

## Biosorption of Heavy Metals, Dyes and Contaminants Emerging of Concern by Lignocellulosic Biomass

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### Abstract

Biosorption on lignocellulosic biomass (LCB) has the potential of being a replacement of existing technologies applied for removal of heavy metals ion, dye and contaminants of emerging concern (CECs) from wastewater streams. This paper reviews the utilization of modified and natural LCB produced from different agricultural and agro-industries byproducts as biosorbents. The characteristics of each biosorbent are discussed with respect to the operating conditions such as pH, equilibrium time, kinetic and isotherm models, preparation methods, chemical modification, sorption capacity, and the thermodynamics properties. This paper also summarizes the regeneration techniques and continuous operation of the biosorption process.

**Keywords:** Biosorption; Metals, Dyes; Contaminants of emerging concern; Lignocellulosic biomass (LCB); Dynamic operation; and Regeneration of biosorbent;

### Introduction:

Water is an essential and scarce commodity for human existence in the world especially in the developing countries. Anthropogenic activities, population growth, unplanned urbanization, and rapid industrialization have caused the deterioration and quality of water. In addition, the development of industrial and agricultural activities has resulted in the contamination of water with various pollutants such as heavy metals, dyes, pesticides, toxic, organic compounds, and chemicals of emerging concern (CECs). These types of pollutants have entered the food chain and resulted in toxic effects, caused diseases in humans, and affected the aquatic biota. In addition, wastewaters derived from municipalities and from various industries, which are highly loaded with various pollutants have become serious global environmental issues in the last decades [1]. Therefore, the removal of these contaminants is necessary for the production of safe drinking water and the environmentally responsible discharge of wastewater. Among the many chemical and physical technologies that have been developed and used for the removal of these contaminants from industrial effluents are, adsorption, ion exchange, reverse osmosis, chemical precipitation, membrane filtration and evaporation. Among these methods' adsorption stands out as one of the most competitive method in view of its low processing power cost as well as its

economic benefits. Commercial activated carbon has been used as an effective adsorbent industrially due to these properties porous structure and large surface area that makes it a highly effective adsorbent for wastewater treatment, but it has the disadvantage of the high production cost.

Biosorption processes, a branch of biotechnology, are very important in environmental and conventional biotreatment processes. Biosorption has been defined as the removal or recovery of metals, organic and inorganic substances from solution by plant materials and agricultural wastes of natural origin as well as live or dead biomass or their derivatives from aqueous solutions [2]. In this review, the definition of Ali et al. (2016) of biosorption is adopted which stated that biosorption is a physico-chemical and metabolically-independent process based on a variety of mechanisms including absorption, adsorption, ion exchange, surface complexation onto lignocellulosic biomass (LCB) [3]. These materials contain cellulose, lignin, pectin and several other compounds that have functional groups such as hydroxyl, carbonyl, amino, carboxylic and alkoxy, which have great affinity for the aforementioned contaminants. Biosorption onto lignocellulosic biomass (LCB) have been shown to be an efficient and low-cost method for the removal of heavy metal ions from wastewater effluents [4]. This process is flexible in design and operation

generating high-quality treated effluents. In addition, in some cases the process is reversible permitting the regeneration of the adsorbents through desorption [5].

Biosorption is a promising process based on the following advantages namely low operating cost, ease of handling, avoidance of generating secondary pollutants (e.g. toxic sludge), and high efficiency over a wide range of pollutants [1]. For industrial-scale application, a biosorbent must exhibit the following properties namely high adsorption capacity; availability in large quantity within one location; relatively cheap; and high reusability potential (regeneration) compared to other purification technologies such as chemical precipitation, carbon adsorption, ion exchange, evaporation, and membrane filtration [1]. Even though there has been a significant increase in publications on this topic as well as progress in our understanding of this complex phenomenon, commercial applications of biosorption technologies have been limited [1, 6-9].

One of the most important properties of LCB affecting its adsorption characteristics is its chemical composition. The compositions of LCB have been covered the reviews of Abdolali et al. (2014), Dai et al. (2018) and Tran et al (2015) [6, 8 and 9]. According to these authors, LCBs are products of photosynthesis and are therefore have been called photomass. LCB is the primary building block of plant cell walls, containing cellulose, hemicellulose, lignin and a little amount of pectin, protein, vitamins, and lipids, extractives, combined with ash. Cellulose, which is 35–50%, is a linear polymer of  $\beta$ -D-glucopyranose sugar units whose average chain has a degree of polymerization of about 9,000–10,000 units, hemicellulose (20–40%) and lignin (15–25%) [6]. Approximately 65% of the cellulose is highly oriented and crystalline with no accessibility to water and other solvents. As a result of its partial accessibility to water and other solvents a variety of characteristics such as hydrophilicity, chirality and degradability are exhibited by the molecular structure of cellulose. In addition, the high donor reactivity of the OH groups in cellulose molecules imparts a strong chemical reactivity. The hemicellulose the second major component consists of a group of polysaccharide polymers has a lower degree of polymerization than cellulose and are not crystalline but vary in structure and polymer composition depending on the source [6]. Lignins, the third major component are composed of nine carbon units derived from substituted cinnamyl alcohol of which the structure and chemical composition are a function of their source are highly branched without crystalline structure [6]. The adsorption capacities of biosorbents are affected by some factors such as polarity and aromaticity and as such, lignin being aromatic in nature would therefore influence the adsorption capacity of organic pollutants, the higher lignin content the higher the affinity for CECs [9]. Tran et al. (2015) reported that the adsorption potential of lignin was seriously affected by polar components suggesting that low sugar content which are polar components could enhance adsorption ability of LCBs for CECs [9]. The minor components such as ash, also play active role in the adsorption process of CECs. The ionic structure of silica ( $\text{SiO}_4 \cdot 4\text{H}_2\text{O}$ ) in ash enhances the capability of LCBs to adsorb polar molecules such as phenols. The functional groups which are sites for adsorption of metals, dyes and CECs on LCBs are hydroxyl ( $-\text{OH}$ ), carboxyl ( $-\text{COOH}$ ) and silanol ( $\text{Si-OH}$ ).

Surface morphology which is determined by scanning electron microscope (SEM) also plays a significant role in the adsorption process. SEM indicates the pores and opening structure on the surface of LCBs which provides LCBs the ability to absorb specific organic pollutants (SOPs). In addition, adsorption capacity of organic pollutants on biosorbents can be enhanced by modifications of raw materials with various methods. Removal of organic matter such as cellulose from LCBs increased its surface area and porosity hereby improving organic pollutant removal [9].

There have been four reviews on the application of LCB in biosorption process [6-9]. These reviews focused on the composition of LCB, their biosorption characteristics, parameters affecting biosorptive capacities, as well as the mechanism of adsorption inorganics and organics. In contrast this literature review covers studies conducted in the last three years on the use of LCBs for the biosorption of heavy metals, dyes and contaminants of emerging concern (CECs) with focus on modifications for enhancement of biosorption capacity, characterization of the LCBs, their kinetic models and thermodynamic parameters during biosorption applications, dynamic operation in fixed-bed columns and regeneration.

### Preparation and Characterization of LCB

The properties of LCBs which make them amenable for biosorption are that they require little processing, have good adsorption capacity, very selective in the adsorption of contaminants such as (heavy metal ions, dyes and CEC), low cost, free availability and easy regeneration. More important is the simplicity of the process. However, these LCBs need to be treated because of the release of soluble organic compounds contained in the plant materials leading to several problems such as low adsorption capacity, high chemical oxygen demand (COD) and biological chemical demand (BOD) as well as high total organic carbon (TOC) resulting in the depletion of oxygen content of water thus threaten aquatic life. There is therefore a need for modification by drying, grinding or chemically treatment before being applied for adsorption of heavy metals, dyes and CECs. These modifications increase the functional groups present on the adsorbent surfaces hereby increasing the adsorption capacity.

Noli et al. (2019) modified Aloe vera leaves (AL) for the biosorption of cadmium by treating the natural biomass with 1.5 M of either NaOH or  $\text{H}_3\text{PO}_4$  for 24h at room temperature [10]. The pH<sub>pzc</sub> values of the natural biomass (AL), acid treated biomass (AL-at) and base treated (AL-bt) were found to be 2.6, 2.2 and 2.8 respectively which meant that the surface of these biosorbents were negatively charged above these pH values due to the dissociation of carboxylic and phenolic groups (Bronsted acid sites). The acidic character surface therefore complexes easily with positively charged particles [10]. When the Fourier-transform infrared (FTIR) spectra of the natural (AL) and modified (AL-at, AL-bt) and the loaded biosorbent were compared it indicated that hydroxyl and carboxyl groups participated in the binding with the metal ions. The complexation therefore occurred between the metal and the hydrogen atom and carboxyl groups through ion exchange. The surface area of the sorbents had a value of 2.35  $\text{m}^2/\text{g}$  and the calculated cumulative volume for AL using the Brunauer, Emmett and Teller (BET) equation was 0.0003  $\text{cm}^3/\text{g}$  [10]. The X

ray diffraction (XRD) patterns of the raw, modified biosorbents and the biosorbent after sorption indicated amorphous structure. In contrast to the SEM images of AL which showed rough heterogeneous structure the morphologies of AL-at and AL-bt were characterized as being irregular with formation of random orientations and cavities. These cavities were characterized as channels onto the surface of the sorbents instead of pores, considering the small surface area calculated from BET analysis. The Energy-Dispersive X-ray spectroscopy (EDS) analysis indicated that AL contained mainly carbon (60 wt. %) and oxygen (35–38 wt. %) which are the basic constituents of cellulose, hemicellulose, lignin and protein, and also small quantities of metals (silicon, calcium, magnesium, phosphorus). In addition, AL- bt was found to contain Na (0.35 wt. %) [10].

Saraeian et al. (2018) investigated the biosorption of cadmium onto modified Sorghum x drummondii commonly called Sudan grass (SG). SG was modified chemically with NaOH [11]. It was suggested that NaOH improved the sorption ability of SG by removing the base-soluble materials and increasing the ratio of active sites, saponification of ester functional groups to carboxylates, and improving ion-exchange ability of SG by implanting sodium ions on the surface [11]. The BET surface area significantly decreased from 3.33 to 0.76 m<sup>2</sup> /g after modification, suggesting that sodium hydroxide removed some water- and base-soluble materials thereby plugging some of the pores. The resulting pore size was large enough for Cd (II) ion penetration and adsorption on both sorbents, with NaOH-SG having a larger pore size than the natural (SG) [11]. It was suggested that the decrease in surface area and increase in Cd (II) uptake after modification occurred mainly due to more available binding sites per unit area of NaOH-SG, indicating effective chemical modification [11]. Comparison of the FTIR spectra of SG before Cd(II) sorption to that after sorption suggested the involvement of hydroxyl groups in the adsorption of Cd (II). SEM images revealed that the modification process removed some components of the biomass resulting in a smoother outer surface and created gaps in biomass structure in agreement with larger average pore width obtained from N<sub>2</sub> sorption studies [11]. EDX analysis confirmed the adsorption of Cd(II) ions on the surface of both sorbents and validated the effectiveness of sodium hydroxide modification by exhibiting the presence of Na<sup>+</sup> ions on the surface of the biomass. In addition the higher oxygen content after modification also showed that Cd(II) ions were adsorbed on the surface while Na<sup>+</sup> ions were desorbed, suggesting an ion-exchange process [11].

A byproduct of the cellulose and paper industry Pinus bark was modified chemically with hydrogen peroxide, sulfuric acid and sodium hydroxide and investigated for its biosorption characteristics of Cd (II), Pb (II) and Cr (III) [12]. SEM micrographs of the P- nature presented a spongy and fibrous surface with irregular and heterogeneous structure; the P-H<sub>2</sub>O<sub>2</sub> showed a heterogeneous surface, resembling spongy aspect of the P-in nature; P-H<sub>2</sub>SO<sub>4</sub> presented a relatively heterogeneous surface, with many pits and fissures prominent, and P-NaOH presented irregular, heterogeneous surface, with cracks (breaks) through the surface [12]. The surface area of the modified biosorbents was in general, small. The P-H<sub>2</sub>O<sub>2</sub> had the highest value for surface area (0.76m<sup>2</sup>/g), followed by P- NaOH (0.48m<sup>2</sup>/g) and P-H<sub>2</sub>SO<sub>4</sub> (0.33m<sup>2</sup>/g). The

pore volume for all the biosorbents was 0.00194cm<sup>3</sup>/g. The pH<sub>pzc</sub> values for unmodified P-nature and modified biosorbents P-H<sub>2</sub>O<sub>2</sub>, P-H<sub>2</sub>SO<sub>4</sub> and P- NaOH were 3.50, 2.50, 2.47 and 6.03 respectively [12]. The modifying agents were effective in changing the chemical structure of the Pinus biomass. When an aqueous solution at a higher pH than the pH<sub>pzc</sub>, is exposed to the biosorbent, negative charges predominate on the surface favoring cations adsorption, such as Cd (II), Pb (II) and Cr (III) [12].

Sodium hydroxide modified tomato waste and apple juice residue was studied for the biosorption of lead (Pb (II)) [4]. The Fourier transform IR (FTIR) spectra of the biosorbent before and after biosorption indicated the involvement of OH group in the biosorption of Pb (II). SEM analysis of the biosorbent before NaOH activation had a dense and rigid morphology, revealing homogeneity without any porous structure and a little-damaged surface, caused by liberation of volatile substances in carbonization process (Herald et al. 2018). The NaOH-activated biosorbents had an irregular surface with cavities of several sizes, demonstrating a well-built porous structure and closely packed surfaces confirming the FTIR analysis [4].

Zaidi et al. (2018) investigated the use of modified *Artocarpus odoratissimus* or Tarap leaves (TL) for the biosorption of Pb (II) [13]. The Tarap leaves were surface chemically modified using 0.01M NaOH and EDTA single modification TLN and TLE respectively. Double modification was achieved by exposing TL to NaOH (TLN) followed by EDTA. This double modified TL was denoted TLNE [13]. SEM analysis of these biosorbent presented a rough porous surface for TL, and the surfaces of TLN, TLE and TLNE appeared to be much smoother than that of TL. The decreased roughness of TL upon the chemical treatments was attributed either to removal of wax, lipid, and fat from the surface or the filling up of the pores of TL's surface by the chemicals, especially EDTA [13]. FTIR spectra revealed that the TL and modified TL had OH, CO, COOH and NH<sub>2</sub> as their functional groups. The amount of these functional groups was dependent on the introduction of NaOH and EDTA onto TL, as EDTA consists of functional groups COOH and NH<sub>2</sub> and NaOH has OH groups. The presence of these functional groups made the surface of the adsorbents to be more hydrophilic and thus enhanced the adsorption of positive metal ions [13].

Ogata et al. (2018) studied the biosorption of molybdenum onto virgin wheat bran (WB) and calcined wheat bran. WB200, WB400, WB600, WB800, and WB1000 were prepared by treating virgin WB in a muffle furnace at temperatures of 200, 400, 600, 800, and 1000 °C for 2 h respectively [14]. WB0.01, WB0.1, WB1.0, and WB6.0 were also prepared by treating Virgin WB with hydrochloric acid at concentrations of 0.01, 0.1, 1.0, and 6.0 M respectively. The pH<sub>pzc</sub> value of WB decreased with increasing the concentration of hydrochloric acid (WB > WB0.01>WB0.1> WB1.0>WB6.0) [14]. Increase in calcination temperatures treatment produced pores on the surface of WB samples resulting in increased specific surface area of the WB samples. The specific surface area of WB, WB200, WB400, WB600, WB800, and WB1000 were 1.5, 1.9, 0, 10.0, 260.9, and 197.1 m<sup>2</sup>/g respectively [14].

Peat has been investigated as a biosorbent for nickel and lead [15]. FT-IR spectra identified hydroxyl, ether, carbonyl groups in peat samples. Analysis of the FTIR spectra of the peat before and

after adsorption confirmed the important role played by these functional groups on the peat surface in the metal ion adsorption process [15]. The specific surface area of peat as a natural adsorbent is small, amounting to 1.40 m<sup>2</sup>/g. The total pore volume of the peat is 0.01 cm<sup>3</sup>/g, while the average pore size is 14.6 nm [15]. The electrokinetic curve from the plot of the zeta potential as a function of pH suggested that the zeta potential of peat was strongly dependent on the pH. The zeta potential values were negative over the whole range of pH investigated, namely for pH from 1.7 to 11, where the electrokinetic potential varied from -3 to -25 mV [15]. The zeta potential values suggested that the functional groups in the peat was highly deprotonated and negatively charged, indicating that the major binding sites were acidic groups [15].

Raw banana peels (RBP) were modified with sulfuric acid and then mixed with polyaniline to improve their electrical conductivity and were studied to remove zinc ions from wastewater as sensor in a working electrode [16]. Physical analysis indicated that the activated banana peels (ABP) had a specific surface area value of 0.4 m<sup>2</sup>/g. The FTIR spectra of the RBP and ABP had a complex chemical structure of carboxylic acid, ether, ester and amine, which provided the adsorption capacity [16].

Modified water hyacinth plants (*Eichhornia crassipes*) was studied for biosorption of Pb<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup> ions in a tri-element system [17]. The water hyacinth plant was treated with sodium hydroxide, nitric acid to obtain the base modified BWH and the acid modified AWH. FTIR spectra of BWH indicated that the alkali treatment reduced the carboxylic and phenolic functional groups concentration and increased the basic group's concentration present on the lignocellulosic fiber surface, while the acid treatment provided the opposite effect [17]. The BWH FTIR spectra obtained before and after biosorption of Ni<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> ions indicated that carboxylate and hydroxyl ions were the functional groups responsible for the biosorption [17].

Eucalyptus leaf residue (ELR) was modified to improve its biosorption of metals in a multi-metal system [18]. Modification was achieved by treating ELR with nitric acid to form (AELR) and sodium hydroxide to form (BELR). BELR was found to be a better biosorbent than AELR. The surface area calculated by the BET equation were 0.05m<sup>2</sup>/g and 1.87m<sup>2</sup>/g for ELR and BELR respectively; and the pore volume values were 2.0×10<sup>-4</sup> cm<sup>3</sup>/g and 1.3×10<sup>-3</sup> cm<sup>3</sup>/g for ELR and BELR respectively [18]. Thus, the available surface area of BELR was important for the metal's removal. It was observed that, there was a loss of the approximately 23–27% of biomass during the treatment of ELR with NaOH solution [18].

Chemically and enzymatically treated flax fibrous material was investigated as biosorbent for methylene blue [19]. Chemical modification involved sodium hydroxide (5g/L) (FFMSH); Sodium borohydride (2g/L) and Sodium hydroxymethanesulfonate (6 g/L) (FFMSHMS). Enzymatic modification involved hydrolysis of the flax fiber material by a cellulolytic preparation, which contains endoglucanases, (FFMCP), a mixture of the cellulolytic preparation and an exogalactosidase (FFMCPG), a mixture of the cellulolytic preparation and an exoxylosidase (FFMCPX), a mixture of all the three enzymes (FFMCPGX) (Koksharov et al. 2019). The specific surface area of the biosorbents were 14.7, 21.9, 14.3, 14.5, 28.5, 28.1, 28.3, 27.8 m<sup>2</sup>/g for FFM, FFMSH, FFMSB, FFMSHMS, FFMCP,

FFMCPG, FFMCPX, FFMCPGX respectively. The total pore volume was 0.007, 0.012, 0.009, 0.010, 0.020, 0.020, 0.020, 0.020 cm<sup>3</sup>/g for FFM, FFMSH, FFMSB, FFMSHMS, FFMCP, FFMCPG, FFMCPX, FFMCPGX respectively. The specific surface area was doubled by the enzymatic treatment while the total pore volume almost tripled [19].

Cellulose extracted from rice husk was functionalized through free radical grafting with a binary vinyl monomer mixture of 2-acrylamido-2-methylpropane sulfonic acid and acrylic acid in the presence of N-N-methylene bisacrylamide cross-linker to form a biosorbent (Cell-g-AASO<sub>3</sub>HCO- AAc) [20]. Cell-g-AASO<sub>3</sub>HCOAAc was used as a biosorbent for the removal of model malachite green, crystal violet, Congo red dyes, Ni (II) and Cu (II) metal ions from aqueous solutions [20]. Cell-g-AASO<sub>3</sub>HCO-AAc was characterized by Field emission scanning electron microscopic (FESEM), FTIR, XRD and thermal analytical techniques. The surface morphology was greatly influenced by the grafting of comonomers onto the cellulose backbone [20]. FESEM images showed pure cellulose to have long and smooth fiber like threads grafted while Cell-g-AASO<sub>3</sub>H- CO-AAc polymer had highly thick, flaky and layered structures. The swelling behavior of the grafted copolymer analyzed as a function of pH followed the order 7.0 > 9.4 > 2.2 [20].

Liu et al (2019) reported the use of walnut shell (WS) for the biosorption of methylene blue. FTIR spectra analysis indicated the presence of ionizable groups (carboxyl and hydroxyl) that easily bind to positive dye ions [21]. The SEM image indicated that walnut shell had amorphous and heterogeneous morphology while XRD scan exhibited the typical cellulose structures favouring biosorption [21].

