

Review Article

Review on the Effectiveness of using Bio-Char as an Adsorbent for the Removal of Water Pollutants**Lame Elsie Othugile, Tumeletso Lekgoba*, Freeman Ntuli and Emmanuel Makhura***Department of Chemical, Materials and Metallurgical Engineering, Botswana International University of Science and Technology, Private Bag 16, Palapye, Botswana*

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Abstract

In the last few decades, biochar has been effectively used in water remediation and for improving soil fertility. Due to an aggravated desire for zero pollution and green technology, biochar application is gaining interest in wastewater treatment. Adsorption has been regarded as a clean and less costly technology to decontaminate water laden with harmful materials including heavy metals, dyes, pesticides, herbicides etc. Therefore, a review of the effectiveness of biochar derived from different feedstocks used as adsorbents is given in this paper. These include biochar from agricultural and forest residues, industrial by-products and waste, municipal solid waste materials, waste tyres and paper. In addition, this study reveals the effect of surface functional groups, surface charges, surface area, elemental composition and other parameters such as pyrolysis temperature, adsorbent and adsorbate concentrations, solution pH and others on the removal efficiencies. To achieve this, studies have been compiled using biochar derived from agricultural and forest residues. It was found that biochar feedstocks and pyrolysis temperature determine most of the biochar characteristics and their behaviour during removal of contaminants. Among these characteristics are the oxygenated surface functional groups which were found to aid in the removal of positively charged contaminant due to their negative charge hence electrostatic attraction. Furthermore, other reaction mechanisms involved during adsorption include surface complexation, ion exchange, chelation etc. Kinetic models were used to predict these mechanisms while kinetic isotherms predicted whether monolayer or multilayer adsorption occurred. This study has revealed that conversion of biomass to biochar offers an excellent alternative to waste management, wastewater treatment and green technology therefore intensive research on this topic should be of priority.

Keywords: Adsorbent, Adsorption, Biochar, Pollutants, Wastewater

1. Introduction

The quality of our environment is gradually degrading due to increased population growth, industrialization, domestic and agricultural activities which utilises environmentally unfriendly technologies and materials in their operations especially during wastewater disposal. Recently, water pollution is a serious global issue which adversely affects our lives and is expected to worsen in the coming decades [1]. Water pollutants include inorganics such as heavy metals, nitrates, sulphates, chlorides, fluorides, phosphates etc., organics such as pesticides including herbicides, fungicides and insecticides, dyes and hydrocarbons. The main sources of these pollutants include manufactures of cosmetics, pharmaceuticals, fertilisers, food, textiles, steel and mining industries [2]. In response to this, several treatment technologies have been adapted by these industries to treat wastewater before being disposed to the environment. They include ion exchange, chemical precipitation, adsorption and membrane technologies such as nanofiltration, ultrafiltration and reverse osmosis [3]. To date, adsorption has proved to be the best technology due to its cost effectiveness and cleanliness from utilizing cheap and naturally available adsorbents. As a result, the desire for green technology and

zero pollution gave rise to research on adsorption and adsorbent materials that are environmentally friendly, hence the birth of bio-char (pyrogenic black carbon produced from burning of carbon rich biomass in an oxygen limited environment) for water treatment processes [4]. Its application in wastewater led to rapid growth in its market due to its adsorptive characteristics and low-cost nature. A report from the International Biochar Initiative Organization (IBIO) shows that by 2050, there will be a conversion of about 80% of crops and forests to bio-char and energy, hence an emphasis to its significance [5]. On the other hand, this process has been found to have some drawbacks during the removal of these contaminants. For instance, there are some limitations to the amount and type of contaminants removed. The ease of adsorbent regeneration and reusability of the adsorbent [6]. The production of biochar also involves an energy intensive process of pyrolysis which uses heat to carbonize biomass.

The overarching aim of this work is to provide a comprehensive review on the findings of the effectiveness of biochar produced from different natural sources in its application as an adsorbent, with a firm focus on how biochar is used as an adsorbent, production and adsorptive characteristics.

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2. Adsorption as a treatment process

Economic, social and environmental issues regarding the use of some treatment technologies such as ion exchange, adsorption, chemical precipitation and membrane technology have led to intensive research on them and development of other cost effective and green technologies. It is evident that some of these are not economically viable such as the use of ion exchange and membrane technology which utilizes expensive and complicated systems. This led to increased application of adsorption processes since the early 1900s and continual studies on this technology has revealed that adsorption remains the highly used technique due to its renewability and low-cost nature [2]. Adsorption is a separation process where molecules of a substance bind to the surface of a solid material known as the adsorbent and it is mostly applicable in treatment of industrial and domestic wastewater [7]. Two key substances in adsorption are the adsorbate which is termed as the substance that binds to the surface and the adsorbent which is defined as the substance whose surface the process of adsorption occurs. The affinity between the two substances helps the process to occur and the two main types of adsorption are physical (physisorption) and chemical adsorption (chemisorption), which are differentiated by the manner in which adsorbate is attracted to the surface of the adsorbent. Physisorption occurs due to weak non-specific Van der Waal's forces and occurs at relatively low enthalpies of 20-40 kJ/mol. Reversibility in this type of adsorption is due to the weak bonds and takes place at lower temperatures, normally below the boiling point of the adsorbate, hence a lower the adsorption capacity at higher temperatures [8]. Chemical adsorption occurs at higher enthalpies of about 80-240 kJ/mol and its non-reversibility is due to the formation of chemical bonds since there is sharing of electrons between the adsorbent and the adsorbate. Adsorption is considered as a clean method that contributes less to environmental pollution as solid natural adsorbents are utilised [9]. For a solid-liquid adsorption, the mechanisms which drives the process are boundary layer diffusion (external mass transfer) or intraparticle diffusion (mass transfer through the pores). Boundary layer diffusion occurs for processes with lower concentrations of adsorbate, poor mixing and small particle size while intraparticle diffusion occurs when there is good mixing, high concentration of adsorbate and big particle size [10]. Studies show that adsorption dynamics occurs in 3 consecutive steps which are: firstly the adsorbate molecules are transported from the bulk solution to the adsorbent external surface by a boundary layer diffusion, then the adsorbate diffuses from the external surface into the pores of the adsorbent and lastly, adsorption of the adsorbate on the active sites on the internal surface of the pores [11].

3. Biochar as an adsorbent

Applications of biochar in the adsorption process can be divided into two subsections being its use on organic and