Peanut shell was modified for the biosorption of methylene and tetracycline by refluxing it with H<sub>2</sub>SO<sub>4</sub> [22]. Refluxing with concentrated H<sub>2</sub>SO<sub>4</sub> resulted in the carbonization and sulfonation of the peanut shell. The zeta potential at pH 1.54 was measured to be -10 mV; however, the negative zeta potential increased with the increase in pH. The Brunauer–Emmett–Teller (BET) surface area of the PNS-SO<sub>3</sub>H was determined to be about 3.7 m<sup>2</sup>/g [22]. The modified peanut shell (PNS- SO<sub>3</sub>H) presented a flake-like microstructures. The particles exhibited random shapes and sizes. Analysis of the magnified SEM spectra of the PNS-SO<sub>3</sub>H presented an uneven and rough surface morphology of the microparticles. There were smaller particles on the surface of the bigger particles [22]. The EDS spectrum confirmed that the PNS-SO<sub>3</sub>H was chemically composed of carbon, oxygen, and sulfur. The high-resolution X-ray photoelectron spectroscopy (XPS) also confirmed the qualitative elemental composition of the different functional groups of the PNS- SO<sub>3</sub>H to be composed of carbon, oxygen, and sulfur [22]. Analysis of the FTIR spectra of the pristine peanut shell (PS) indicated the presence of hydroxyl (O-H), aromatic (C-H), aliphatic (C- H), and carbonyl (C=O) functional groups [22]. In contrast, the FTIR spectrum of the PNS-SO<sub>3</sub>H indicated some new features, which demonstrated the change in the functional groups of the peanut shell. In addition, complete removal of O-H, C-H, and the C-O ether groups was observed, indicating the dehydration of the peanut shell by the H<sub>2</sub>SO<sub>4</sub> acid reflux. From the results of the EDS, XPS, and the FTIR analyses it was concluded that the sulfuric acid reflux converted the peanut shell into a carbonaceous material while incorporating the sulfonic acid functional group. It was also

observed that the zeta potential of the PNS-SO<sub>3</sub>H was negative throughout the pH range [22].

Microwave assisted tea leaves were used in the biosorption of Eriochrome black T (EBT) [23]. Spent tea leaves (STL) were treated with aqueous solution of H<sub>2</sub>SO<sub>4</sub> and then subjected to microwave irradiations at 600 W under N<sub>2</sub> atmosphere to produce the microwave-assisted spent black tea leaves (MASTL). The specific surface area of STL was 25.2 m<sup>2</sup>/g while that for MASTL was calculated to be 42.3 m<sup>2</sup>/g [23]. The point of zero charge (pHpzc) of MASTL was determined to be 4.6. Analysis of the SEM images of MASTL before adsorption indicated that the surface was composed of a rough and regularly arranged layered morphology with spaces in between them, which enhanced the biosorption of EBT [20]. After EBT adsorption the dye molecules occupied the available pores and resulted in a more dispersed and irregular mass. The FTIR spectra showed that MASTL surface is composed of a number of functional groups such as -OH, C-H, -C-O, C=O, N-H and -CH<sub>3</sub> groups [23].

Heat treated Phragmites australis fiber was used in the study of the biosorption of methylene blue (MB) [24]. The pHpzc value of the Phragmites australis fibers was 6.62 which explained the positive charges on the surface at lower pH values below this point, and the negative charges on surface at higher pH value that provided a better biosorption of MB which is an alkaline and hydroxyl cationic dye. Using the Boehm method [25], the surface functions of the Phragmites australis were determined to be the acidic functions, carboxylic, phenolic and lactonic which are more important than basic functions; leading to the conclusion that the surface of the biomass was acidic confirmed by the pHpzc of 6.62 [24]. Analysis of the FTIR spectra of the native Phragmites australis and Phragmites australis with MB indicated the presence of the functional groups involved in the biosorption such as the formation of hydrogen bonds between azote of methylene blue and hydroxyl groups of Phragmites australis -OH due to the presence of cellulose, hemicellulose, and lignin. The SEM images indicated the presence of the typical compact lignocellulosic fibrous structure [24].

Modified Grape stalk (MGS) modified with phosphoric acid was investigated for biosorption of caffeine. The biosorbent characteristics such as specific surface areas and micropore volumes were 6.23 and 4.21 m<sup>2</sup>/g and 0.003 and 0.002 cm<sup>3</sup>/g for native grape stalk and modified grape stalk respectively [26].

Modified wheat bran waste (MWB) was investigated as a biosorbent for Enrofloxacin (ENR), which belongs to the class of fluoroquinolone antibiotics used extensively in veterinary pharmaceuticals [27]. Modification involved acid (10% H<sub>2</sub>SO<sub>4</sub>) treatment followed by an alkali treatment (KOH, pH 8) and lastly suspension of the solid in a nitric acid solution (pH 3). The point of zero charge (pHpzc) value of MWB was found to be 4.1. The specific surface area using the Brunauer-Emmett-Teller method (BET) was equal to 11 ± 3 m<sup>2</sup>/g. Analysis of the SEM spectra indicated a fibrous morphology. The percentage elemental composition of MWB was C: 49.6; N: 1.7; H: 6.6; O: 42.1 and a total concentration of acidic sites on MWB surface equal to 0.56 mmol/g [27].

Tea leaves and coffee waste modified with sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) to form two new carbonaceous materials (TW-SO<sub>3</sub>H) and (CW-SO<sub>3</sub>H) were studied for their biosorption of two contaminants

of emerging concern (CEC): sulfamethoxazole (SMX) and bisphenol A (BPA) [28, 29]. Based on the Zeta potential analysis the surface charge of both biosorbents were highly negative surface charges -24.4 mv and 23.6 mv for TW-SO<sub>3</sub>H and CW-SO<sub>3</sub>H respectively after the sulfonation process due to the presence of sulfonic acid groups which suggested that these biosorbents would have strong electrostatic interactions with the cationic pollutants [28].

Analysis of the Scanning electron microscopy (SEM) indicated that the particles were mostly micrometer in size and had an irregular morphology. SEM images showed the formation of the irregular microparticles of CW-SO<sub>3</sub>H biosorbent after the sulfuric acid treatment (sulfonation). Energy dispersive X-ray spectroscopy (EDS) and elemental mapping confirmed the presence of carbon, oxygen, and sulfur in TW, CW, and biosorbents TW-SO<sub>3</sub>H, CW-SO<sub>3</sub>H [29]. Analysis of the Fourier-transform infrared (FTIR) spectra of TW-SO<sub>3</sub>H and CW-SO<sub>3</sub>H indicated the presence of aliphatic, aromatic compound, carbonyl, amino and sulfonyl groups. Raman spectroscopic analysis showed the graphitic nature of the both TW-SO<sub>3</sub>H and CW-SO<sub>3</sub>H samples and the sp<sup>2</sup> and sp<sup>3</sup> nature of its carbon types [29].

## Adsorption of heavy metals

Rapid industrialization and urbanization in the last century have resulted in the excessive discharge of heavy metal-containing wastewater into the environment, which has negatively affected human health [8]. The two main sources of heavy metals in wastewater effluents are natural and anthropogenic. The former is caused by soil erosion, volcanic activities, weathering of rocks and minerals, whereas the latter is because of human activities such as mineral processing, fuel combustion, street run-offs, landfills, agricultural activities, and industrial activities such as mining, printed board manufacturing, metal finishing and plating, semiconductor manufacturing [5]. Heavy metals are stable, have high solubility, migrate easily in aqueous media, and if untreated or inadequately treated in wastewater effluents causes a variety of health and environmental impacts when released into water bodies [5]. Unlike organic wastes, heavy metals are non-biodegradable and they accumulate in living tissues, causing various diseases and disorders. It is therefore imperative that wastewater containing heavy metals be treated prior to its discharge to the environment in order to avoid these negative consequences and polluting drinking water. So far, several chemical and physical technologies have been developed and are used to remove metals from industrial wastewater effluents such as, ion exchange, chemical precipitation, membrane filtration, evaporation, reverse osmosis and adsorption [30, 31]. Adsorption is considered one of the most competitive and optimal techniques that is simple to design and economically efficient [32].

## Arsenic

According to World Health Organization (WHO) arsenic has been reported as one of the major toxic elements to humans. Arsenic contamination has been found in the drinking water of over 140 million people in 70 countries around the world. Chronic arsenic intoxication has been determined to cause several types of cancer and affects numerous organs including the central nervous system, skin and caused vascular diseases as well as visceral cancer

[33]. Gupta et al. (2015) reported the biosorption of As (III) and As (V) ions onto functionalized sugarcane bagasse (SCB-S) from aqueous solution [34]. The adsorption data fitted both Langmuir and Freundlich isotherm models. The Langmuir monolayer capacities for As (III) and As(V) were determined to be 28.57 and 34.48 mg/g of SCB-S, respectively (Table 1). The adsorption capacity for both arsenic species increased as the pH increased from 2 to 7 after which it decreased. Between pH 4 and 7, As (V) predominantly existed as negatively charged  $\text{HAsO}_4^{2-}$  and  $\text{H}_2\text{AsO}_4^-$  species [34]. In addition, the prevalent acidic conditions supported the presence of the proton in the ( $-\text{SH}^+$ ) group. Thus, there exists an electrostatic attraction between the  $\text{H}^+$  ions and the negatively charged arsenic species consequently leading to an increased adsorption in this pH range. The biosorption of As (III) and As (V) with SCB-S followed pseudo first order (PFO) kinetics. The adsorption of As (III) and As(V) onto the SCB-S adsorbent involved pore, surface or intraparticle diffusion and as such was fitted Weber and Morris model which describes the probability of intraparticle diffusion. This model relates the amount of the solute adsorbed to the square root of time with a proportionality constant the intraparticle rate constant ( $k_{\text{int}}$ ). The value of intraparticle diffusion constant ( $k_{\text{int}}$ ) of As (III) and As (V) were found to be 11.40 and 12.39 (g/mg)/(min<sup>0.5</sup>) respectively [32]. The adsorption data showed good fit to both Langmuir and Freundlich isotherm models. The thermodynamic parameters such as the standard enthalpy ( $\Delta H^\circ$ ), standard entropy ( $\Delta S^\circ$ ) for As(III) and AS (V) were (4.42 kJ/mol and 1.794 J/mol K) and (6.67 kJ/mol and 2.738 J/mol K) respectively (Table 4) [34]. The positive value of  $\Delta H^\circ$  indicated a chemisorption process. The positive value of entropy suggested the irreversibility and stability of the adsorption process. The  $\Delta G$  values were negative indicating that the process was feasible and adsorption was spontaneous. Total arsenic removal was observed when adsorption studies were performed with samples of arsenic contaminated ground water at a dose rate of 5.0 g of SCB-S, [34].

## Cadmium

Cadmium (Cd) is an extremely toxic metal and has no known biological function. Cadmium accumulates in the human body, especially in the kidneys incapacitating renal function. The World Health Organization's permissible limit of cadmium in drinking water is 0.005 mg/L [8], while the World Health Organization (WHO) has set a maximum guideline concentration of 0.003 mg/L [35]. Dirbiz et al. (2018) studied the biosorption of cadmium ions onto different microalgae *Parachlorella* sp., *Spirulina* sp., *Scenedesmus* sp., and *Nannochloropsis* sp. [36]. The biosorption capacity of the *Parachlorella* sp. at 30 °C and pH of 7 was determined to be 90.72 mg/g. The PFO kinetic model was more consistent with the experimental kinetic data while the equilibrium data fitted the Langmuir isotherm best with the maximum biosorption capacity ( $q_m$ ) varying from 75.87 mg/g to 104 mg/g with increasing temperature (Table 1) [36]. The dimensionless separation factor ( $R_L$ ) of the Langmuir equation that confirms the favorability of the sorption if  $0 < R_L < 1$ , had values between 0.032 and 0.673 indicating the favorable sorption of Cd (II) onto *Parachlorella* sp. The thermodynamic parameters standard enthalpy ( $\Delta H^\circ$ ) and standard entropy ( $\Delta S^\circ$ ) were (77.01 to 91.86 kJ/mol) and (349.01 to 393.71 J/mol /K) respectively (Table 4). The positive value of  $\Delta H^\circ$  indicated an endothermic adsorption process while the positive value of  $\Delta S^\circ$

confirmed a favorable process. In addition, these values indicated the spontaneity and desirability of the process. The negative values of  $\Delta G^\circ$  indicated that the biosorption of Cd (II) by *Parachlorella* sp. was a spontaneous process. The decrease in  $\Delta G^\circ$  with increase of both temperature and pH indicated the enhanced feasibility of the biosorption at higher pH and temperatures values [36].

Noli et al. (2019) investigated the biosorption of cadmium with modified Aloe vera leaves [10]. The optimum pH for biosorption of cadmium onto all the biosorbents (AL, AL-at, AL-bt) was 5-6. The specific uptake decreased when the sorbent dosage increased from 1.5 to 5.0 g/L. The optimum sorbent dosage for the three biosorbents was 1.5 g/L. The presence of  $\text{H}_3\text{O}^+$  ions at low pH values inhibited the metal uptake due to the competition with the sorbate ions for the existing sorption sites while at elevated pH values, increase of the metal uptake was observed [10]. The equilibrium data for cadmium was a better fitted to Freundlich isotherm model for AL but AL-at and AL-bt fitted Langmuir isotherm model. The maximum absorption capacity for cadmium were 66.23 mg/g and 104.2 mg/g for AL- at and AL-bt respectively (Table 1) [10]. The presence of sodium ions caused a decrease in metal removal with AL as sorbent (24.9% for cadmium) due to ion competition. The effect of ionic strength signified ion exchange or outer-sphere complexation because  $\text{Na}^+$  ions competed with cadmium ions for the same sorption sites. The Weber and Morris intra-particle diffusion plots for the temperature of 285 K were linear over the entire time range. These results suggested that the sorption was driven by physical interaction between sorbent and sorbate due to the controlling influence for the diffusion process at 285 K. When the temperature was increased to 298 K and further to 313 K, the plots were not linear over the entire time range, meaning that intraparticle diffusion was not the rate controlling step. In this case, a multi-step process occurred thus indicating that more steps were involved in the sorption process [10]. The thermodynamic parameters, standard enthalpy ( $\Delta H^\circ$ ) and standard entropy ( $\Delta S^\circ$ ), for biosorption of cadmium onto AL were (1.5 kJ/mol and 64.0 J/mol K) (Table 4). The positive value of  $\Delta H^\circ$  indicated the endothermic nature of adsorption and the biosorption is a physical process while the positive value of  $\Delta S^\circ$  confirmed the increased randomness at the solid-solute interface during adsorption processes. The calculated negative values of  $\Delta G^\circ$  indicate that the sorption process occurred spontaneously at the temperatures studied [10].

Saraeian et al. (2018) studied the biosorption of cadmium onto *Sorghum x drummondii* commonly called Sudan grass (SG) and NaOH modified Sudan grass (NaOH-SG) [11]. Both sorbents were characterized and various parameters including particle size, agitation speed, pH, sorbent dosage, time, and temperature were investigated on their sorption performance. Cadmium sorption was improved as particle size decreased from 250 to 150  $\mu\text{m}$ . This can be accounted for by the increase in total surface area of smaller particles leading to their higher number of binding sites for adsorption of Cd (II) ions [11]. Cadmium uptake was increased by a factor of two as agitation speed increased from 50 to 200 rpm. Equilibrium time was reduced from 90 min to 20 min after modification. The optimal pH for SG and NaOH-SG were 7.5 and between 5 and 7 respectively. Percentage of cadmium removed increased as the sorbent dose increased for both sorbents due to higher number of available binding sites for Cd (II) ions. However, the sorption

capacity behaved differently. For SG, adsorption capacity decreased from 3.49 to 1.32 mg/g by increasing sorbent dosage from 1–20 g/L (Table 1) [11]. Higher capacity at lower sorbent dosage was attributed to exposure of binding sites to excessive amount of Cd (II) ions, leading to unobstructed saturation of adsorption sites and eventually higher sorption capacities. Unlike SG, NaOH-SG sorption capacity initially increased with sorbent loading up to 10 g/L, after which it decreased significantly. This observation was explained by the fact that the initial increase in adsorption capacity was due to increased availability of sorbent surface area, while the subsequent decrease was attributed to overlapping, saturation, or aggregation of sorption sites leading to their lower availability relative to the amount of metal ions. Intra-particle diffusion and pseudo-second order kinetic models were found as the best-fitting models for Sudan grass and NaOH-modified Sudan grass, respectively. Langmuir isotherm model described equilibrium data with the highest accuracy. Maximum monolayer adsorption capacity of cadmium onto SG and NaOH-SG was 1.52 and 7.76 mg/g, respectively, showing a five-fold improvement for cadmium sorption (Table 1) [11]. The Intra-particle diffusion model of Weber and Morris only fitted the sorption data for SG indicating that the pore diffusion is the only rate controlling step. The thermodynamic parameters such as the standard enthalpy ( $\Delta H^\circ$ ), standard entropy ( $\Delta S^\circ$ ) for biosorption of cadmium onto SG and NaOH-SG were (-21.53 kJ/mol and -87.18 J/mol K) and (2.214 kJ/mole and 14.11 J/mole/K) respectively (Table 4) [11]. The negative value of  $\Delta H^\circ$  for SG suggested an exothermic process while the positive value of  $\Delta H^\circ$  for NaOH-SG suggested the endothermic nature of the biosorption process. The positive value of  $\Delta S^\circ$  confirmed the increased randomness at the solid-solute interface during adsorption processes while negative entropy for Cd(II) sorption onto SG suggested a decrease in randomness at sorption interface as a result of cadmium uptake, which could be an indication of physical sorption process. The calculated values of  $\Delta G^\circ$  for SG were positive while those for NaOH-SG were negative. The negative values of  $\Delta G^\circ$  suggested that the sorption process was feasible and that it occurred spontaneously at the temperatures studied. The mean free energy of adsorption (E) determined from Dubinin-Radushkevich (D-R) isotherm for SG and NaOH-SG were 7.5 kJ/mol and 10 kJ/mol respectively (Table 4) [11]. These values indicated a physisorption process for SG and a chemisorption mechanism for NaOH-SG, which explained the significant reduction of equilibrium time after modification, as chemisorption (dominantly ion-exchange) processes, occur much faster than physisorption processes [11].

Schwantes et al. (2018) investigated the biosorption of Cd (II) onto modified Pinus bark, a byproduct of the cellulose and paper industry [12]. The modified biosorbents (P-nature, P-H<sub>2</sub>O<sub>2</sub>, P-H<sub>2</sub>SO<sub>4</sub>, P-NaOH) were evaluated with respect the effect of contact time and equilibrium. The maximum biosorbent dosage was 4g/L for all metal ions. The kinetic data fitted well the pseudo second order kinetics model for all biosorbents and all metals ions. Equilibrium data for Cd (II) onto P-nature, P-H<sub>2</sub>O<sub>2</sub>, and P-H<sub>2</sub>SO<sub>4</sub> fitted Freundlich isotherm well while Cd onto P-NaOH fitted Langmuir isotherm with a q<sub>m</sub> value of 26.08 mg/g [12]. The thermodynamic parameters standard enthalpy ( $\Delta H^\circ$ ), standard entropy ( $\Delta S^\circ$ ) for biosorption of cadmium onto P-H<sub>2</sub>O<sub>2</sub>, P-H<sub>2</sub>SO<sub>4</sub>, P-NaOH were (52.8 kJ/mol and -178.3 J/mol/K), (18.2 kJ/mol and -72.1 J/mol/K) and (-35.3 kJ/mol and 125.5 J/mol/K) respectively [12]. The calculated values

of  $\Delta G^\circ$  for Cd (II) onto P-NaOH was negative while the  $\Delta G^\circ$  for Cd (II) onto P-H<sub>2</sub>O<sub>2</sub> and P-H<sub>2</sub>SO<sub>4</sub> was positive. The positive values of  $\Delta H^\circ$  suggested an endothermic process and a negative  $\Delta G^\circ$  suggested a spontaneous process [12].

Peng et al. (2018) investigated the biosorption behavior and the mechanism of cadmium (Cd) ions onto foxtail millet shell as a natural biosorbent in aqueous solution [37]. Batch experiments were conducted in which the effects of pH (2.0–6.0), contact time (5.0–240.0 min), initial metal ions concentration (25.0–300.0 mg/L), particle size (0.25–2.0 mm) and biosorbent dosage (1.0–6.0 g/L) on the adsorption efficiency of the target metals using foxtail millet shell were studied. The optimal operational conditions were to be pH of 5.0, biosorbent dosage of 4.0 g/L, contact time of 120.0 min and temperature of 25.0°C. The kinetics data for the biosorption of Cd (II) ions was best explained by PSO kinetic model [37]. Furthermore, the intraparticle diffusion model revealed multiple curves which did not pass through the origin, indicating that the boundary layer diffusion controlled the biosorption to some degree. Nonlinearity was observed, indicating that three steps took place during the whole adsorption process. The first step was attributed to the diffusion of metal ions through the solution to the external surface adsorbent, or the boundary layer diffusion of solute molecules. The second step described the gradual biosorption stage, where intraparticle diffusion was the rate-limiting step. The third step was attributed to the final equilibrium stage where the intraparticle diffusion started to slow down [37]. The rate constant for intraparticle diffusion suggested that Cd ions had a high boundary layer effect and could more easily diffuse and transport into the inside of the shell. The biosorption isotherm for Cd (II) ions was well represented by Langmuir model with a biosorption capacity of 12.48 mg/g [37].

Kebede et al. (2018) investigated the biosorption of cadmium (Cd (II)) ions onto Moringa stenopetala seed powder from industrial effluent [38]. The optimum pH at an equilibrium time of 15 min was found to be 5.0. The results of the adsorption equilibria fitted the Freundlich isotherm ( $R^2 \geq 0.926$ ) more than Langmuir isotherm. The maximum adsorption capacity (q<sub>m</sub>) was found to be 23.26 mg/g (Table 1) [38]. The kinetic adsorption data was well defined by the PSO model ( $R^2=1$ ). The calculated thermodynamic parameters  $\Delta H^\circ$  and  $\Delta S^\circ$  were 54.59 kJ/mol and 201.94 J/K/mol respectively (Table 4). The positive value of  $\Delta H$  suggested that the sorption of cadmium onto Moringa stenopetala seed powder was an endothermic process [38].

## Chromium

Health effects caused by chromium include allergic reactions, dermatitis, eczema, bronchitis and rhinitis, and carcinogenic [8]. Chromium exists in aqueous media in two oxidation states, hexavalent Cr (VI), and trivalent Cr (III) and the toxicity of chromium depends upon its oxidation state. The form in which chromium exists in a solution depends upon the pH., these include chromate (Cr<sub>2</sub>O<sub>4</sub><sup>2-</sup>), hydrochromate (HCrO<sub>4</sub><sup>+</sup>), or dichromate (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) [8]. Schwantes et al. (2018) studied the biosorption of Cr (III) onto modified Pinus bark, a byproduct of the cellulose and paper industry [12]. The modified biosorbents (P-nature, P-H<sub>2</sub>O<sub>2</sub>, P-H<sub>2</sub>SO<sub>4</sub>, P-NaOH) were evaluated with respect the effect of contact time and equilibrium. The maximum biosorbent dosage

was 4g/L. The kinetic data fitted well the PSO kinetics model for all biosorbents. Equilibrium data for Cr (III) onto P-nature and P-H<sub>2</sub>SO<sub>4</sub> fitted Freundlich isotherm well while Cr(III) onto P-H<sub>2</sub>O<sub>2</sub>, P-H<sub>2</sub>SO<sub>4</sub> and P-NaOH fitted Langmuir isotherm with  $q_m$  values of 3.77, 10.06 and 18.35 mg/g respectively (Table 1) [12]. The standard enthalpy ( $\Delta H^\circ$ ), standard entropy ( $\Delta S^\circ$ ) for biosorption of Cr(III) onto P-H<sub>2</sub>O<sub>2</sub>, P-H<sub>2</sub>SO<sub>4</sub>, P-NaOH are (12.1 kJ/mol and 51.0J/mol/K), (48.3kJ/mol and 14.7J/mol/K) and (22.3 kJ/mol and 73.8 J/mol/K) respectively (Table 4) [12]. The calculated values of  $\Delta G^\circ$  for Cr (III) onto P-H<sub>2</sub>O<sub>2</sub> and P-NaOH were negative while that for Cr (III) onto P- H<sub>2</sub>SO<sub>4</sub> was positive. The positive values of  $\Delta H^\circ$  suggested an endothermic process and a negative  $\Delta G^\circ$  indicated a spontaneous process [12].

Peng et al. (2018) investigated the biosorption behavior and the mechanism of chromium (Cr) ions onto foxtail millet shell as a natural biosorbent in aqueous solution [37]. The effects of pH, contact time, Cr ions concentration, and particle size and biosorbent dosage on the adsorption efficiency of chromium ions using foxtail millet shell were evaluated in batch experiments [37]. The kinetics data of biosorption of chromium ions processes was best explained by pseudo-second- order kinetic model. In addition, the intraparticle diffusion model revealed multiple curves lines which did not pass through the origin; thus, the boundary layer diffusion controlled the biosorption to some degree. Nonlinearity was observed, indicating that three steps took place during the whole adsorption process. The first step was attributed to the diffusion of metal ions through the solution to the external surface adsorbent, or the boundary layer diffusion of solute molecules. The second step described the gradual biosorption stage, where intraparticle diffusion was the rate-limiting step. The third step was attributed to the final equilibrium stage where the intraparticle diffusion started to slow down [37]. The biosorption isotherm for Cr ions was well represented by Langmuir model. The optimal conditions were pH of 5.0, temperature of 25.0°C and contact time of 120.0 min. The biosorption capacity was 11.70 mg/ g for Cr ions at the optimal conditions at a biosorbent dosage of 4.0 g/L (Table 1) [37].

## Copper (Cu (II))

Low concentrations of Cu are essential and required by the body for enzyme synthesis, and tissue and bone development; however, excess amounts are toxic and carcinogenic. The acceptable limit of copper in drinking water is 1.3ppm according to the EPA [8]. Cu (II) is a dangerous and toxic heavy metal when its concentration exceeds this standard limit. Several technologies have been employed to remove copper from wastewater including as precipitation, cementation, classical and advanced oxidation process and ion exchange. These techniques are too expensive and ineffective when the metal ion concentrations in solution are less than 100 ppm [39]. Ben-Ali et al. (2017) studied the biosorption of copper (Cu (II)) onto untreated pomegranate peel (PGP) [39]. The studied parameters were, the initial metal concentration, the pH of the solution, the particle size, the temperature and contact time. The optimal operating conditions for Cu (II) adsorption were pH 5.8, for a particle size of 630  $\mu$ m, at a temperature of 313K, and a contact time of 2 h. The adsorption capacity increased from 1.54 mg/g to 6.64 mg/g when the initial metal concentration increased from 10 mg/L to 50 mg/L until it reached a constant value when no more copper ion was removed [39]. Langmuir isotherm model fitted quite well with the experimental data with a  $q_m$  value of

30.12mg/g at 303K. The Langmuir constant RL was in the range of (0.034-0.344 (L/mg).) for initial metal concentration values ranging from 10 to 100 mg/L. This value suggested a favorable adsorption of the copper ions onto PGP. The kinetic data fitted well to pseudo-second order. The thermodynamic parameters the standard enthalpy ( $\Delta H^\circ$ ), standard entropy ( $\Delta S^\circ$ ) for biosorption of copper onto PGP were 67.20 kJ/mol) and 239J/mol/K suggesting a spontaneous endothermic adsorption of Cu (II) on pomegranate peel (Table 4) [39]. The calculated negative value for  $\Delta G^\circ$  suggested a spontaneous process and a positive value for  $\Delta S^\circ$  indicated the affinity of the adsorbent to copper ions [39].

Karuiki et al. (2017) studied the potential of roger's mushroom (*Lepiota hystrix*) biomass in the biosorption of copper from aqueous solutions [40]. The efficiency of biosorption was tested in batch experiments and the analysis of FTIR spectrum revealed that the metal ions uptake by roger mushroom involved interaction of Cu (II) ion and hydroxyl, carboxyl and carbonyl groups of the biomass at an optimum pH of 4.5 and sorbent mass of 1.5g [40]. Biosorption capacity was found to be 8.9 mg/g at a contact time of 40 min and initial metal ion concentration of 500  $\mu$ g/L. The biosorption process followed second order kinetics and fitted the Langmuir isotherm model [40].

Ferreira da Silva et al. (2018) performed batch studies on the adsorption of Cu (II) ions using carnauba straw powder (CSP) as biosorbent [41]. The following parameters were evaluated copper solution concentration, pH, biosorbent size and dosage, adsorption time, and temperature. The optimal conditions were obtained at pH 6, 50 °C, and 10 g/L of biosorbent with a biosorption capacity of 9.5 mg Cu (II)/g biosorbent [41]. A decrease in copper ions uptake was observed with the increase of Cu (II) concentration and Cu (II) removal capacity was improved with reduction of CSP granule size. Adsorption data fitted well to the Langmuir isotherm and pseudo-second order kinetic models. The process was both spontaneous and exothermic (Table 1) [41].

Sostarić et al. (2018) studied the biosorption of Cu (II) onto raw apricot shell (SH) and alkali- modified apricot shell (SHM) [42]. The kinetic data of biosorption of Cu (II) onto SH and SHM fitted well with pseudo- second order model indicating that the biosorption of Cu (II) involved complexation and ion exchange mechanism [42]. The equilibrium data for biosorption of Cu (II) onto SH and SHM both fitted best the Sips isotherm model and the maximum biosorption capacity  $q_m$  from Langmuir isotherm were 4.24 and 8.99 mg/g for SH and SHM respectively (Table 1) [42].

Peng et al. (2018) investigated the biosorption behavior and the mechanism of copper (Cu) onto foxtail millet shell as a new natural biosorbent in aqueous solution [37]. The effects of pH (2.0– 6.0), contact time (5.0–240.0 min), initial metal ions concentration (25.0–300.0 mg/L), particle size (0.25–2.0 mm) and biosorbent dosage (1.0–6.0 g/L) on the adsorption efficiency of the target metals using foxtail millet shell were evaluated in batch experiments. The kinetics data for the biosorption of Cu (II) ions fitted well to the PSO kinetic model. The intraparticle diffusion model revealed multiple curved lines which did not pass through the origin; thus, the boundary layer diffusion controlled the biosorption to some degree. Nonlinearity was observed, suggesting that three steps took place during the whole adsorption process.

The first step was attributed to the diffusion of metal ions through the solution to the external surface adsorbent, or the boundary layer diffusion of solute molecules. The second step described the gradual biosorption stage, where intraparticle diffusion was the rate-limiting step. The third step was attributed to the final equilibrium stage where the intraparticle diffusion started to slow down. The biosorption isotherm for Cu ions fitted well to the Freundlich isotherm indicating that of Cu biosorption was a multi-layer process at solution pH of 5.0, temperature of 25.0°C and contact time of 120.0 min. From the Langmuir model, the biosorption capacity was 11.89 mg/g at the operational conditions of pH of 5.0, biosorbent dosage of 4.0 g/L, contact time of 120.0 min and temperature of 25.0°C (Table 1) [37].

Singh et al. (2017) investigated the biosorption of Cu<sup>2+</sup> onto powder derived from Aloe vera leaves from aqueous solution [43]. The highest removal percentage were observed at the optimal conditions of: 2 h contact time, 20 mg/L of initial Cu<sup>2+</sup> concentration, adsorbent dose 2 g, pH 5 and temperature 45 °C. The biosorption of Cu<sup>2+</sup> ions was a spontaneous and endothermic process. The negative  $\Delta S^\circ$  value suggested a decrease in randomness at the solid/liquid interface during the adsorption process [43].

Kebede et al. (2018) studied the biosorption of copper ions from industrial effluent onto Moringa stenopetala seed powder [38]. The optimal absorption conditions were pH 5.0 and an equilibrium time of 30min. The adsorption equilibria data fitted the Freundlich isotherm ( $R^2 = 0.974$ ) more than the Langmuir isotherm. The maximum adsorption capacity ( $q_m$ ) was found to be 10.20 mg/g (Table 1) [36]. The kinetic adsorption data were well defined by the pseudo-second order model ( $R^2=1$ ). The calculated thermodynamic parameters  $\Delta H^\circ$  and  $\Delta S^\circ$  were 54.55 KJ/mol and 199.45 J/K/mol respectively (Table 4). The positive value of  $\Delta H$  suggested that the adsorption of copper ions on Moringa seed powder was an endothermic process [38].

Kumar et al. (2018) investigated the use of cellulose extracted from rice husk that has been functionalized through free radical grafting with a binary vinyl monomer mixture of 2-acrylamido-2-methylpropane sulfonic acid and acrylic acid in the presence of N, N'-methylene bisacrylamide cross-linker (Cell-g-AASO3Hco-AAc) as a biosorbent for copper (Cu(II)) from aqueous solution [20]. The adsorption characteristics of the grafted copolymer (Cell-g- AASO3Hco-AAc) were studied as a function of contact time, temperature, pH, and concentration. The optimal adsorption conditions for Cu (II) ions were pH 6.0, temperature of 30°C and a contact time of 120 min [20]. Among the various kinetic and adsorption isotherm models, the experimental adsorption data were best fitted to pseudo-second-order kinetic model and Langmuir isotherm model. The maximum sorption capacity from Langmuir isotherm was 109.77 mg/g for Cu (II) ions (Table 1) [20].

## Lead

When Lead and its compounds enter the body, they negatively impact the nervous, cardiovascular, hematopoietic, kidney, digestive, endocrine and other systems. For example, long term

drinking of water containing high levels of lead can cause anemia, brain damage, mental deficiency, anorexia, and the inhibition of enzyme activity [8]. Zaidi et al. (2018) reported the biosorption of Pb (II) from simulated wastewater by modified *Artocarpus odoratissimus* (Tarap leaves) [13]. The following parameters were investigated: pH, ionic strength, interference effect, regeneration and column (dynamic) studies. The NaOH modified Tarap leaves (TLN) and EDTA modified TL (TLE) had enhanced biosorption capacity compared to the pristine *A. odoratissimus* Tarap leaves (TL). All the biosorbents reached equilibrium within 60 min of shaking. The initial rate of biosorption increased for all biosorbents the first 10 min indicating fast adsorption of Pb (II) onto the surface of the biosorbent. The removal rate was in the order TLNE > TLN > TL > TLE. The adsorption of Pb (II) by all of the biosorbents was affected by the pH of medium. The optimum pH for the removal of Pb(II) was observed between pH 5 and 6. The effect of ionic strength was also investigated, for all the four adsorbents, At very low salt concentration (0.01 mol/L), TL was the most affected by ionic strength compared to the others. At high salt concentrations (1.0 mol/L) TLNE showed greatest decrease in the adsorption of Pb (II). This meant that TLNE was very sensitive to the presence of salt and the existence of salt in the adsorption of Pb (II) by TL was less impactful when compared to TLNE. Adsorption isotherm data point for the double modified adsorbent (TLNE) had the highest adsorption capacity. The Redlich-Peterson (RP) model showed the highest correlation coefficient ( $R^2$ ) compared to the other models for the adsorption of Pb (II) onto TL, TLN and TLE, while the Langmuir model had the best fit for TLNE. This study also showed that the kinetics of all the adsorbents followed the PSO model suggesting that the adsorption processes were all chemisorption. The dynamic study concluded that column containing higher bed heights of the adsorbent took more time to exhaust and able to adsorb a large amount of the Pb (II) [13]. The thermodynamic properties standard enthalpy ( $\Delta H^\circ$ ) and standard entropy ( $\Delta S^\circ$ ) for biosorption of Pb (II) onto TL, TLE, TLN and TLNE were (-14.68 kJ/mol and 34.84J/mol.K), (-72.26kJ/mol and -134.20J/mol.K), (11.50 kJ/mol and 110.06J/mol.K) and (-35.15 kJ/mol and -27.40 J/mol/K) respectively (Table 4) [13]. TL, TLE and TLNE were found to show negative  $\Delta H^\circ$  but positive  $\Delta H^\circ$  for TLN; this meant that the adsorptions of Pb (II) were endothermic for the first three of mentioned adsorbents and exothermic for TLN. In addition, negative values of  $\Delta S^\circ$  were observed for TLE and TLNE and positive values for TL and TLN indicating that the randomness of TLE and TLNE with Pb (II) at the interface of solid-liquid were increased with the increase of temperature while the opposite was true for TL and TLN. The calculated values of  $\Delta G^\circ$  negatively increased with the increase of temperature for TL and TLN while the reverse was true for TLE and TLNE. This suggested that the adsorption processes for TL and TLN were spontaneous but not for TLNE. None of the  $\Delta G^\circ$  values was in the range of 0 to 20 kJ/mol implying that the key reaction was due to chemisorption, thus supporting the results obtained from kinetics [13].

Šoštarić et al. (2018) investigated the biosorption of Pb (II) onto raw apricot shell (SH) and alkali-modified apricot shell (SHM) [42]. The kinetic data of biosorption of Pb (II) onto SH and SHM fitted well with PSO model. The applicability of this kinetic model

indicated that the biosorption of Pb (II) involved complexation and ion exchange mechanism. The equilibrium data for biosorption of Pb (II) onto SH fitted best the Sips isotherm model while that for SHM fitted the Freundlich isotherm. The maximum absorption capacity  $q_m$  from Langmuir isotherm were 22.19 and 33.39 mg/g for SH and SHM respectively (Table 1) [42].

Bartczak et al. (2018) studied the biosorption of lead Pb (II) ions onto peat [15]. Langmuir's isotherm model fitted the equilibrium data very well with a biosorption capacity of 82.31 mg (Pb<sup>2+</sup>)/g (Table 1) [15]. The optimal biosorption conditions were 15 min and pH 5.0. Irrespective of the pH of the reaction system, the effectiveness of the process was found to be significantly high for the biosorption of Pb (II) ions. This result was explained by the presence of acidic functional groups on the surface of peat [15]. At low pH values (1–3) there were no changes in the binding properties, which were modified only when the pH of the system was increased, due to the dissociation of hydrogen from the acid functional groups. The kinetic data fitted well to the pseudo-second-order kinetics model [15].

Herady et al 2018 investigated the biosorption of lead (Pb (II)) onto tomato waste (TW) and apple juice residue (AR) [4]. The effects of contact time, the pH of the solution, and sorbent dosage on the Pb (II) removal process were optimized. The equilibrium data fitted the Freundlich isotherm more than Langmuir isotherm model. The kinetic study data followed the PSO model. The biosorption capacity ( $q_m$ ) of Pb (II) onto tomato waste and apple juice residue biosorbents were found to be 152 mg/g and 108 mg/g, respectively (Table 1) [4]. The optimum pH for sorption of Pb (II) onto both biosorbent was 4.0. The sorption of Pb (II) rose with the increase in sorbent dosage from 0.025 mg to 0.100 mg/25 mL and reached a maximum at 95.6% removal (for TW biosorbents) and 90.8% (for AR biosorbents) [4].

Karuiki et al. (2017) studied the potential of rogers mushroom (*Lepiota hystrix*) biomass in biosorption of lead from aqueous solutions [40]. Batch experiments were conducted to test the efficiency of lead biosorption. The biosorption process followed the PSO kinetics model and fitted the Langmuir isotherm model. The analysis of FTIR spectrum revealed that the Pb (II) ions uptake by roger mushroom involved the interaction of Pb (II) ion and hydroxyl, carboxyl and carbonyl groups on the biomass at the optimum pH of 6.0 and sorbent mass of 2.1 g. The biosorption capacity was found to be 3.9 mg/g at a contact time 25 min and initial metal ion concentration of 300 µg/L (Table 1) [40].

Kebede et al. (2018) investigated the removal of lead (PbII) from industrial effluent using *Moringa stenopetala* seed powder [38]. The equilibrium isotherms, kinetic and thermodynamic models were studied. The optimum pH for biosorption of Pb (II) at an equilibrium time of 15 min was 5.0. The results of the adsorption equilibria fitted the Langmuir isotherm ( $R^2=0.983$ ) more than Freundlich isotherm. The maximum adsorption capacity ( $q_m$ ) was found to be 16.13 mg/g. The kinetic biosorption data fitted well to PSO model ( $R^2=1$ ). The calculated thermodynamic parameters  $\Delta H^\circ$  and  $\Delta S^\circ$  were 52.01 kJ/mol and 194.79 J/mol. K respectively (Table 4). The positive value of  $\Delta H$  indicated that the adsorption of metal ions on the adsorbent was an endothermic process [38].

Khoshsang & Ghaffarinejad (2018) investigated the biosorption of lead Pb (II) from aqueous solution onto Saffron flower waste [44]. Parameters studied included the effects of pH, the initial concentration, mixing method and time on the removal of lead ions. The adsorption results showed that the biosorption process reached equilibrium rapidly in 9 min. The maximum biosorption capacity for ultrasonic and shaking process, are 36.97 mg/g and 45.62 mg/g respectively. The biosorption kinetic data fitted well to PSO order model (Table 1) [44]. Three errors functions including Chi-square statistic ( $\chi^2$ ), root mean square error (RMSE) and average relative error (ARE) were used for isotherm optimization prediction that had the best fitting with Langmuir model [44].

### Iron and Manganese

Nunez-Gomez et al. (2019) recently studied the sorption equilibrium of the removal of metal ions and acids present in coal acid mine drainage (AMD) using shrimp shell (SS) as a biosorbent as well as the behavior of the continuous-flow removal process [45]. The Freundlich isotherm model was the most appropriate for fitting the experimental data with both synthetic solutions and natural AMD, indicating a metallic removal via a physisorption mechanism. The adsorption capacities obtained for Fe and Mn were 17.43 and 3.87 mg/g, respectively [45].

### Molybdenum

Ogata et al. (2018) investigated the biosorption of molybdenum (Mo) onto virgin and calcined wheat bran (WB) at different temperatures [14]. The amount of Mo biosorbed increased with increasing temperature and decreasing pH of the solution. The amount of Mo adsorbed on virgin WB was greater than that adsorbed on WB treated with different concentrations of hydrochloric acid, which suggested that the adsorption mechanism was related to the three-dimensional protein structure [14]. The optimal pH for biosorption of Mo was approximately 1.5 and as the pH increased, the amount of Mo biosorbed decreased. At neutral pH, the biosorption site (hydroxyl groups) were negatively charged, which increased electrostatic repulsion between Mo species and WB surface. The biosorption capacity  $q_m$  was dependent on the concentration of the hydrochloric acid treatment WB6.0 (16.1 mg/g) < WB 1.0 (19.9 mg/g) < WB 0.1 (21.7 mg/g) < WB0.01 (23.2 mg/g) < WB (24.7 mg/g) [14]. The amount of Mo adsorbed decreased with decreasing pH, which suggested that the protein structure was altered by hydrochloric acid, and subsequently the biosorption sites for Mo were destroyed. The experimental data fitted well to PSO kinetic model, which indicated that the adsorption of Mo was controlled by chemical sorption involving valence forces, through sharing or exchanging of electrons between adsorbate and biosorbent [14]. The thermodynamic parameters standard enthalpy ( $\Delta H^\circ$ ), standard entropy ( $\Delta S^\circ$ ) for WB and WB1000 were (10.6 kJ/mol and 28.6 J/mol K) and (11.6 kJ/mol and 41.2 J/mol) respectively (Table 4) [14]. The positive values of  $\Delta H^\circ$  suggested that the biosorption process was endothermic while the positive value of  $\Delta S^\circ$  indicated increased randomness at the solid/solution interface during the biosorption of Mo onto the biosorbents. The values of  $\Delta G^\circ$  for all the ions-biosorbent systems were negative at different temperatures indicating the spontaneous behavior of the system [14].

## Nickel

Nickel is an essential life element, with minimal quantity required in the human body. The normal body requirement is 10.00 mg of the nickel and the blood normal concentration is 0.11 mg/L. Nickel ions can penetrate through the pores and sebaceous glands inside the skin, leading to allergic inflammation of the skin [8]. Excessive body daily intake in excess of 250mg causes dermatitis, respiratory disorders and respiratory tract cancer, anemia, encephalopathy, hepatitis, gastrointestinal distress, pulmonary fibrosis, renal edema, skin allergies, headaches, dizziness and virulent tumors [46]. Using artificial neural network (ANN) and adaptive neuro-fuzzy interference system (ANFIS) modelling Souza et al. (2018) compared the biosorption of nickel ( $\text{Ni}^{2+}$ ) onto four agro-wastes (sugarcane bagasse (SB), orange peel (OP), passion fruit waste (PF) and pineapple peel (PP) [46]. The adsorption capacity was 63.50 mg/g, 58.79 mg/g, 46.84 mg/g and 39.15 mg/g for SB, OP, PF and PP respectively (Table 1) [46]. The results of the biosorption experiments revealed that sugarcane bagasse and orange peel presented the best adsorption performance for  $\text{Ni}^{2+}$  removal from aqueous solutions; even better than those of commercial activated carbon. The study also revealed that the biosorption capacity was affected by  $\text{pH}_{\text{ZPC}}$  and surface area. The  $\text{pH}_{\text{ZPC}}$  for SB, OP, PF and PP were 4.6, 4.9, 4.6 and 6.0 respectively. ANN and ANFIS were compared with the experimental data to determine the relationship of four input parameters on  $\text{Ni}^{2+}$  biosorption capacities: initial biosorbent concentration, adsorption time,  $\text{pH}_{\text{ZPC}}$  and surface area [46]. The developed ANN and ANFIS accurately predicted the experimental data with correlation coefficient of 0.9926 and 0.9943, respectively. The Pearson's Chi-square measure was found to be 0.9508 for ANN and 0.5959 for ANFIS, indicating a small advantage of ANFIS over ANN [46].

Bartczak et al. (2018) studied the biosorption of nickel ( $\text{Ni}$  (II)) ions onto peat [15]. The equilibrium data fitted well with Langmuir's isotherm model with sorption capacity of 61.27 mg ( $\text{Ni}^{2+}$ )/g. Equilibrium adsorption was attained within 60 min (Table 1). The effectiveness of adsorption of  $\text{Ni}$  (II) ions from model solutions with a concentration of 50 mg/L increased as the pH increased. The kinetic data of the adsorption of  $\text{Ni}$  (II) ions on natural peat fitted well with pseudo-second-order kinetics model [15].

Kumar et al. (2018) studied the biosorption of nickel onto cellulose extracted from rice husk that has been functionalized through free radical grafting with a binary vinyl monomer mixture of 2-acrylamido-2-methylpropane sulfonic acid and acrylic acid in the presence of  $N,N'$ -methylene bisacrylamide cross-linker (Cell-g-AASO<sub>3</sub>Hco-AAc) [20]. The biosorption characteristics of Cell-g-AASO<sub>3</sub>Hco-AAc copolymer was studied as a function of contact time, temperature, pH, and concentration. The optimal biosorption conditions were pH 6.0 at a temperature of 30 °C after a contact time of 120 min. The kinetic and equilibrium experimental adsorption data were best fitted to PSO model and Langmuir isotherm model. The reported Langmuir adsorption isotherm maximum sorption capacity ( $q_m$ ) was 112.74 mg  $\text{Ni}$  (II) /g (Table 1) [20].

## Palladium

Gold and platinum group metals (Pd, Pt and Rh) exist on the earth's crust and are very important economically. Pd is especially

indispensable and used as a material for catalysts, fuel cells and electric devices. Its increasing economic importance and scarcity value has stimulated the importance of research for recovering Pd from industrial waste. Sato et al. (2019) investigated the biosorption of palladium Pd (II) ions onto silk fibroin (SF) fiber from silkworm, *Bombyx mori* [47]. The amount of Pd (II) adsorbed to SF was highest among the metals ( $\text{Pt}^{2+}$ ,  $\text{Os}^{4+}$ ,  $\text{Ir}^{4+}$ ,  $\text{Rh}^{3+}$  and  $\text{Ru}^{4+}$ ) used in both single and mixture solutions, which suggested high selectivity biosorption for  $\text{Pd}^{2+}$ . The optimum contact time for the biosorption of Pd (II) onto SF at 25 °C was 180 minutes and the PSO kinetic model was adequate for this system. Langmuir isothermal model fitted the isothermal experimental data with the parameters  $q_m$  and  $KL$  of 46.3 mg/g and 3.85 L/mg, respectively (Table 1) [47]. The calculated thermodynamic properties  $\Delta H^\circ$  and  $\Delta S^\circ$  were 5.34 kJ/mole and 64.1 J/mole.  $K$  respectively (Table 4) [47]. Negative values of  $\Delta G^\circ$  (from -13.0 to -17.5 kJ/mol at 298–353 K) were obtained, which indicated that the adsorption process was thermodynamically feasible and spontaneous at 298–353 K. Positive value of enthalpy change means the adsorption of  $\text{Pd}^{2+}$  onto SF was endothermic. This implies that the change of entropy is dominant to adsorption of  $\text{Pd}^{2+}$  to SF [47].

## Zinc

Acute zinc poisoning as a result of excessive zinc intake can cause, vomiting, diarrhea and other gastrointestinal symptoms while chronic zinc poisoning may result in anemia and other symptoms [8]. Šoštarić et al. (2018) studied the biosorption of Zn (II) on raw (SH) and alkali-modified apricot shell (SHM) [42]. The kinetic data of biosorption of Zn (II) onto SH and SHM fitted well with PSO model. The applicability of this kinetic model suggested that the biosorption of Zn (II) involved complexation and ion exchange mechanism. The equilibrium data for biosorption of Zn(II) onto SH fitted best the Langmuir and Sips isotherms model while that for SHM fitted the Freundlich isotherm. The maximum biosorption capacities ( $q_m$ ) from Langmuir isotherm were 5.06 and 8.65 mg/g for SH and SHM respectively (Table 1) [42]. Analysis of the cations released during the biosorption showed that the number of cations released from SHM was almost equal to the amount of metal ions adsorbed suggesting ion-exchange mechanism. Sodium ions were exchanged first, followed by  $\text{H}^+$  and other exchangeable cations [42].

Ngabura et al. (2018) studied the removal of zinc by hydrochloric acid modified durian peels (HAMDP) from wastewater [48]. Spectroscopic studies indicated that the predominant groups for Zn (II) biosorption onto HAMDP were hydroxyl, carbonyl, carboxyl and amides. The optimal conditions for biosorption of zinc onto HAMDP were pH 8, 0.5 g biosorbent dose, 4 h contact time at a reaction temperature of 313 K. Non-linear isotherm models suggested applicability of Tempkin and Langmuir models at 313 K. The Langmuir maximum adsorption capacity was 36.73 mg Zn /g (Table 1) [48]. Kinetic studies data fitted well to PSO model and Webber-Morris model indicating the possible role of diffusion of Zn (II) within the particles of HAMDP during the biosorption process. Freundlich constant and activation energy values confirmed the physical nature of the process. Thermodynamic studies indicated that the process was exothermic and spontaneous. Regeneration studies depicted that hydrochloric acid modified durian was economically viable. HCl served two significant purposes, namely, a

good modification reagent and best eluent for Zn (II) recovery [48].

Benakouche and Bounoughaz (2017) reported the electrosorption of zinc ions from aqueous solution on an artificial electrode based on banana wastes [16]. Langmuir isotherm model fitted the equilibrium experimental data with a maximal biosorption capacity ( $q_m$ ) of 3.42 mg/g [16]. Houda and Moussa (2017) studied the electro-sorption of Zn from wastewater onto activated banana peels treated with sulfuric acid then mixed with polyaniline to improve their electrical conductivity [47]. The study of electro-sorption process involved the optimization of different operational conditions of applied potentials, contact time and initial zinc concentrations. The effect of increase in initial zinc

concentration on the electro-sorption for low concentrations varied between 0.02M and 0.1M, rapidly increased Zn retention capacity that was explained by the occupation of the active sites available on the biosorbent surface and the rapid diffusion of the zinc ions onto the surface layer of biosorbent. Langmuir isotherm model fitted the equilibrium experimental data with a maximal biosorption capacity of 3.42mg/g (Table 1) [47]

**Table 1:** List of the best isotherm and kinetic models for biosorption of heavy metals on LCB

LCB	Heavy metals	Optimum pH/ time	Isotherm Modela	Kinetic Modelb	Maximum mono-layer adsorption capacity (mg/g)	Reference
Thiol Modified Sugarcane bagasse	As (III)	7.0/120 min	F	PFO	28.57	[34]
Thiol Modified Sugarcane bagasse	As(V)	7.0/120 min	F	PFO	34.48	[34]
Foxtail millet shell	Cd <sup>2+</sup>	5.0/120min	L	PSO	12.48	[37]
Aloe vera leaves	Cd (II)	5.0-6.0/90	F	PSO		[10]
Acid Modified Aloe vera leaves	Cd (II)	5-6.0/90min	L	PSO	66.23	[10]
Base Modified Aloe vera leaves	Cd (II)	5-6.0/90min	L	PSO	104.2	[10]
microalgae Parachlorellasp.	Cd (II)	7.0/20min	L	PFO	96.2	[36]
NaOH modified Sudan grass	Cd (II)	5-7/20min	L	PSO	7.76	[11]
Sudan grass	Cd (II)	7.5/90min	L	PSO	1.52	[11]
Eucalyptus leaf residue (ELR)	Cd (II)	3.8/500min	L	PSO	15.18	[18]
NaOH modified Eucalyptus leaf residue (BELR)	Cd (II)	3.8/240min	L	PSO	16.86	[11]
Moringa stenopetala seed powder	Cd (II)	5.0/15 min	L	PSO	23.26	[38]
Foxtail millet shell	Cr (VI)	5.0/120min	L	PSO	11.7	[37]
Acrylonitrile grafted banana peels	Cr (VI)	3.0/120min	L	PSO	6.17	[3]
Apricot shell (SH)	Cu <sup>2+</sup>	NA	S	NA	4.24	[42]
Modified Apricot shell (SHM)	Cu <sup>2+</sup>	NA	S	NA	8.99	[42]
Untreated Pomegranate peel	Cu <sup>2+</sup>	5.8/120min	L	NA	30.12	[39]
Foxtail millet shell	Cu <sup>2+</sup>	5.0/120min	F	PSO	11.89	[37]
Mushroom biomass	Cu <sup>2+</sup>	4.5/40min	L	PSO	8.9	[40]
Moringa stenopetala seed powder	Cu <sup>2+</sup>	5.0/15 min	L	PSO	10.2	[38]
Grafted cellulose (Cell- g-AASO3Hco- AAC)	Cu <sup>2+</sup>	6.0/120min	L	PSO	109.77	[20]
Shrimp Shell	Fe <sup>2+</sup>			NA	17.43	[45]
Peat	Pb <sup>2+</sup>	5.0/15min	L	PSO	82.31	[15]
Modified Apple juice residue	Pb <sup>2+</sup>	4.0/60min	F	PSO	108	[4]
Eucalyptus leaf residue (ELR)	Pb <sup>2+</sup>	3.8/900min	L	PSO	44.71	[18]
NaOH modified Eucalyptus leaf residue (BELR)	Pb <sup>2+</sup>	3.8/900min	L	PSO	48.9	[18]
Modified Tomato waste	Pb <sup>2+</sup>	4.0/75min	F	PSO	152	[4]
Tarap Leaves (TL)	Pb <sup>2+</sup>	5-6/60min	RP	PSO	75.14	[13]
EDTA modified Tarap Leaves (TLE)	Pb <sup>2+</sup>	5-6/60min	RP	PSO	53.26	[13]
NaOH Modified Tarap leave (TLN)	Pb <sup>2+</sup>	5-6/60min	RP	PSO	109.7	[13]
NaOH-EDTA modified Tarap leaves (TLNE)	Pb <sup>2+</sup>	5-6/60min	L	PSO	154.8	[13]
Mushroom biomass	Pb <sup>2+</sup>	6.0/25min	L	PSO	3.9	[40]
Moringa stenopetala seed powder	Pb <sup>2+</sup>	5.0/15 min	L	PSO	16.13	[38]

Saffron flower waste	Pb <sup>2+</sup>	6.0/9min	L	PSO	45.62	[44]
Banana peel	Pb <sup>2+</sup> /Ni <sup>2+</sup>	4.5/60min	L	PSO	13.4/7.29	[50]
Coconut shell	Pb <sup>2+</sup> /Ni <sup>2+</sup>	4.0/60min	L	PSO	10.5/2.11	[50]
Eucalyptus	Pb <sup>2+</sup> /Ni <sup>2+</sup>	4.5/90min	L	PSO	11.7/2.79	[50]
Piassava	Pb <sup>2+</sup> /Ni <sup>2+</sup>	4.5/210min	L	PSO	7.37/1.56	[50]
Spent coffee grounds	Pb <sup>2+</sup> /Ni <sup>2+</sup>	4.5/90min	L	PSO	14.8/2.35	[50]
Water hyacinth	Pb <sup>2+</sup> /Ni <sup>2+</sup>	3.5/30min	L	PSO	15.2/6.06	[50]
Grafted cellulose (Cell- g-AAS03Hco-AAC)	Ni <sup>2+</sup>	6.0/120min	L	PSO	112.74	[20]
Silk fibroin (SF) fiber	Pd <sup>2+</sup>	/180min	L	PSO	46.3	[47]
Shrimp Shell	Mn	8.0/	F	NA	3.87	[45]
Wheat bran	Mo	1.5/6h	L	PFO	80.6	[14]
Calcined Wheat bran	Mo	1.5/6h	L	PFO	84	[14]
Eucalyptus leaf residue (ELR)	Ni <sup>2+</sup>	3.8/500min	L	PSO	10.68	[18]
NaOH modified Eucalyptus leaf residue (BELR)	Ni <sup>2+</sup>	3.8/240min	L	PSO	14.09	[18]
Peat	Ni <sup>2+</sup>	5.0-7.0/30min	L	PSO	61.27	[15]
Orange peel	Ni <sup>2+</sup>	NA	NA	NA	63.5	[46]
Passion fruit waste	Ni <sup>2+</sup>	NA	NA	NA	46.84	[46]
Pineapple	Ni <sup>2+</sup>	NA	NA	NA	39.15	[46]
Sugarcane bagasse	Ni <sup>2+</sup>	NA	NA	NA	63.5	[46]
Aloe vera leaves	U(VI)	4.0/90min	F	PSO	NA	[10]
Acid modified Aloe Vera leaves	U(VI)	4.0/90min	L	PSO	370.4	[10]
Base modified Aloe vera leaves	U(VI)	4.0/90min	L	PSO		[10]
Banana peel	Zn <sup>2+</sup>	5.8/5-10min	L	NA	3.42	[49]
Foxtail millet shell	Zn <sup>2+</sup>	5.0/120min	F	PSO	10.59	[37]
Modified banana peels	Zn <sup>2+</sup>	-/10min	L	NA	3.42	[16]

### LCB: lignocellulosic biomass

A L: Langmuir model  $q = \frac{q_m \cdot K_a \cdot C_e}{1 + K_a \cdot C_e}$ ; F: Freundlich model  $q = K_f \cdot C_e^{\frac{1}{n_f}}$ ;

T: Temkin model  $q = B \ln a_r + B \ln C_e$   $B = \frac{RT}{b_r}$ ; S: Sips:  $q = \frac{q_m \cdot K_a \cdot C_e^n}{1 + K_a \cdot C_e^n}$

BS: Brouers-Sotolongo  $q = q_m \left(1 - \exp(-K_{BS} C_e^\alpha)\right)$

T: Toth:  $\left(\frac{C_{eq}}{q_{eq}}\right)^m = \frac{1}{q_{max} b_T} + \frac{1}{(q_{max})^{n_T}} C_{eq}^{n_T}$

B PFO: Pseudo-first order kinetic model; PSO:  $q_t = q_e \left(1 - \exp(-k_1 t)\right)$ ;

PSO Kinetic model  $q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$

NA: Not available

### Biosorption of multiple metal ions

Metals are leached into natural water bodies such as rivers, lakes and groundwaters resulting in the coexistence of different metal ions in aqueous solution. Wastewater from industries and mining operations also contain different ions in their compositions. It is therefore imperative that biosorption of multi metal systems is important [17]. da Silva Correira et al. (2018) [50] studied the biosorption of Pb(II) and Zn(II) simultaneously from water onto six residual plant materials (coconut shell, banana peel, spent coffee grounds, eucalyptus bark, piassava (*Attalea funifera*) and water hyacinth (*Eichornia crassipes*). The effect of pH on biosorption of Pb<sup>2+</sup> and Ni<sup>2+</sup> ions was investigated. The highest values for

biosorption capacity were found at pH equal to 4.0, 4.5 and 3.5 for Pb<sup>2+</sup>, for coconut shell, eucalyptus bark and water hyacinth respectively while for banana peel, spent coffee grounds and piassava had the maximum biosorption capacity at pH 4.5. For Ni<sup>2+</sup> the maximum biosorption capacity for all the residual plant materials was obtained at pH 5. The percent removal of Pb<sup>2+</sup> at the pH of maximum adsorption was over 94% by all the biosorbents, whereas the percent removal of Ni<sup>2+</sup> ranged from 29.87% (piassava) to 72.35% (banana peel). The biosorption of Ni<sup>2+</sup> was lower than that of Pb<sup>2+</sup> regardless of the pH value. The adsorption kinetics were fitted to the PSO model for the both metals. The Langmuir isotherm was used to estimate the biosorption capacity of the biosorbents for mono and bicomponent solutions [50].

Zolgharnein et al. (2017) reported the biosorption of a ternary system of metals by modified *Buxus sempervirens* tree leaves [51]. Response surface methodology and desirability function were applied in the study of the ternary system made up of the simultaneous removal of Cu (II), Zn (II) and Ni (II) ions. *B. sempervirens* tree leaves successfully removed Cu (II), Zn (II) and Ni (II) from the aqueous solution. Modification of *B. sempervirens* tree leaves with various chemical agents, such as NaOH, HNO<sub>3</sub>, NaCl, H<sub>3</sub>PO<sub>4</sub> and SDS improved the uptake capacity of the biosorbent. The best modifier was NaOH. The Simplex lattice mixture design was successfully employed for optimization of the biosorption process. The effective factors on the biosorption process, such as pH, amount of biosorbent and initial concentrations of metal ion, were considered via the use of a crossed mixture process design. The biosorbent was characterized by SEM micrographs, a pH of point

of zero charge ( $\text{pH}_{\text{pzc}}$ ), a BET analysis of surface area, XPS, energy dispersive X-ray microanalysis (EDX) for elemental analysis/composition [51].

Corral-Bobadilla et al. (2019) recently reported the use of the Spent Mushroom Substrate (SMS) of *Agaricus bisporus* in a bioreactor for the removal of heavy metals present in industrial waters [52]. These metals include chromium, lead, iron, cobalt, nickel, manganese, zinc, copper and aluminum. The bioreactor containing 5 kg of SMS with a hydraulic retention times of 10- and 100- days in industrial waters with different groups of heavy metals resulted in the removal of between 80 to 98% of all contaminants. The best removal efficiencies and longevities were achieved when removing iron (III), nickel and cobalt from contaminated water at a pH of 2.5 [52].

Neris et al. (2019) studied modified water hyacinth (*Eichhornia crassipes*) as a biosorbent for  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  ions in a and tri-element system [17]. Water hyacinth was modified with NaOH (BWH) and  $\text{HNO}_3$  (AWH). The kinetic model that best fitted the single and tri-element experimental data for all the ions was the PSO model. The single-element adsorption data fitted the Redlich-Peterson, Freundlich and Sips isotherm model, while the multi-element system did not fit any of the models adequately. The maximum single-element adsorption capacities for BWH at 25.0 °C for  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  ions were  $28.6 \pm 3.9$ ,  $18.9 \pm 1.6$  and  $76.8 \pm 4.7$  mg//g, respectively. The selectivity order of BWH fiber in single and tri-element systems was  $\text{Pb}^{2+} \gg \text{Zn}^{2+} \geq \text{Ni}^{2+}$ . This order was attributed to the stability of the complexes formed by metal ions and the biosorbent material functional groups [17].

Feisther et al. (2019) reported the study of modified eucalyptus leaf residue (ELR) for the biosorption of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Ni}^{2+}$  from an aqueous solution in a single and tri metal system [18]. Raw eucalyptus leaf residue (ELR) was modified with 0.4M  $\text{HNO}_3$  (AELR) and 0.4M NaOH (BELR). The Langmuir model fitted the experimental equilibrium data very well. The maximum biosorption capacity (qm) at pH 3.8 for the raw ELR, for  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Ni}^{2+}$  in a single metal system, was 15 mg/g, 45 mg/g and 5mg/g, respectively. For the multi-metal system using the same molar concentrations of lead, cadmium and nickel in solution the best removal efficiency was obtained for the lead, followed by cadmium and then nickel. The biosorption capacities for lead and removal efficiencies obtained in the kinetics for lead were 2.53/ 2.61 mg/g and 50/54%, cadmium 2.47/ 2.59 mg/g and 10/11% and nickel 1.103/ 1.409 mg/ g and 7/8%, for ELR and BELR, respectively [18]. However, the biosorption equilibrium using the  $\text{Pb}^{2+}/\text{Cd}^{2+}/\text{Ni}^{2+}$  mixture revealed that there was competition between the metal ions for the active sites. The results of multi- metal equilibrium, according to the selectivity coefficients, showed a higher affinity of ELR for lead ions, followed by cadmium and nickel ions. The basic treatment of the biomass improved the metal removal capacity. The biosorption behavior in the batch system was modeled using a mass transfer kinetic model, considering that the biosorption rate was controlled by a Linear Driving Force model (LDF). The initial rate of removal of the Pb, Cd and Ni is faster using BELR, followed by AELR. The percent removal were 62, 70 and 52 for  $\text{Pb}^{2+}$ , 22, 26 and 20 for  $\text{Cd}^{2+}$  and 9, 11 and 8 for  $\text{Ni}^{2+}$  for ELR, BELR and AELR samples respectively. Therefore, the basic treatment improved the biosorption efficiency of the metal ions; the acid treatment

impaired the process against the results obtained with the sample without treatment [18].

Kebede et al. (2018) investigated the biosorption properties of *Moringa stenopetala* seed powder of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  ions at pH 5.0, 30oC, biosorbent dosage of 10g/L, and 200 rpm for 60min [38]. The maximum percentage adsorption of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  ions from synthetic wastewater were 99.65, 99.66 and 99.42%, as opposed to industrial effluent were 94.17, 94.67 and 92.81 respectively [38].

## Adsorption of Dyes

Dai et al. (2018) has reported that there are one hundred thousand types of commercial dyes with an annual production of over seven hundred thousand tons, most of which eventually are directly discharged into the aqueous environment [8]. The presence of these dyes in the aquatic environment is having a negative environmental impact on the quality of ecosystems. The deleterious human health impact of these dyes include allergy, dermatitis, skin irritation, cancer, and mutations. In addition, they prevent the transmission of light, which in effect interfere with the biological metabolism processes of the aquatic ecosystem. Most textile dyes in wastewater have complex aromatic molecular structures making them recalcitrant to biological degradation.

Adsorption is one of the most promising alternative of the various physio-chemical methods for removing dyes from aqueous media, due to its efficiency, high selectivity, low cost, ease of operation, simplicity, and availability in a wide range of experimental conditions. However, all these advantages are closely related to the nature of adsorbent material used in the dye adsorption processes. Dyes have been categorized as anionic dyes (direct, acid and reactive dyes); cationic dyes (alkaline dyes) and non-ionic dyes (disperse dyes). Anionic dyes are dependent on negative ions. They include many compounds from different types of dyes, structural differences (azo, anthraquinone, triphenyl methane and nitro dyes). They have a shared trait such as water-soluble ionic substituents. Acidic dyes, direct dyes and reactive dyes are anionic dyes [8].

## Anionic dyes

Stavrinou et al. (2018) investigated the biosorption of anionic (Orange G) dyes from wastewater onto Banana peels (BP), cucumber peels (CP) and potato peels (PP) [53]. The effects of pH, biosorbent dose, contact time and dye concentration were studied. The biosorption capacity for Orange G (OG) onto these biosorbent decreased in the order  $\text{CP} > \text{PP} > \text{BP}$  over the whole concentration range (10–300 mg/L). The equilibrium data for the biosorption of OG on BP, PP and CP fitted well with Langmuir isotherm. The maximum monolayer adsorption capacities for OG at pH 2 were found to be 20.9, 23.6 and 40.5 mg/g for BP, PP and CP respectively (Table 2). Adsorption kinetic models revealed that chemisorption was the dominant biosorption mechanism [53].

Juchen et al. (2018) studied the biosorption of reactive blue BF-5G dye, a reactive dye, by malt bagasse (MB) [54]. The effects of particle size, biosorbent dosage, effect of pH on the kinetics of biosorption isotherm and desorption were studied. The results

indicated that reactive blue BF-5G biosorption onto MB had optimum pH of 3.0 at a biosorbent dosage of 14 g /L while by the particle size had little influence on biosorption. The  $pH_{PZC}$  of MB was determined to be 5.4. The kinetic and equilibrium biosorption data fitted well to PSO model and the Langmuir isotherm model with a  $q_{max}$  of 42.58 mg/g (Table 2) [54].

Khan et al. 2108 studied the biosorption of reactive dye Eriochrome Black T (EBT) from aqueous solutions onto Microwave-assisted spent black tea leaves (MASTL) [25]. The effects of pH, contact time, temperature, adsorbent dose and EBT concentration, were optimized to evaluate the interaction of EBT with MASTL [25]. The biosorption of EBT was strongly dependent on pH with an optimum at pH 2.0. Langmuir model fitted well the equilibrium data with the monolayer biosorption capacity ( $q_m$ ) of 242.72 mg/g at 25°C (Table 2) [25]. The separation factor  $R_L$  varied from 0.0319 to 0.5693 at 25°C, which indicated that the biosorption process was favorable. The mean free energy of sorption ( $E_a$ ), which is the amount of energy released when one mole of ions is transferred to the solid surface from infinity in solution, was calculated to be 0.8737, 1.0071, and 1.4618 at 25, 40 and 60°C respectively. The thermodynamic  $\Delta H^\circ$  and  $\Delta S^\circ$  calculated from the temperature-dependent adsorption isotherms were 31.82 kJ/mol and 189.32 J/mol. K (Table 4) [25]. The negative  $\Delta G^\circ$  values (-24.55, -27.55 and -31.18 kJ/mol at 298, 313 and 333 K respectively) indicated that the adsorption was fairly feasible and spontaneous under the applied conditions. The decrease in  $\Delta G^\circ$  values with the increase of temperature suggested that the sorption of EBT was a favorable process, because of its rapid dehydration at higher temperature.  $\Delta G^\circ$  values from 0 to -20 kJ/mol indicates physisorption, while more negative than -40 kJ/mol represents chemisorption [25]. Similarly, adsorption is controlled by both physical and chemical interactions, when the corresponding values of  $\Delta G^\circ$  fall in the range of -20 to -40 kJ/mol. The positive values of  $\Delta S^\circ$  indicated that the adsorption process was random at solid/solution interface. The thermodynamic study concluded that the adsorption of EBT onto STL was thermally feasible, spontaneous, endothermic, highly random at solid/solution interface and physicochemical in nature [25].

Krishna et al. (2017) investigated the potential of Bengal gram fruit shell (BGFS), an agricultural byproduct to adsorb Acid Blue 25 (AB25) [55]. The effects of biosorbent dose, different dye concentration, solution pH, and temperature on the removal of Acid Blue 25 (AB25) were investigated in a batch system. The optimal conditions for the biosorption of AB25 onto BGFS were pH of 2 with 83.84% removal, biosorbent dose of 200 mg of BGFS with equilibrium being reached within 180 minutes. Equilibrium data were found to fit well with both the Langmuir and Freundlich models with a maximum monolayer biosorption capacity ( $q_m$ ) of 29.41 mg/g of AB25 onto BGFS (Table 2) [55]. The kinetic studies experimental data suggested that the PSO model was the best fit. In addition, thermodynamic parameters  $\Delta H^\circ$  and  $\Delta S^\circ$  values were -16.7920 kJ/mol and 196.6 J/mol. K respectively (Table 4) [55]. The biosorption process was spontaneous and exothermic in nature with negative values of  $\Delta G^\circ$  (-1.6031 to -0.1089 kJ mol<sup>-1</sup>). The negative  $\Delta G^\circ$  indicated the feasibility of physical biosorption process [55].

Feisther et al. (2019) studied the biosorption of Congo red

from aqueous solution onto functionalized cellulose extracted from rice husk (Cell-g-AASO<sub>3</sub>Hco-AAC) [20]. The functionalization was through free radical grafting with a binary vinyl monomer mixture of 2-acrylamido-2-methylpropane sulfonic acid and acrylic acid in the presence of N, N'-methylene bisacrylamide cross-linker. The effects of contact time, temperature, pH, and concentration on biosorption of Congo red dye onto Cell-g-AASO<sub>3</sub>Hco-AAC copolymer were studied. Congo red dye was removed under acidic pH of 2.2 in 8 h. PSO model and Langmuir isotherm model fitted the kinetic and equilibrium experimental adsorption data. The maximum sorption capacity ( $q_m$ ) from Langmuir adsorption isotherm was 15.54 mg/g, (Table 2) [20].

da Silva et al. (2019) studied the biosorption of Reactive Yellow B2R textile dye from aqueous solutions Residual onto chia-seed-oil-extraction (CSOE) biomass in a batch system [56]. The optimal biosorption conditions were pH 2.0 at 303K for an equilibrium time of 60 min. The kinetic and equilibrium experimental data were best fitted to pseudo second order and Toth isotherm with the maximum biosorption capacity ( $q_{eq}$ ) of 70.95 mg/g and the heterogeneity parameter of 1.2785 while the Langmuir isotherm gave a biosorption capacity ( $q_{eq}$ ) of 76.34 mg/g (Table 2) [56]. The thermodynamic parameters  $\Delta H^\circ$  and  $\Delta S^\circ$  were 1.5269 kJ/mol and 9.6 J/mol. K respectively (Table 4) [56]. These values indicated an endothermic process and that there was increased mobility and consequently disorganization of the molecules after the process. The  $\Delta G^\circ$  for this biosorption process evaluated at temperatures of 303, 313, and 323 K was -1.1395, -1.5038, and -1.5885 kJ mol<sup>-1</sup> respectively. These values indicated that the biosorption process was favorable, spontaneous and a physical adsorption [56].

### Cationic dyes

Stavrinou et al (2018) studied the biosorption of cationic dye Methylene blue from wastewater onto Banana peels (BP), cucumber peels (CP) and potato peels (PP) [53]. The effects of pH, biosorbent dose, contact time and dye concentration were investigated. The biosorption capacity over the methylene blue concentration range 10–80 mg/L decreased in the order BP > PP > CP while in the methylene blue concentration 80–300 mg/L the biosorption capacity decreased in the order BP > CP > PP [53]. The biosorption of MB on BP and PP followed the Langmuir isotherm whereas biosorption on CP followed the Freundlich isotherm for low MB concentration values and the Langmuir isotherm for high MB concentrations (Stavrinou et al 2018). The maximum monolayer adsorption capacities ( $q_m$ ) for MB at pH 6 were 211.9, 107.2 and 179.9 mg/g for BP, PP and CP respectively (Table 2) [53].

Gautam et al. (2018) investigated the removal of malachite green (MG) using acetylated sodium 2, 3 dicarboxyhemiacellulose (ASDCH) synthesized from pine needles [57]. Extracted hemicellulose was converted to sodium 2, 3-dicarboxyhemiacellulose (SDCH) without the acetylation reaction. The MG removal was very rapid reaching equilibrium within 60 min with  $q_{max}$  value of 88.84 mg/g, and 57.6 mg/g for ASDCH and SDCH, respectively (Table 2) [57]. The acetylated and dicarboxylated hemicellulosic material showed efficient dye adsorption with Langmuir adsorption capacity of 456.23 mg/g. PSO kinetic model and Freundlich isotherm fitted the kinetic and isotherm models, and experimental data closely [57]. The thermodynamic parameters standard enthalpy ( $\Delta H^\circ$ ), standard

entropy ( $\Delta S^\circ$ ) were 49.9 kJ/mol and 172.02 J/mol. K) respectively (Table 4) [57]. The positive value of  $\Delta H^\circ$  suggested the endothermic nature of adsorption while the positive value of  $\Delta S^\circ$  confirmed the increased randomness at the solid-solute interface during adsorption processes [57].

Kumar et al. (2018) investigated the use of functionalized cellulose extracted from rice husk (Cell-g-AASO<sub>3</sub>Hco-AAc) for the biosorption of cationic dyes malachite green and crystal violet from aqueous solutions [20]. The extract was functionalized through free radical grafting with a binary vinyl monomer mixture of 2-acrylamido-2-methylpropane sulfonic acid and acrylic acid in the presence of N, N'-methylene bisacrylamide cross-linker. The effects of contact time, temperature, pH, and concentration of dye on the biosorption characteristics of, Cell-g-AASO<sub>3</sub>Hco-AAc copolymer were studied. The optimal conditions were pH 7.0 in 90 min contact time. The PSO kinetic model and Langmuir isotherm model fitted the kinetic and equilibrium experimental adsorption data for both dyes. From Langmuir adsorption isotherm, maximum sorption capacities ( $q_m$ ) were 4.42 and 9.57 mg/g for malachite green and crystal violet respectively (Table 2) [20].

Koksharov et al. (2019) studied enzymatically and chemically modified flax fibrous material for the biosorption of methylene blue [19]. Flax fibrous material was chemically modified with sodium hydroxide (FFMSH), sodium borohydride (FFMSB), and sodium hydroxymethanesulfonate (FFMSHMS). Enzymatic modification involved cellulolytic preparation (FFMCP), CP and exo-galactosidase (FFMCPG), CP and exo-xylosidase (FFMCPX) and CP, G and X (FFMCPGX). The biosorption capacity to methylene blue were 18.4, 26.6, 53.8, 65.7, 51.963.5, 66.2 and 75.3 mg/g for FFM, FFMSH, FFMSB, FFMSHMS, FFMCP, FFMCPG, FFMCPX, FFMCPGX respectively [19].

Batch and dynamic biosorption studies of methylene blue (MB) onto walnut shell (WS) were performed by Liu et al. (2019) [21]. The biosorption capacity ( $q_m$ ) of MB onto WS was 80.4 mg/g at 318 K and the process was endothermic (Table 2) [21]. The adsorption kinetics and equilibrium processes were predicted by PSO kinetic model and Langmuir model, respectively [21].

Mokhtar et al. (2017) studied the potential of biosorption of azo dye, Methylene Blue (MB) onto five indigenous species of marine red, green and brown macro-algae [58]. The effect of various operational parameters such as pH (2–11), biosorbent dosage (0.2–1.2 g/L) and initial concentration (50–200 mg/L) were optimized. The optimal biosorption conditions were reported as 27 °C, pH 8 and 1.4 g/L dosage, where the MB removal achieved was 84% for an equilibrium time within 60–80 min for all algae species. The maximum biosorption capacities ( $q_m$ ) of MB at pH 8 and pH 11 were 84.5 mg/g and 85.1 mg/g, respectively (Table 2) [58]. Increase of initial MB concentration lead to increase of biosorption capacity. This suggested that *E. spinosum* has a high affinity towards MB dye. Both Freundlich and Langmuir isotherms were well represented by the equilibrium data with the maximum monolayer biosorption capacity ( $q_{max}$ ) estimated at 833.33 mg/g. The value of RL for this study was estimated as 0.37 indicating the biosorption was favorable. PSO kinetic model better fitted to the kinetic data [58].

Dallel et al. (2018) studied the potential for the biosorption

of cationic dye methylene blue (MB) onto the fibers of a Tunisian biomass "*Phragmites Australis*" in a batch system [24]. The effects of operational parameters such as pH, contact time, temperature, the mass of the fibers, the concentration of methylene blue, competition in adding salt and detergent were investigated. The optimal biosorption conditions were pH 8, biosorbent dosage of 0.5 g for an initial dye concentration 10 mg/L [24]. The biosorption capacity increased from 11.25 mg/g to 44.5 mg/g with an increase of the initial dye concentration from 10 mg/L to 50 mg/L. The biosorption capacity  $q_m$  for MB decrease from 7.4 mg/g to 0.8 mg/g at the optimal conditions when the amount of detergent increased [24]. To investigate the effect of salt, NaCl (0.5, 0.8 and 1.25 g) was added at the optimum condition, the presence of the salt decreased the biosorption capacity of methylene blue onto *Phragmites australis*. This was attributed to the competitive effect between methylene blue cations and salt cations for the sites available on the biosorption process onto the surface of biomass. Since Na<sup>+</sup> cations were smaller than methylene blue cations, they occupied the sites easily and quickly [24]. The kinetic and equilibrium data fitted well the PSO model and the Brouers-Sotolongo isotherm model respectively, thus assuming the fractal character of the process by (Dallel et al. 2018) [24]. The  $\Delta H^\circ$  and the  $\Delta S^\circ$  for the biosorption processes were -35.78 kJ/mol and -104.59 J/mol. K (Table 4) [24]. The negative value of  $\Delta H^\circ$  suggested the exothermic nature of the biosorption processes while the negative value of  $\Delta S^\circ$  revealed the decreased randomness at the solid-solution interface during the fixation of the dye cations on the sites of the *Phragmites australis* fibers. The values of  $\Delta G^\circ$  were negative indicating that the biosorption is spontaneous. The thermodynamic study revealed a spontaneous phenomenon of biosorption and confirms the chemisorption shown in desorption tests [24].

Shao et al. (2017) investigated the potential biosorption of methylene blue (MB) onto Defatted *Luminaria japonica* biomass (DLB) modified with sulfuric acid (DLB-S) [59]. The effects of biosorbent dose, initial pH, contact time, temperatures and initial MB concentrations were studied. The optimal biosorption conditions were pH 6, low biosorbent dose of 0.6 g/L, quasi-equilibrium time within 60 min and temperature of 308 K. The maximum MB biosorption capacities ( $q_{max}$ ) of DLB and DLB-S were 418.41 mg/g and 549.45 mg/g at the optimum conditions, respectively (Table 2) [59]. Langmuir models and Sips models described the equilibrium biosorption data while the PSO kinetic model fitted the kinetic biosorption data. The  $\Delta H^\circ$  and the  $\Delta S^\circ$  for the biosorption processes were (0.0134 kJ/mol and 198.09 J/mol. K) and (0.011 and 174.56 J/mol. K) for DLB and DLB-S respectively (Table 4) [59]. These thermodynamic parameters indicated that the biosorptions were spontaneous, endothermic processes. The biosorption of MB onto DLB-S mainly involved electrostatic interaction and complexation. The biosorption capacity of DLB-S was enhanced and the organic content leaching from DLB-S was effectively decreased after DLB was modified by sulfuric acid [59]. The free energy changes ( $\Delta G^\circ$ ) were negative, confirming the spontaneity of the adsorption process. The decrease in  $\Delta G^\circ$  value with increasing temperature indicated that adsorptions of MB on DLB and DLB-S became more favorable at higher temperature. The positive value of  $\Delta H^\circ$  further revealed that the adsorption processes were endothermic in nature. The positive value of  $\Delta S^\circ$  showed the increased randomness at the solid/solution interface during the adsorption of MB on the DLB

and DLB-S [59]. In addition, positive value of  $\Delta S^\circ$  reflected affinity of the adsorbent for MB. These results suggested MB adsorption on DLB, and DLB-S could occur spontaneously under the experimental conditions [59].

Islam et al (2019) investigated the biosorption of methylene blue (MB) with sulfonated peanut shells (PNS-SO<sub>3</sub>H) [22]. The effects of adsorption of pH, time, initial adsorbate concentration, and temperature in a batch system were evaluated. The biosorption capacity for MB increased from pH 3 to 10. The maximum biosorption capacity ( $q_m$ ) was 1250 mg/g for MB. In comparison

to the pristine peanut shell, the PNS-SO<sub>3</sub>H demonstrated about 100 higher adsorption capacity for MB [22]. Langmuir isotherm model fitted the equilibrium data while the kinetic data fitted the PSO model [22]. The thermodynamic properties  $\Delta H^\circ$  and  $\Delta S^\circ$  for biosorption of MB were found to be 12.24 kJ/mol and 55.26 J/mol.K respectively suggesting an endothermic process. The Gibbs free energy changes ( $\Delta G$ ) were calculated as -39.71, -46.34, and -67.92 kJ/mol at the experimental temperature of 23, 45, and 75 °C, respectively for the adsorption of MB indicating that the adsorption of MB onto PNS-SO<sub>3</sub>H was spontaneous under the experimental conditions [22].

**Table 2:** List of the best isotherm and kinetic models for biosorption of dyes on LCB

LCB	Dyes	Optimum pH/ time	Isotherm Model <sup>a</sup>	Kinetic Model <sup>b</sup>	Maximum monolayer adsorption capacity (mg/g)	Reference
Bengal gram fruit shell (BGFS)	Acid blue 25	2.0/180min	L & F	PSO	29.41	[55]
Microwave treated tea leaves	Eriochrome black T	2.0/250min	L	PSO	242.72	[23]
Modified Pine needles (ASCDH)	Malachite green	6.5/60 min	F	PSO	456.23	[57]
Grafted cellulose (Cell-g- AASO <sub>3</sub> Hco-AAc)	Malachite green	7.0/120min	L	PSO	4.42	[20]
Grafted cellulose (Cell-g-AASO <sub>3</sub> Hco- AAc)	Crystal violet	7.0/120min	L	PSO	9.57	[20]
Grafted cellulose (Cell-g- AASO <sub>3</sub> Hco-AAc)	Congo red	2.2/8h	L	PSO	15.54	[20]
Macro-alga of <i>Euchema Spinosum</i>	Methylene blue	4.0 /60-80 min	F & L	PSO	833.33	[58]
Walnut shell	Methylene blue	/90min	L	PSO	33.5	[21]
Defatted <i>Laminaria japonica</i> biomass (DLB)	Methylene blue	4.0-6.0/60 min	L, S	PSO	418.41	[59]
Modified Defatted <i>Laminaria japonica</i> biomass (DLB-S)	Methylene blue	4.0-10.0/60 min	S	PSO	549.45	[59]
Flax fibrous material	Methylene blue	NA	NA	NA	18.4	[19]
NaOH modified flax fibrous material (FFMSH)	Methylene blue	NA	NA	NA	26.6	[20]
NaBH <sub>4</sub> modified flax fibrous (FFMSB) material	Methylene blue	NA	NA	NA	53.8	[20]
CH <sub>3</sub> NaO <sub>3</sub> modified flax fibrous material (FFMSHMS)	Methylene blue	NA	NA	NA	65.7	[20]
Cellulolytic hydrolyzed- flax fibrous material (FFMCP)	Methylene blue	NA	NA	NA	51.9	[20]
Cellulolytic galactosidase hydrolyzed- flax fibrous material (FFMCPG)	Methylene blue	NA	NA	NA	63.5	[20]
Cellulolytic – xylosidase hydrolyzed flax fibrous material (FFMCPX)	Methylene blue	NA	NA	NA	66.2	[20]
Cellulolytic- Galactosidase –Xylosidase hydrolyzed flax fibrous material (FFMCPGX)	Methylene blue	NA	NA	NA	75.3	[20]

Sulfonated peanut shell	Methylene blue	10/30min	L	PSO	1250	[22]
Malt bagasse	Blue BF-5G	3.0/4h	L	PSO	42.58	[54]
KOH modified cypress cone chips	Rhodamine B	4/120min	L	PSO	239.5	[60]
Chia seed residue	Yellow B2R	2/60min	L & T	PSO	76. /70.95	[56]

### LCB: lignocellulosic biomass

A L: Langmuir model  $q = \frac{q_m \cdot K_a \cdot C_e}{1 + K_a \cdot C_e}$ ; F: Freundlich model  $q = K_f \cdot C_e^{1/n_f}$ ;

T: Temkin model  $q = B \ln a_r + B \ln C_e$   $B = \frac{RT}{b_r}$ ; S: Sips:  $q = \frac{q_m \cdot K_a \cdot C_e^{n_s}}{1 + K_a \cdot C_e^{n_s}}$

BS: Brouers-Sotolongo  $q = q_m \left(1 - \exp(-K_{BS} C_e^\alpha)\right)$

T: Toth:  $\left(\frac{C_{eq}}{q_{eq}}\right)^n = \frac{1}{q_{max} b_T} + \frac{1}{(q_{max})^{n_T}} C_{eq}^{n_T}$

B PFO: Pseudo-first order kinetic model; PSO:  $q_t = q_e \left(1 - \exp(-k_1 t)\right)$ :

PSO Kinetic model  $q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$

NA: Not available

### Biosorption of contaminants of emerging concern (CECs)

Contaminants of emerging concern (CECs) are chemicals present in many commercial products such as drugs (human and veterinary), illicit drugs, personal care products (PCPs), steroids and hormones, pesticides, surfactants, gasoline additives, industrial additives. They are organic chemicals found in treated wastewater in low concentrations, which can cause harm to human and animal health if not completely removed during the water treatment process [61]. Pharmaceuticals compounds have received more attention among the CECs because, of their increased worldwide consumption. These substances have persistent characteristics as they are developed to resist biodegradation and their metabolic stability increases the pharmacological action [62]. These CECs interact with biological systems, thus leading to acute and chronic damage to environmental biodata [63]. For example, endocrine disrupting chemicals have been linked to increased number of intersex fish, elevated female-to-male ratios, and physiological alterations in male fish [64]. In addition, human exposure to endocrine disruptors (through drinking water or from skin contact) is associated with cancerous tumors, birth defects and other developmental disorders [65]. The US Geological Survey (USGS) has reported that pharmaceutical compounds and hormones are frequently detected in wastewater treatment facilities [66] as well as in groundwater and/or untreated drinking water sources [67]. Several methods have been used to treat these CECs including chemical precipitation, activated carbon adsorption, ion exchange, evaporation and membrane processes with little success [68].

### Caffeine

Caffeine found in cold medicines, analgesics, anorectics, stimulants and cosmetics with transdermal uptake is a nervous system stimulant is sometimes classified as a pharmaceutical. Many advanced technologies, such as ozonation, advanced oxidative

processes, reverse osmosis, membrane filtration and adsorption have been investigated for the removal of caffeine from aqueous solution. Among these ozonation and adsorption onto activated carbon are methods with potential for large scale application, considering efficiency, cost and energy requirement of these processes. Unfortunately, both methods present disadvantages, such as possibility of forming toxic byproducts in the case of ozonation, and reduction of activated carbon efficiency caused by natural organic matter presence in water. In the case of adsorption processes, the cost of commercial activated carbons is limiting, leading to the necessity for the development of new materials with lower investment cost. One of the alternative potentials is grape stalk, which has been studied by [26]. Grape stalk (GS) was modified with phosphoric acid (MGS). The effects of pH, residence time and adsorbent concentration were investigated. The optimal conditions were found to be pH 2.0, 25 g/L of biosorbent and 15min as an incubation time for both GS and MGS. The equilibrium data fitted well the Sips model with correlation coefficients  $R^2$  equal to 0.994 and 0.999 and maximum adsorption capacities equal to 89.2 and 129.6 mg/g for both GS and MGS respectively [26].

### Pharmaceuticals

The use of pharmaceutical active compounds has been increasing all over the world. Most of these compounds end up in the environment or wastewater treatment plants, households, hospitals, industrial units and intensive animal-breeding farms [69]. Thus, their past and ongoing usage produces significant residues, which are introduced into the aquatic and terrestrial environments [27]. Human and veterinary antibiotics have been detected in many different matrices, inducing antibiotic-resistance among several bacterial strains, thus, reducing the therapeutic efficiency of antibiotics [27]. Most wastewater treatment plants (WWTPs) were not designed for treating pharmaceuticals resulting in partial removal efficiency. Despite public concerns about the negative impact of pharmaceuticals on the aquatic ecosystems, there are currently no regulations defining the amount of these chemicals permitted in wastewater streams or in drinking water. [27, 69].

Bi et al. (2018) investigated the biosorption of antibiotics tetracycline (TC) and oxytetracycline (OTC) onto furfural residues (FR) [70]. The equilibrium biosorption data of TC and OTC on FR fitted Langmuir isotherm model suggesting the homogeneity of the adsorption process due to the surface being covered with a single layer of adsorbate. The maximum biosorption capacities ( $q_{max}$ ) of TC and OTC on FR were 162 mg/g and 335 mg/g respectively indicating FR had a better adsorption capacity for OTC than TC at the same conditions (Table 3) [70]. The kinetic data for the biosorption of TC and OTC onto FR fitted well with the PSO model. The  $q_e$  values obtained from the PSO model were closer to experimental  $q_e$ . This indicated that the biosorption of TC and OTC onto FR was chemisorption in nature and the chemical adsorption

was the rate-controlling step [70].

Oickle et al. (2010) investigated the biosorption properties of LCB derived from wheat bran for its ability to remove enrofloxacin fluoroquinolone antibiotic from water [27]. The effects of contact time, pH and concentration were studied. The optimum pH at a contact time of 60min was 6.0. Three kinetic (PFO, PSO and intra-particle diffusion) and three isotherms (Langmuir, Freundlich and Sips) models were tested at pH 3.7 and 6. The kinetics followed the PSO model at both pH with a higher constant rate  $k_2$  at higher pH (3.88 g/mg/h at pH 6). The slower kinetics at pH 3.7 was due to intra-particle diffusion. The isotherm best fit obtained with Sips model indicated a heterogeneous monolayer adsorption of the antibiotic with a high maximum adsorption capacity of 91.5 mg/g at pH 6 (Table 3) [27].

Aruajo et al. (2018) studied the biosorption of Diclofenac (DCF), a widely used anti-inflammatory drug, onto *Moringa oleifera* (MO) seed husk in batch system [61]. Scanning electron microscopy (SEM) showed that the MO biomass possesses an enormous number of pores and a large specific area, indicating powerful adsorption capacity. The optimum pH for biosorption was 5. The kinetic data better fitted the PSO model, while the adsorption equilibrium data better fitted the Freundlich model [61]. Thermodynamic study revealed that the process was endothermic and non-spontaneous in nature. The mechanism proposed to explain the large amount of DCF adsorbed was the chemisorption process, which was facilitated by the electrostatic attraction between the DCF molecules and the functional groups present on the surface of the biosorbent, in addition to the pore volume and surface area of the adsorbent. It was postulated that the mechanism of biosorption was chemisorption facilitated by electrostatic attraction, volume and surface area of the biosorbent [61].

Biosorption of two CECs antibiotics sulfamethoxazole (SMX) and endocrine disrupting chemical bisphenol A (BPA) from contaminated water onto functionalized carbonaceous material derived from tea leaves (TW-SO<sub>3</sub>H) was studied by Ahsan et al. (2018a) [28]. The optimum pH for biosorption of both SMX and BPA onto TW-SO<sub>3</sub>H was 4.0. The Langmuir and Temkin isotherm models best fitted the experimental data for the BPA and SMX adsorption processes, respectively. From the Langmuir isotherm at 25 °C, the biosorption maximum capacities ( $q_{max}$ ) of SMX and BPA onto TW-SO<sub>3</sub>H were 258.87 mg/g and 236.80 mg/g respectively (Table 3) [28, 29]. The new biosorbent had the ability to form electrostatic interaction and  $\pi$ - $\pi$  stacking that allow the efficient removal of SMX and BPA. The kinetic studies data for the biosorption of SMX and BPA onto TW-SO<sub>3</sub>H fitted well with the PSO model. The thermodynamic parameters the standard enthalpy ( $\Delta H^\circ$ ), standard entropy ( $\Delta S^\circ$ ) for SMX and BPA were (-9.22 kJ/mol and -26.67 J/mol. K) and (-8.48 kJ/mol and -23.55 J/mol. K) respectively (Table 4) [28, 29]. The negative value of  $\Delta H^\circ$  indicated that the biosorption process was physical and exothermic in nature. The negative standard entropy change ( $\Delta S^\circ$ ) reflected decreased randomness at the solid-liquid interface during the adsorption of BPA on TW-SO<sub>3</sub>H. A negative  $\Delta G^\circ$  indicated that the adsorption process was spontaneous (Ahsan et al. 2018a).

Ahsan et al. (2018b) [29] also reported the biosorption of bisphenol (BPA) and sulfamethoxazole (SMX) on sulfonated coffee waste. The biosorption capacity increased with increasing initial concentration from 100 to 400mg/L for both CECs. The maximum biosorption of BPA onto CW-SO<sub>3</sub>H was observed at acidic pH range but showed little change in biosorption capacity over the whole acidic pH range. The calculated biosorption capacities of CW-SO<sub>3</sub>H were 271 mg/g and 256 mg/g towards the removal of BPA and SMX, respectively (Table 3) [29]. The synthesized biosorbent was capable to form  $\pi$ - $\pi$  interaction and electrostatic interaction that allow the efficient biosorption of BPA and SMX. The equilibrium data was best fitted to the Temkin isotherm model for the biosorption of BPA, while the Temkin and Langmuir models fitted better the biosorption of SMX. The calculated  $R_L$  value for SMX biosorption was 0.284 indicating the biosorption of SMX onto CW-SO<sub>3</sub>H is favorable at the studied experimental conditions [29]. The kinetic data for the biosorption of BPA and SMX onto CW-SO<sub>3</sub>H fitted well to PSO kinetic model. The Intra-particle diffusion model of Weber and Morris indicated that the pore diffusion was not the only rate controlling step since two straight lines were obtained none of which passed through the origin [29]. The thermodynamic parameters such as the standard enthalpy ( $\Delta H^\circ$ ), standard entropy ( $\Delta S^\circ$ ) for SMX and BPA were (-6.82 kJ/mol and -19.30 J/mol. K) and (-7.98 kJ/mol and -23.43 J/mol. K) respectively (Table 4) [29]. The negative value of  $\Delta H^\circ$  demonstrated the biosorption was physical and exothermic in nature. The negative standard entropy change ( $\Delta S^\circ$ ) reflected decreased randomness at the solid-liquid interface during the adsorption of BPA on CW-SO<sub>3</sub>H. The negative  $\Delta G^\circ$  value obtained in this study indicated the spontaneous nature of SMX and BPA biosorption onto CW-SO<sub>3</sub>H. In addition, the value of  $\Delta G^\circ$  increased with the increasing temperature indicating that the biosorption processes of BPA and SMX are more favorable at a lower temperature. The obtained  $\Delta G^\circ$  values were in the range of 0.08 to 1.07 kJ/mol indicating that the biosorption process was mostly physical in nature [29].

Islam et al. (2019) investigated biosorption of tetracycline (TC) onto sulfonated peanut shell (PNS-SO<sub>3</sub>H) [22]. The effects of pH, time, initial adsorbate concentration, and temperature on the biosorption process were evaluated. The biosorption capacity decreased from pH 3 to 10 [22]. The equilibrium and kinetic data for the biosorption of TC onto PNS fitted well with Langmuir isotherm model and PSO respectively. The maximum biosorption capacity for TC on PNS ( $q_{max}$ ) was 303 mg/g [22]. The thermodynamic properties  $\Delta H$  and  $\Delta S$  were estimated to be 14.55 kJ/mol and 49.08 J/mol. K respectively indicating an endothermic process. The  $\Delta G$  was calculated as -0.20, -9.72, and -25.72 kJ/mol at the experimental temperature of 23, 45, and 75 °C, respectively suggesting that the adsorption of TC onto PNS-SO<sub>3</sub>H was spontaneous under the experimental conditions [22].

**Table 3:** List of the best isotherm and kinetic models for biosorption of Contaminants of emerging concern on LCB

LCB	CEC	Optimum pH/time of maximum adsorption	Isotherm Model <sup>a</sup>	Kinetic Model <sup>b</sup>	Maximum monolayer adsorption capacity (mg/g)	Reference
Sulfonated Coffee waste	Bisphenol A	4.0/	T	PSO	271	[29]
Grape Stalk	Caffeine	2.0/40min	S	NA	68.63	[26]
Modified Grape stalk	Caffeine	2.0/30min	S	NA	96.4	[26]
Modified Wheat bran	Enrofloxacin	6.0/60min	S	PSO	91.5	[27]
Furfural residues	Oxytetracycline	-NA	L	PSO	335	[70]
Sulfonated Coffee waste	Sulfamethoxazole	4.0/	T & L	PSO	256	[29]
Sulfonated peanut shell	Tetracycline	3.0/60min	L	PSO	303	[22]
Sulfonated tea leaves	Sulfamethoxazole	4.0/	T	PSO	258.87	[28, 29]
Sulfonated tea leaves	Bisphenol A	4.0/	L	PSO	236.8	[28, 29]
Furfural residues	Tetracycline	-	L	PSO	162	[70]

A L: Langmuir model  $q = \frac{q_m \cdot K_a \cdot C_e}{1 + K_a \cdot C_e}$ ; F: Freundlich model  $q = K_f \cdot C_e^{\frac{1}{n_f}}$ ;

T: Temkin model  $q = B \ln a_T + B \ln C_e$   $B = \frac{RT}{b_T}$ ; S: Sips:  $q = \frac{q_m \cdot K_a \cdot C_e^{\gamma}}{1 + K_a \cdot C_e^{\gamma}}$

BS: Brouers-Sotolongo  $q = q_m (1 - \exp(-K_{BS}(C_e)^{\alpha}))$

T: Toth:  $\left(\frac{C_{eq}}{q_{eq}}\right)^{nt} = \frac{1}{q_{max} b_T} + \frac{1}{(q_{max})^{n_T}} C_{eq}^{n_T}$

B PFO: Pseudo-first order kinetic model; PSO:  $q_t = q_e (1 - \exp(-k_1 t))$ ;

PSO Kinetic model  $q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$

NA: Not available

**Table 4:** Thermodynamic parameters of LCB and different adsorbate

LCB	Adsorbate	$\Delta H_o$ (kJ/mol)	$\Delta S_o$ (J/mol.K)	$E_s$ (kJ/mol)	Reference
<i>Moringa stenopetala</i> seed powder	Cd <sup>2+</sup>	54.59	201.94	NA	[38]
Microalgae <i>Parachlorella</i> sp.	Cd <sup>2+</sup>	71.85	331.28	NA	[36]
Aloe vera leaves	Cd <sup>2+</sup>	1.5	64	34.9	[10]
NaOH modified Sudan grass	Cd <sup>2+</sup>	2.214	14.11	10	[11]
Sudan grass	Cd <sup>2+</sup>	-21.53	-87.18	7.5	[11]
<i>Moringa stenopetala</i> seed powder	Cu <sup>2+</sup>	54.55	199.45	NA	[38]
Raw pomegranate peel	Cu <sup>2+</sup>	67.2	239	32.60-40.57	[39]
<i>Moringa stenopetala</i> seed powder	Pb <sup>2+</sup>	52.01	194.79	NA	[38]
Tarap Leaves (TL)	Pb <sup>2+</sup>	-14.68	34.84	NA	[13]
EDTA modified Tarap Leaves (TLE)	Pb <sup>2+</sup>	-72.26	-134.2	NA	[13]
NaOH Modified Tarap leave (TLN)	Pb <sup>2+</sup>	11.5	110.06	NA	[13]
NaOH-EDTA modified Tarap leaves (TLNE)	Pb <sup>2+</sup>	-35.15	-27.4	NA	[13]
Silk fibroin (SF) fiber	Pd <sup>2+</sup>	5.34	64.1		[47]
Wheat bran	Mo	10.6	28.6	NA	[14]

Calcined Wheat bran	Mo	11.6	41.2	NA	[14]
Aloe vera leaves	U(VI)	2.2	61.2	23.2	
Bengal gram fruit shell (BGFS)	Acid blue 25	-16.792	196.6	NA	[55]
Microwave treated tea leaves	Eriochrome black T	31.82	189.32	32.7	[23]
Modified Pine needles (ASCDH)	Malachite green	49.9	172.02	NA	[57]
Defatted <i>Laminaria japonica</i> biomass (DLB)	Methylene blue	0.0134	198.09	NA	[59]
Modified Defatted <i>Laminaria japonica</i> biomass (DLB-S)	Methylene blue	0.011	174.56	NA	[59]
<i>Phragmites australis</i> fibers	Methylene blue	-35.78	-104.59	NA	[24]
Sulfonated peanut shell	Methylene blue	12.24	55.26	NA	[22]
Chia seed residue	Yellow B2R	1.5269	9.6	NA	[56]
Sulfonated tea leaves	Sulfamethoxazole	-9.22	-26.67	NA	[28, 29]
Sulfonated tea leaves	Bisphenol A	-8.48	-23.55	NA	[28, 29]
Sulfonated coffee waste	Bisphenol A	-7.98	-23.43	NA	[28, 29]
Sulfonated coffee waste	Sulfamethoxazole	-6.82	-19.3	NA	[28, 29]
Sulfonated peanut shell	Tetracycline	14.55	49.08	NA	[22]

NA Not available

### Dynamicoperation

Continuous flow in which the polluted water passes through a column filled with adsorbents is more practical for the treatment of wastewater than batch adsorption mode [71]. Zaidi et al. (2018) studied the biosorption of Pb (II) onto NaOH modified tea leaves (TLN) in a dynamic system [13]. The relationship between the bed height of TLN and the time taken for the column to reach breakthrough was investigated. As the bed heights of TLN were increased, more volume of the Pb(II)solution could be processed through the column before the breakthrough time where the biosorption was drastically decreased to almost zero percent was achieved [13]. Possible reason for this consequence was attributed to the larger amount of the TLN used in higher bed height that lead to the higher performance of the biosorbent. The implication was that the higher bed height tended to improve the operation of the column and as such, the need to change the biosorbent was delayed due to its long-lasting good performance in treating the effluents. In this study, only 10 cm of the bed height of TLN was used yet it was able to adsorb 850 mL achieving 100% removal [13].

The dynamic mode was studied for the biosorption of cadmium, copper, lead and zinc in a continuous fixed-bed multimetal binding biosorbent (MMBB) containing a combination of tea waste (TW), maple leaves (ML) and mandarin peel (MP) in the weight ratio of 3, 2 and 1, respectively by Abdolali et al. (2017) [72]. The effects of influent flow rate, metal concentration and bed depth were investigated at pH 5.5 for a synthetic wastewater sample. Results indicated that the total amount of metal adsorption decreased with increased influent flow rate and increased when each metal concentration increased [72]. The maximum biosorption capacities ( $q_{max}$ ) in a 31 cm bed height, a flow rate of 10 mL/min and an initial concentration of 20 mg/L for Cd, Cu, Pb and Zn were 38.25, 63.37, 108.12 and 35.23 mg/g respectively. The Thomas model gave the best description of the whole column dynamic behavior compared to the Dose Response and Yoon– Nelson models [72].

Calero et al (2018) studied the continuous biosorption of copper in fixed-bed column of olive stone and pinion shell [73]. The effects of feed flow rate (2–6 ml/min), inlet copper concentration

(40– 100 mg/L) and bed-height (4.4–13.4 cm) was analyzed. Optimization of the percentage of copper removal and the retention capacity in the column was analyzed using Artificial Neural-Fuzzy Inference System (ANFIS) [73]. The highest percentage of copper retained was achieved at 2 ml/min, 40 mg/L and 4.4 cm. However, the optimum biosorption capacity was obtained at 6 ml/min, 100 mg/L and 13.4 cm. The traditional mathematical models of Adams-Bohart, Thomas, Yoon and Nelson and Dose-Response) and ANFIS model were applied to the breakthrough curves [73]. When the calculated results obtained with each model were compared with, experimental data the best results were predicting biosorption of copper with high accuracy were given by ANFIS model. This model permitted the prediction of the best operating conditions for the biosorption process [73].

In a similar study Nakkeeran et al. (2018) [74] reported the column biosorption studies of Cr (VI) from simulated aqueous solution onto *Strychnos nux vomica* tree fruit shell (STFS). The effects of the bed height (3, 5, 7 cm), flow rate inside the column (5, 10, 15 mL/min) and initial concentration of Cr(VI) in aqueous solution (50, 100, 150 mg/L) for the biosorption of Cr(VI) were investigated. At an initial concentrations of Cr (VI) of 50mg/L and flow rate of 5ml/min the Cr (VI) biosorption capacity ( $q_{max}$  mg/g) increased from 32.52 to 77.21mg/g as the bed height increased from 3 to 7 cm [74]. When the equilibrium data was analyzed, using the biosorptioncolumn models of Adams-Bohart, Thomas, Yoon-Nelson, the Thomas and BDST model gave the best fit with the maximum equilibrium adsorption capacity values of 32.52 mg/g and 20.31 mg/g respectively [74].

Qu et al. (2019) [75] recently reported the biosorption of Pb (II) ions from aqueous solution onto sodium hydroxide modified *Auricularia* (a mushroom) Matrix Waste (AMW) and immobilized into granular adsorbent with sodium alginate in a fixed-bed column. The effects of bed length, flow rate and lead ions concentration on the breakthrough characteristics of lead (II) biosorption were investigated. The optimal conditions were an initial concentration of 150 mg/L at a flow rate of 25 mL/min resulting in a maximum biosorption capacity of 151.7 mg/g. The equilibrium data fitted Thomas model better than the Bohart-Adams model for the

description of the performance of the immobilized AMW for the biosorption of lead (II) [75].

Nag et al. (2019) [76] also recently reported the biosorption of Cd (II) from synthetic wastewater onto three biowaste materials, jackfruit (AHL), mango (MIL) and rubber (HBL) leaves in continuous down flow in packed bed columns. Using a hybrid network modelling of Genetic algorithm and artificial neural network (GA-ANN) technique model the influence of influent concentration (20–80 mg/L), flow rate (10–25 ml min<sup>-1</sup>) and bed depth (3–9 cm) on Cd(II) removal were investigated at pH 6. [76]. Results showed that 21%, 80.32% and 66.44% Cd(II) was removed at a 5 cm bed depth; and removal was enhanced to 95.52%, 98.62% and 90.68% at a bed depth of 9 cm for MIL, AHL and HBL respectively at breakthrough concentration when the influent concentration was 20 mg/L and 15 ml/min flow rate. At breakthrough, Cd (II) removal efficiency decreased from 75.21–42.16%, 80.32–48.29% and 66.44–38.23% for MIL, AHL and HBL respectively at a bed height of 5 cm and flow rate of 15 ml/min (Nag et al. 2019). Increase in bed height favored the adsorption process whereas the decrease in bio-sorption efficiency was observed at high influent flow rate and concentration. 98.26% Cd (II) was removed at breakthrough by jackfruit leaves (AHL) at a flow rate of 10 ml/ min when the influent concentration was 20 mg/L and 5 cm bed height [76]. The following kinetic models Thomas, Yoon-Nelson, Bohart-Adams and Wolborska were evaluated for their scale-up comparative applicability. Thomas and Yoon-Nelson model were found to be the best kinetic models for scale- up design [76].

Biosorption of Cd<sup>2+</sup>, Pb<sup>2+</sup>, and Ni<sup>2+</sup> onto modified eucalyptus leaf residue (ELR) in the dynamic mode in a fixed bed column was studied by Feisther et al. (2019) [18]. The dimensions of the fixed bed glass column used were 2.5 cm internal diameter and 35 cm in length. A synthetic solution containing an initial concentration of 0.1mM of each metal at pH value 3.8 was pumped at a flow rate of 10 mL/min through the column. The biosorption capacities obtained in the fixed bed column experiments were lower than those obtained in a batch system. A Linear Driving Force model (LDF) model was able to predict biosorption by ELR in the fixed bed successfully. The breakthrough curves obtained represented a normal biosorption curve presenting the typical S, indicating resistance to mass transfer [18]. The breakthrough time in a single metal system was 35, 12 and 4 h, respectively for lead, cadmium and nickel, which corresponded to a service capacity of 646, 232, and 75 bed volumes (BV), respectively. In contrast, for the multi-metal system, the saturation occurred rapidly because a higher metal concentration (mM) came in contact with the biosorbent within the same time interval, causing a decrease of these parameters. The breakthrough time obtained was 24.0, 1.0, and 0.7 h, respectively for lead, cadmium, and nickel, which corresponded to a service capacity of 440, 18, and 13 BV. In a batch operation with 24 g of biomass when only lead is removed, a 14.4 L of a feed solution containing three metal mixture (cadmium, nickel and lead ions) at a metal concentration of 0.10 mM can be treated [18].

Desorption of methylene blue (MB) from MB loaded Liu et al. (2019) investigated walnut shell in a column [21]. The shape of the breakthrough curves was dependent on the dye concentration and flow rate. The breakthrough times decreased with the initial concentration of MB concentration resulting in a shorter mass

transfer zone, which significantly affected the saturation rate and breakthrough time (Lui et al. 2019). In a secondary biosorption operation, the MB-loaded walnut shell column efficiently removed Congo red (CR) an anionic dye. Yan model fitted well the equilibrium data. Parameter trends were similar to those observed in the batch MB biosorption [21].

Islam et al. (2019) reported a column study of the biosorption of methylene blue with sulfonated peanut shell (PNS-SO<sub>3</sub>H) [22]. The dimension of the fritted chromatographic glass column was 26mm x 457mm (Inner Diameter x Length). About 14 cm of the column was packed with the mixture of adsorbent (PNS-SO<sub>3</sub>H) and sea sand. The column processed up to 36 liters of 20 ppm MB solution in tap water at pH 7 under continuous flow condition achieving 100% removal efficiency. After processing 42 liters, the removal efficiency decreased to 96%. In addition, the breakthrough curve was consistent with 100% removal efficiency even after 80 hr. operation after which the column removal efficiency decreased with time [22].

Dynamic biosorption of Arsenic (V) in contaminated water at pH 8.0 onto a fixed bed column filled with chitosan was investigated by Brion-Roby et al. (2018) [33]. The effects of bed diameter, bed depth, arsenic inlet concentration, flow direction and flow rate were studied using breakthrough curves (BTC) acquired in real-time using a chromatographic instrument. Experimental data indicated that dynamic adsorption capacities were dependent on flow rate and inlet concentration but independent of the other factors considered. In addition, an enlargement of the column did not affect the maximal capacity (50 mg As/g). The height and the moving rate of the exchange zone were also determined for all experimental conditions studied. The BTC were fitted to Thomas, Yoon-Nelson and Adams-Bohart models. Both the Thomas and Yoon-Nelson were found to be adequate [33].

## Desorption and Regeneration of Biosorbent

Regeneration of biosorbents will reduce the amount of waste biosorbents and increase the possibility of reusing natural adsorbents multiple times increasing the attractiveness of the biosorption process. It is therefore imperative that regeneration of biosorbent be part of biosorption studies. An important element of the regeneration process is the development of an effective method for the regeneration agent. A successful desorption process requires the proper selection of eluents, which strongly depends on the type of biosorbent and the mechanism of desorption [8]. At present, commonly used adsorbent regeneration methods include solvent extraction. The solvent extraction method uses an appropriate solvent to extract the adsorbate from the adsorbent. Bartczak et al. (2018) [15] used water and hydrochloric acid in various concentrations (0.05 and 0.1 M) as the regenerating agent for the removal of nickel and lead from peat. It was found that as the concentration of the hydrochloric acid used increased, there was an improvement in the effectiveness of the biosorbent regeneration process. The mechanism of desorption is based on the exchange of hydrogen ions (H<sup>+</sup>) with the adsorbed metal ions [15].

Desorption of Pb(II) from modified *Artocarpus odoratissimus* tea leaves with HCl, NaOH and water was studied by Zaidi et al. (2018) [13]. All of the desorbing agents showed similar trends

with respect to desorption efficiency for the first four cycles and it was evident that there was a need for treatment with desorbing agents before the adsorbents can be reused for the next cycle. When treated with NaOH, the biosorption efficiencies of all the adsorbents were consistent for the four cycles but the biosorption efficiencies increased after treatment of natural tea leaves (TL) and EDTA modified tea leaves (TLE) [13]. Second best desorbing agent was HCl followed by water. Washing the spent biosorbents with water was slightly better than without washing treatment. It was found that water treatment with continuous shaking was better than by rinsing only as the biosorption efficiency slightly improved especially for NaOH modified tea leaves (TLN) and NaOH EDTA modified tea leaves (TLNE) [13].

Schwantes et al. 2018 [12] studied the desorption of cadmium, lead and chromium from modified Pinus bark (P-H<sub>2</sub>O<sub>2</sub>, P-H<sub>2</sub>SO<sub>4</sub>, P-NaOH) with 1M HCl as the eluent. The % desorption were 96%, 51%, 49%, 29%, 46%, 53% for Cd-P-NaOH, Cd-P-H<sub>2</sub>SO<sub>4</sub>, Pb-P-H<sub>2</sub>SO<sub>4</sub>, Pb-P-NaOH, Cd-P-H<sub>2</sub>O<sub>2</sub>, Pb-P-H<sub>2</sub>O<sub>2</sub>, respectively. The desorption of Cr (III) from any of the modified biosorbent was less than 5% [12].

The desorption of copper and lead from roger's mushroom with 0.1M each of EDTA and HCl in the batch mode for 2 h at a speed of 150 rpm was studied by Karuiki et al. (2017) [40]. After desorption step, solutions were filtered with 0.45 mm filter membrane and the filtrate was analyzed for metal concentration and the residual was reused for a second batch adsorption. The adsorption-desorption process was repeated three times. The recycling of the biomass showed that it can be used up to three times without losing efficiency and the desorption efficiency of the metal ions from the mushroom biomass with HCl was higher compared with the one performed with EDTA [40].

Gautam et al. (2018) using functionalized hemicellulose, extracted from Pine needles (*Pinus wallichiana*) studied the removal of cationic dyes and malachite green [57]. The synthesized biosorbent was regenerated with sodium hydroxide and the biosorption maximum capacity after the 15<sup>th</sup> cycle was 29.07 mg/g [57].

Abdolali et al (2017) investigated the desorption of multi-metals (cadmium, copper, lead and zinc) in a fixed bed column. The column biosorbent is composed of tea waste (TW), maple leaves (ML) and mandarin peel (MP) in weight ratio of 3, 2 and 1, respectively. The desorbing agents were 0.1M HCl followed with 1M CaCl<sub>2</sub> at a flow rate of 10mL/min to regenerate the column [72]. Calcium chloride increased the stability and reusability of MMBB by repairing the damage caused by the desorbing agents. It also removed the excess protons after each elution and thereby providing new binding sites. The observed mechanical stability and stiffness of the MMBB made it amenable for fixed-bed column applications. The reusability of MMBB for the removal of heavy metal from real wastewater was conducted using 0.1 M HCl at a flow rate of 10 mL/min [72]. After three cycles of sorption, desorption and regeneration, the metal uptake at the exhaustion time were 49.94, 50.76, 56.38 and 53.87% for Cd, Cu, Pb and Zn, respectively which were adequate for practical applications. The desorption efficiency decreased as the number of cycles increased from 48.08, 47.61, 57.37 and 45.88% during the first cycle to 22.80, 23.69, 34.44 and 23.80% in the third cycle for Cd, Cu, Pb and Zn, respectively. In effect biosorption and

desorption efficiencies decreased progressively as the biosorption and desorption cycles increased [72].

Adsorbed molybdenum (Mo) on wheat bran (WB) was easily desorbed by treatment with sodium hydroxide solution. The recovery percentage of Mo using 1- and 100-mM sodium hydroxide solution was 95.0% and 94.2% respectively [14].

Feisther et al. (2019) studied the desorption of Cd<sup>2+</sup>, Pb<sup>2+</sup>, and Ni<sup>2+</sup> from modified eucalyptus leaf residue (ELR) [18]. Solutions of 0.1M HNO<sub>3</sub>, HCl, H<sub>3</sub>PO<sub>4</sub>, and ultrapure water were tested as eluents. ELR was subjected to three cycles of reuse with over 80% elution efficiencies for all metal ions during the first desorption cycle, greater than 80% for all desorbing agents (HCl, HNO<sub>3</sub>, and H<sub>3</sub>PO<sub>4</sub>) as eluent except H<sub>2</sub>O which had a much lower desorption rates with less than 10% elution efficiency [18]. The desorption of the Pb<sup>2+</sup>, Cd<sup>2+</sup> and Ni<sup>2+</sup> ions from ELR decreased in the order HNO<sub>3</sub> > HCl > H<sub>3</sub>PO<sub>4</sub> > H<sub>2</sub>O. After three cycles of biosorption/desorption, the decrease in the biosorption efficiency of ELR for % for Pb<sup>2+</sup>, Cd<sup>2+</sup> and Ni<sup>2+</sup> was of approximately 25, 46 and 57, respectively using HNO<sub>3</sub> as the desorbing agent [18].

During the desorption study of methylene blue from *Phragmites australis* fibers it was observed that the desorbed amount increased at lower pH. The desorption capacity (q<sub>dmax</sub>) and efficiency at pH=6.0 were 3.52 mg/g and 35.2% respectively, which was a very low value compared to the values at pH=2.0 which were 9.24 mg/g and 92.4% [24]. Hence, it was confirmed that the optimum pH was 2.0. The desorption process was attributed to the negative charges on the surface of *Phragmites* fibers and the free electrons of nitrogen atoms on the dye molecules competing to bind hydrogen bonds on the desorbing agents the stronger acid hereby reducing the interaction between dye and the biomass [24].

Sodium hydroxide was investigated as a desorbing agent for Reactive blue BF-5G from malt bagasse at different concentration (0.01 -1.0M). The desorbed efficiency increased with the increase in desorbing agent, with the best result of 38.54% being obtained at the highest sodium hydroxide concentration of (1M NaOH) [54]. The dye desorption is favored at higher pH, because when pH > pH<sub>pzc</sub> the surface of the biosorbent has a negative net charge. The increase of the eluent concentration (pH=13.82) promotes an increase in the amount of OH<sup>-</sup> ions present in solution that causes the equilibrium displacement in the sense that the biosorption of OH<sup>-</sup> ions is favored, consequently contributing to the desorption of the dye [54]. The effects of temperature (30, 40 and 50 °C) and time was investigated. The optimum desorption temperature was found to be 50 °C for 1hr duration with desorption capacity q<sub>dmax</sub> and efficiency 5 mg/g and 70.8% respectively [54].

Ethanol was used to desorb sulfamethoxazole and Bisphenol A from functionalized tea leaves in order to regenerate it for successive adsorption. The functionalized tea leaves were easily regenerated and recycled for three cycles with a nominal loss in biosorption capacity [28].

## Discussion and conclusion

This literature review revealed that biochemically and chemically modified biosorbent showed better adsorption

capacities than unmodified biosorbents. Biochemical and chemical modification of LCBs have been shown to increase the number of active binding sites. Chemicals that were used in the modification include sodium hydroxide, sodium borohydride, sodium hydroxymethanesulfonate, and calcium carbonate. Alkaline treatment improved the biosorption capacity of LCBs as a result of several factors such as: increased degree of dissociation of superficial functional groups, increased porosity and surface area, increased hydrogenated groups, formation of more carboxylic (-COOH) and hydroxyl groups (-OH), which in effect increased the functional groups available for biosorption. Biochemical modification involved hydrolysis with enzymatic preparations of endoglucanases, exo-galactosidase and exo-xylosidase. Biocatalytic conversion of polycarbohydrates present in LCBs by exogenous enzymes provide the generation of the highly reactive reducing agents needed for redox transformations of lignin. Exogenous enzymes separated mono or dimeric units at the end of polymer links inside LCBs, which practically changed the state of the high-molecular components. Exo-glucanases hydrolyzed the oligomeric fraction with a low degree of polymerization. These modification lead to improvement in the internal pore structure of the material and the stimulation of its polymer components to different types of interparticle and intermolecular interactions. The ion exchange properties were improved and new functional groups that favor metals, dyes, and CECs removal from aqueous media were formed. In addition, the specific surface area of the modified LCBs was increased hereby affecting the biosorption capacity.

Factors affecting the efficiency of biosorption of heavy metal, dyes, and contaminants of emerging concerns removal from wastewater onto LCB adsorbents were initial concentration, temperature, adsorbent dose, pH, contact time, and stirring speed. The biosorption efficiency increased with increase in the initial concentration, temperature, adsorbent dose, contact time, and stirring speed while the optimum pH for biosorption varied with the adsorbate. With respect to examined pollutants, heavy metals, and contaminants of emerging concern the optimum pH was in the ranges 2 and 6 whereas for dyes it depended on the type of dye. For anionic dyes, the optimum pH was in the ranges 2 and 3 while for cationic dyes it was between 6 and 7. Based on the results of maximum dye biosorption capacities reported in literatures dye biosorption is strongly dependent on pH as well as biosorbent type. In addition, the rough surface of these biosorbent provided a suitable bed for dye binding or entrapping according to SEM images. At higher pH, negatively charged adsorbent sites increased, which enhanced the adsorption of positively charged cations through electrostatic forces of attraction. The principal adsorption mechanisms were ion exchange, electrostatic interaction, and complex adsorption. Predicting the rate of adsorption for a given system is among the most important factors in adsorption system design, since the system kinetics determines the adsorbate residence time and the reactor dimensions. The equilibrium time varied between 10 min and 6 hours for all the adsorbates.

Parameters such as the kinetic, isothermal, and thermodynamic features influenced the biosorption processes. The biosorption kinetics data described the adsorbate concentration profile. The rate constant for biosorption is important to estimate the adsorption rate in planning water treatment process. From the isotherms,

biosorption capacity and energy intensity for adsorption can be evaluated if the adsorption mechanism obeys to the proposed adsorption model. The commonly used Langmuir or Freundlich isotherm models described the biosorption of heavy metals. The Langmuir model was found to be more representative of the biosorption of metals onto LCBs. Although there is a disagreement regarding the effectiveness of the Langmuir and Freundlich models in interpreting the metal adsorption, some parameters of these models, such as the Langmuir maximum adsorption capacity ( $q_{max}$ ) and the Freundlich constant related to the distribution coefficient ( $K_p$ ), were widely acceptable in characterizing the metal sorption capacity of various materials [5]. The pseudo-second order (PSO) kinetic model fitted most of the kinetic data for the biosorption of metals dyes and CECs. The thermodynamic properties such as the specific enthalpy ( $\Delta H^\circ$ ), Gibbs free energy ( $\Delta G^\circ$ ) and specific entropy ( $\Delta S^\circ$ ) suggested whether the adsorption proceeded spontaneously or not. The estimated values offered novel insights into the adsorption mechanism of heavy metals, dyes, and CECs onto LCBs. Positive values of  $\Delta H^\circ$  were observed for most metals, dyes, and CECs biosorption which meant that the biosorption process was endothermic process (while a negative value would suggest an exothermic process). Positive values of  $\Delta S^\circ$  as observed for most adsorbates suggested that randomness increased. The  $\Delta S^\circ$  involved two contributing factors; one is negative contribution due to reducing of degree of freedom of metal ions by adsorption proceeds, and the other is positive contribution due to increasing of degree of freedom of water molecules coordinated to the adsorbate. Randomness is increased because of water molecules being coordinated to the adsorbate and were released during the adsorption process. Thermodynamic feasibility and spontaneity of the biosorption process in the temperature range were indicated by negative values of  $\Delta G^\circ$  observed in all adsorbates [47].

The objective of regeneration is to increase the potential of reuse of biomass in new biosorption cycles and reduce waste generation. In the case of metal biosorption regeneration, it allows the metal ions to be concentrated in the eluent solution and recovered by reducing the environmental problems caused by the deposit of toxic waste in landfills. One additional advantage of regeneration is that the process must result in a biomass with similar characteristics to the initial biomass, with minimal adsorbed metal and without structural damage or changes to the biomass structure. Regeneration studies of the used LCB biosorbents in this review have shown that they can be recycled making the sorption process more economical. The desorption experiments have been mainly conducted by using diluted acids such as HCl or HNO<sub>3</sub> and basic solutions (NaOH). However, in the presence of mineral acid the biosorbent structure suffered some damage resulting in mass loss. To minimize biomass loss, EDTA a chelating agent solution have been applied. EDTA forms steady complexes with metal ions while desorption with HCl is mainly due to the ion exchange mechanism. LCBs biosorbents exhibit different stability and adsorption efficiency after several sequential adsorption-desorption cycles. Papers reviewed indicated a biosorption efficiency of over 90% after three cycle's adsorption/desorption [35].

Biosorbents that adsorb metals and soluble organic pollutants effectively reduce operation cost in wastewater treatment. However, since most wastewater contains a mixture of metals, it is imperative

that future research should be focused on the identification of biosorbents capable of multiple metal absorption in a continuous system. In addition, the low regeneration rate for biosorbents is a great disadvantage to their use in commercial wastewater treatment; thus, developing an optimal regeneration method is a critical factor for biosorbent applications. Therefore, in order to improve the application of LCBs on an industrial scale, more studies on biosorption onto LCBs from multi-element systems, recovery and recycle of these biosorbents after desorption, and their reuse are needed [17].

## References

1. Giannakoudakis DA, Hosseini B and egharae A, Tsafrakidou P, Triantafyllidis KS, Kornaros M, Anastopoulos I. Aloe vera waste biomass-based adsorbents for the removal of aquatic pollutants: A review. *Journal of Environmental Management*. 2018;227:354-364. doi: 10.1016/j.jenvman.2018.08.064
2. Bulgariu L, Escudero L B, Bello O S, Iqbal M, Nisar J, Adegoke KA, et al. The utilization of leaf-based adsorbents for dyes removal: A review", *Journal of Molecular Liquids*. 2019;276:728-747. doi: 10.1016/j.molliq.2018.12.00
3. Ali A, Saeed K, Mabood F. Removal of chromium (VI) from aqueous medium using chemically modified banana peels as efficient low-cost adsorbent. *Alexandria Engineering Journal*. 2016;55(3):2933-2942. doi: 10.1016/j.aej.2016.05.011
4. Heraldry E, Lestari W W, Permatasari D, Arimurti D D. Biosorbent from tomato waste and apple juice residue for lead removal. *Journal of Environmental Chemical Engineering*. 2018;6(1):1201-1208. doi: 10.1016/j.jece.2017.12.026
5. Burakov A E, Galunina E V, Burakova I V, Kucherova A E, Agarwal S, Tkacheva A G, et al. Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: A review. *Ecotoxicology and Environmental Safety*. 2018;148:702-712. doi: 10.1016/j.ecoenv.2017.11.034
6. Abdolali A, Guo W S, Ngo H H, Chen S S, Nguyen N C, Tung K L. Typical lignocellulosic wastes and by-products for biosorption process in water and wastewater treatment: A critical review. *Bioresource Technology*. 2014;160:57-66. doi: 10.1016/j.biortech.2013.12.03
7. Bhatnagar A, Sillanpaa M, Witek Krowiak A. Agricultural waste peels as versatile biomass for water purification - A Review. *Chemical Engineering Journal*. 2015;270:244-271. doi: 10.1016/j.cej.2015.01.135
8. Dai Y, Sun Q, Wang W, Lu L, Liu M, Li J, et al. Utilizations of agricultural waste as adsorbent for the removal of contaminants: A review. *Chemosphere*. 2018; 211:235-253. doi: 10.1016/j.chemosphere.2018.06.179
9. Tran V S, Ngo H H, Guo W, Zhang J, Liang S, Ton That C, et al. Typical low cost biosorbents for adsorptive removal of specific organic pollutants from water. *Bioresource Technology*. 2015;182:353-363. doi: 10.1016/j.biortech.2015.02.003
10. Noli F, Kapashi E, Kapnisti M. Biosorption of uranium and cadmium using sorbents based on Aloe vera Wastes. *Journal of Environmental Chemical Engineering*. 2019;7(2):102985. doi: 10.1016/j.jece.2019.102985
11. Saraeian A, Hadi A, Raji F, Ghassemi A, Johnson M. Cadmium removal from aqueous solution by low-cost native and surface modified Sorghum x drummondii (Sudan grass). *Journal of Environmental Chemical Engineering*. 2018;6(2):3322-3331. doi: 10.1016/j.jece.2018.05.018
12. Schwantes D, Gonçalves Jr A C, Marcelo Angelo Campagnolo M A, Tarley C R T, Dragunski D C, de Varennes A. Chemical modifications on Pinus bark for adsorption of toxic metals. *Journal of Environmental Chemical Engineering*. 2018;6(1):1271-1278. doi: 10.1016/j.jece.2018.01.044
13. Zaidi, N A H, M Lim L B L, Usman A. Enhancing adsorption of Pb (II) from aqueous solution by NaOH and EDTA modified Artocarpus odoratissimus leaves. *J. Environ. Chem. Eng*. 2018; 6(6):7172-7184. doi: 10.1016/j.jece.2018.10.053
14. Ogata F, Nakamura T, Kawasaki N. Adsorption capability of virgin and calcined wheat bran for molybdenum present in aqueous solution and elucidating the adsorption mechanism by adsorption isotherms, kinetics, and regeneration. *Journal of Environmental Chemical Engineering*. 2018;6(4):4459-4466. doi: 10.1016/j.jece.2018.06.047
15. Bartczak P, Norman M, Klapiszewski L, Karwanska N, Kawalec M, Baczynska M, et al. Removal of nickel (II) and lead (II) ions from aqueous solution using peat as a low-cost adsorbent: A kinetic and equilibrium study. *Arabian Journal of Chemistry*. 2018;11(8):1209-1222. doi: 10.1016/j.arabj.2015.07.018
16. Benakouche H, Bounoughaz M. Electrosorption Removal of the Zinc Ions from Aqueous Solution on an Artificial Electrode based in the Banana Wastes. *J. Electrochem. Sci. Technol*. 2017;8(1):77-86. doi: 10.5229/JECST.2017.8.1.77
17. Neris J B, Luzardo FHM, Santos P F, de Almeida O N, Velasco, F G. Evaluation of single and tri-element adsorption of Pb<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup> ions in aqueous solution on modified water hyacinth (*Eichhornia crassipes*) fibers. *Journal of Environmental Chemical Engineering*. 2019;7(1):102885. doi: 10.1016/j.jece.2019.102885
18. Feisther V A, Filho J S, Hackbarth F V, Mayer D A, Ulson de Souza A A, U de Souza SMAG. Raw leaves and leaf residues from the extraction of essential oils as biosorbents for metal removal. *Journal of Environmental Chemical Engineering*. 2019;7(3):103047. doi: 10.1016/j.jece.2019.103047
19. Koksharov S A, Aleeva S V, Lepilova O V. Biomodification of Flax Fibrous Materials for Increase of Sorption to Organic Compounds. *International Journal of Chemical Engineering*. 2019. doi: 10.1155/2019/4137593
20. Kumar R, Sharma R K, Singh A P. Removal of organic dyes and metal ions by cross-linked graft copolymers of cellulose obtained from the agricultural residue. *Journal of Environmental*

- Chemical Engineering. 2018. doi: 10.1155/2019/4137593
21. Liu M, Li X, Du Y, Han R. Adsorption of methyl blue from solution using walnut shell and reuse in a secondary adsorption for Congo red. *Bioresource Technology Reports*. 2019;5:238-242. doi: 10.1016/j.biteb.2018.11.006
  22. Islam M T, Hyder A G, Saenz Arana R, Hernandez C, Guinto T, Ahsan M A. Removal of methylene blue and tetracycline from water using peanut shell derived adsorbent prepared by sulfuric acid reflux. *Journal of Environmental Chemical Engineering*. 2019;7(1):102816. doi: 10.1016/j.jece.2018.102816
  23. Khan A, Wang X, Gul K, Khuda F, Zaynab Aly Z, Elseman A M. Microwave-assisted spent black tea leaves as cost-effective and powerful green adsorbent for the efficient removal of Eriochrome black T from aqueous solutions. *Egyptian Journal of Basic and Applied Sciences*. 2018;5(2):171-182. doi: 10.1016/j.ejbas.2018.04.002
  24. Dallel R, Kesraoui A, Seffen M. Biosorption of cationic dye onto "Phragmites australis" fibers: Characterization and mechanism. *Journal of Environmental Chemical Engineering*. 2018;6:7247-7256. Doi: 10.1016/J.JECE.2018.10.024
  25. Oickle A M, Goertzen S L, Hopper K R, Abdalla Y O, Andreas H A. Standardization of the Boehm titration: part II. Method of agitation, effect of filtering and dilute titrant, *J. Carbon*. 2010;48(12):3313-3322. doi: 10.1016/j.carbon.2010.05.004
  26. Portinho R, Zanella O, Feris L A. Grape stalk application for caffeine removal through adsorption. *Journal of Environmental Management*. 2017;202:178-187.
  27. Sayen S, Ortenbach López M, Guillon E. Sorptive removal of enrofloxacin antibiotic from aqueous solution using a lignocellulosic substrate from wheat bran. *Journal of Environmental Chemical Engineering*. 2018;6(5):5820-5829. doi: 10.1016/j.jece.2018.08.012
  28. Ahsan M A, Islam M T, Hernandez C, Kim H, Lin Y, Curry M L. Adsorptive Removal of Sulfamethoxazole and Bisphenol A from Contaminated Water using Functionalized Carbonaceous Material Derived from Tea Leaves. *Journal of Environmental Chemical Engineering*. 2018;6(4):4215-4225. doi: 10.1016/j.jece.2018.06.022
  29. Ahsan M A, Islam M T, Imam M A, Golam Hyder AHM, Jabbari V, Dominguez N. Biosorption of bisphenol A and sulfamethoxazole from water using sulfonated coffee waste: Isotherm, kinetic and thermodynamic studies. *Journal of Environmental Chemical Engineering*. 2018;6(5):6602-6611. doi: 10.1016/j.jece.2018.10.004
  30. Huang D, Li B, Ou J, Xue W, Li J, Li Z. Megamerger of biosorbents and catalytic technologies for the removal of heavy metals from wastewater: Preparation, final disposal, mechanism and influencing factors. *Journal of Environmental Management*. 2020. doi: 10.1016/j.jenvman.2019.109879.
  31. Wang J, Shih Y, Wang P Y, Yu Y H, Su J F, Huang C. Hazardous waste treatment technologies. *Water Environment Research*. 2019;91: 1177-1198.
  32. Sharifi-Bonab M, Aber S, Salari D, Khodam, F. Synthesis of CoZnAl-layered double hydroxide/graphene oxide nanocomposite for the removal of methylene blue: Kinetic, thermodynamic, and isotherm studies. *Environ. Prog. Sustainable energy*. 2020;39:1-12.
  33. Brion-Roby R, Gagnon J, Deschênes J, Chabot B. Investigation of fixed bed adsorption column operation parameters using a chitosan material for treatment of arsenate contaminated water. *Journal of Environmental Chemical Engineering*. 2018;6:505-511.
  34. Gupta A, Vidyarthi S R, Sankararamakrishnan N. Concurrent removal of As (III) and As (V) using green low cost functionalized biosorbent - *Saccharum officinarum* bagasse. *Journal of Environmental Chemical Engineering*. 2015;3(1):113-121.
  35. Pyrzynska K. Removal of cadmium from waste waters with low-cost adsorbents. *Journal of Environmental Chemical Engineering*. 2019;7:102795.
  36. Dirbaz M, Roosta A. Adsorption, kinetic and thermo-dynamic studies for the biosorption of cadmium on to microalgae *Parachlorella* sp. *Journal of Environmental Chemical Engineering*. 2018;6:2302-2309.
  37. Peng S, Wang R, Yang L, He L, He X and Liu X. Biosorption of copper, zinc, cadmium, and chromium ions from aqueous solution by natural foxtail millet shell. *Ecotoxicology and Environmental Safety*. 2018;165:61-69.
  38. Kebede T G, Mengistie A A, Dube S, Nkambule T T I and Nindi M M. Study on adsorption of some common metal ions present in industrial effluents by *Moringa stenopetala* seed powder. *Journal of Environmental Chemical Engineering*. 2018;6:1378-1389.
  39. Ben Ali S, Jaouali L, Souissi-Najar S and Ouederni A. Characterization and adsorption capacity of raw pomegranate peel biosorbent for copper removal. *Journal of Cleaner Production*. 2017;142:3809-3821.
  40. Kariuki Z, Kiptoo J, Onyancha D. Biosorption studies of lead and copper using roger's mushroom biomass 'Lepiota hystrix'. *South African Journal of Chemical Engineering*. 2017;23:62-70
  41. Ferreira da Silva A J, Paiva de Alencar Moura M C, da Silva S E, Saraiva Pereira J E, Linsde Barros Neto E. Copper removal using carnauba straw powder: Equilibrium, kinetics, and thermodynamic studies. *J. Environ. Chem. Engr*. 2018;6:6828-6835.
  42. Sostaric T D, Petrovic M S, Pastor F T, Loncarevic D R, Petrovic J T, Milojkovic J V and Stojanovic M D. Study of heavy metals biosorption on native and alkali-treated apricot shells and its application in wastewater treatment. *Journal of Molecular*

- Liquids. 2018;259:340–349.
43. Singh K, Sharma S, Jain A, Mandal M, Pandey PK, Removal of copper from synthetic wastewater using aloe vera as an adsorbent. *Eur. J. Adv. Eng. Technol.* 2017;4:249–254.
  44. Khoshsang H and Ghaffarinejad A. Rapid removal of lead (II) ions from aqueous solutions by saffron flower waste as a green biosorbent. *Journal of Environmental Chemical Engineering.* 2018;6:6021–6027.
  45. Nunez-Gomez D, Rodrigues C, Flavio Rubens Lapolli F R and Lobo-Recio MA. Adsorption of heavy metals from coal acid mine drainage by shrimp shell waste: Isotherm and continuous-flow studies. *Journal of Environmental Chemical Engineering.* 2019;7:102787.
  46. Souza PR, Dotto GL, Salau NPG. Artificial neural network (ANN) and adaptive neuro-fuzzy interference system (ANFIS) modelling for nickel adsorption onto agro-wastes and commercial activated carbon. *J. Environ. Chem. Eng.* 2018; 6: 7152-7160.
  47. Sato T, Abe S, Ito S and Abe T. Silk fibroin fiber for selective palladium adsorption: Kinetic, isothermal and thermodynamic properties. *Journal of Environmental Chemical Engineering* 2019;7:102958 <https://doi.org/10.1016/j.jece.2019.102958>.
  48. Ngabura M, Hussain SA, Ghani, WA, Jami MS, and Tan YP. Utilization of renewable durian peels for biosorption of zinc from wastewater. *Journal of Environmental Chemical Engineering.* 2018;6:2528-2539
  49. Houda B, Moussa B. Electrosorption removal of the zinc ions from aqueous solution on an artificial electrode based in the banana wastes. *J. Electrochem. Sci. Technol.* 2017;8:77-86.
  50. da Silva Correia IK, Santos PF, Santana CS, Neris JB, Luzardo FHM and Velasco FG. Application of coconut shell, banana peel, spent coffee grounds, eucalyptus bark, piassava (*Attalea funifera*) and water hyacinth (*Eichornia crassipes*) in the adsorption of  $Pb^{2+}$  and  $Ni^{2+}$  ions in water. *Journal of Environmental Chemical Engineering.* 2018; 6: 2319–2334.
  51. Zolgharnein J, Bagtash M, Feshki S, Zolgharnein P and Hammond D. Crossed mixture process design optimization and adsorption characterization of multi-metal (Cu (II), Zn (II) and Ni (II)) removal by modified *Buxus sempervirens* tree leaves. *Journal of the Taiwan Institute of Chemical Engineers.* 2017;78:104-117.
  52. Corral Bobadilla M, González Marcos A, Eliseo P. Vergara-González, E.P, and Alba Elías F. Bioremediation of Wastewater to Remove Heavy Metals Using the Spent Mushroom Substrate of *Agaricus bisporus*. *Water.* 2019; 11: 454- 468.
  53. Stavrinou A, Aggelopoulos CA, Tsakiroglou CD. Exploring the adsorption mechanisms of cationic and anionic dyes onto agricultural waste peels of banana, cucumber and potato: Adsorption kinetics and equilibrium isotherms as a tool. *J Environ Chem Eng.* 2018;6(6): doi: 10.1016/j.jece.2018.10.063
  54. Juchen PT, Piffer HH, Veit MT, Goncalves GD, Palácio SM and Zanette JC. Biosorption of reactive blue BF-5G dye by malt bagasse: kinetic and equilibrium studies. *J Environ Chem Eng.* 2018;6(6). doi: 10.1016/j.jece.2018.11.009
  55. Krishna LS, Yuzir A, Yuvaraja G and Ashokkumar V. Removal of Acid Blue 25 from aqueous solutions using Bengal gram fruit shell (BGFS) biomass, *International Journal of Phytoremediation.* 2017;19(5):431-438. doi:10.1080/15226514.2016.1244161
  56. Da Silva DCC, Pietrobelli JMTD. Residual biomass of chia seeds (*Salvia hispanica*) oil extraction as low cost and eco-friendly biosorbent for effective reactive yellow B2R textile dye removal: Characterization, kinetic, thermodynamic and isotherm studies. *Journal of Environmental Chemical Engineering.* 2019;7(2):103008. doi: 10.1016/j.jece.2019.103008
  57. Gautam D, Kumaria S, Rama B, Chauhan GS and Chauhan K. A new hemicellulose-based adsorbent for malachite green. *Journal of Environmental Chemical Engineering.* 2018;6(4):3889. doi: 10.1016/j.jece.2018.05.029
  58. Mokhtar N, Aziz EA, Aris A, Ishak WFW and Ali NSM. Biosorption of azo dye using marine macro-alga of *Euchema spinosum*. *Journal of Environmental Chemical Engineering.* 2018;5(6):5721–5731. doi: 10.1016/j.jece.2017.10.043
  59. Shao H, Li Y, Zheng L, Chen T and Jian Liu J. Removal of methylene blue by chemically modified defatted brown algae *Laminaria japonica*. *Journal of the Taiwan Institute of Chemical Engineers.* 2017;80:525–532. doi:10.1016/j.jtice.2017.08.023
  60. Fernandez ME, Nunell GV, Bonelli PR, Cukierman AL. Batch and dynamic biosorption of basic dyes from binary solutions by alkaline-treated cypress cone chips. *Bioresource Technology.* 2012;106:55–62. doi:10.1016/j.biortech.2011.12.003
  61. Araujo LA, Bezerra CO, Cusioli LF, Silva MF, Nishi L, Gomes RG, Bergamasco R. Moringa oleifera biomass residue for the removal of pharmaceuticals from water. *J Environ Chem Eng.* 2018;6(6): 7192–7199. doi: 10.1016/j.jece.2018.11.016
  62. Haro NK, Del Vecchio, P, Marcilio, NR, Feris LA. Removal of atenolol by adsorption- Study of kinetics and equilibrium. *Journal of Cleaner Production.* 2017;54:214-219. doi: 10.1016/j.jclepro.2017.03.217
  63. Vieira W T, de Farias M B, Spaoloni M P, da Silva M G C, and Vieira M G A. Removal of endocrine disruptors in waters by adsorption, membrane filtration and biodegradation. A review. *Environmental Chemistry Letters.* 2020;18:1113–1143.
  64. Phillips PJ, Smith SG, Kolpin DW, Zaugg SD, Buxton HT and Furlong ET. Methods, Description, quality assurance, environmental data, and other information for analysis of

- pharmaceuticals in wastewater-treatment-plant effluents, streamwater, reservoirs, 2004-2009. US Geological Survey. 2010.
65. Rich AL, Phipps LM, Tiwari, S, Rudraraju H and Dokpesi P O. The increasing prevalence in intersex variation from toxicological dysregulation in fetal reproductive tissue Differentiation and development by endocrine-disrupting chemicals. *Environmental health Insights*.2016;10: 163 -171.
66. Vajda AM, Barber LB, Gray JL, Lopez EM, Woodling JD and Norris. Reproductive disruption in fish downstream from estrogenic wastewater effluent. *Environmental Science Technology* 2008;42:3407-3414.
67. Barnes KK, Kolpin DW, Focazio MJ, Furlong ET, Meyer MT, Zaugg SD Haack, SK. Water-quality data for pharmaceuticals and other organic wastewater contaminants in ground water and in untreated drinking water sources in the United States, 2000-01. US Geol Survey.
68. Rajasulochana P and Preethy V. Comparison on efficiency of various techniques in treatment of waste and sewage water. - A comprehensive review. *Resource Technology*2016;2:175-184.
69. De Andrad JR, Oliveira MF, da Silva M GC and Vieira MGA. Adsorption of Pharmaceuticals from Water and Wastewater Using Nonconventional Low-Cost Materials: A Review. *Ind. Eng. Chem. Res.* 2018;57(9):3103-3127.
70. Bi S, Liu W, Wang C. and Zhan H. A versatile approach to the synthesis of biomass derived from furfural residues as a potential adsorbent. *Journal of Environmental Chemical Engineering*. 2018; 6:5049-5052.
71. De Freitas GR, Vieira MGA, da Silva MGA.. Batch and Fixed Bed Biosorption of Copper by Acidified Algae Waste Biomass. *Ind. Eng. Chem. Res.* 2018; 57: 11767-11777.
72. Abdolali A, Ngo HH, Guo W, Zhou JL, Zhang J, Liang, S, et.al Application of a breakthrough biosorbent for removing heavy metals from synthetic and real wastewaters in a lab-scale continuous fixed-bed column. *Bioresource Technology*. 2017; 229:78-87.
73. Calero M, I Ianez Rodriguez, I, Perez A, Martin-Lara MA and Blazquez G. Neural fuzzy modelization of copper removal from water by biosorption in fixed-bed columns using olive stone and pinion shell. *Bioresource Technology* 2018; 252:100-109.
74. Nakkeeran E, Patra C, Shahnaz T, Rangabhashiyam S and Selvaraju N. Continuous biosorption assessment for the removal of hexavalent chromium from aqueous solutions using *Strychnos nux vomica* fruit shell. *Bioresource Technology Reports*. 2018; 3: 256-260.
75. Qu J, Song T, Liang J, Bai X, Li Y, Wei Y, et.al. Adsorption of lead (II) from aqueous solution by modified *Auricularia* matrix waste: A fixedbed column study. *Ecotoxicology and Environmental Safety*. 2019;169:722-729.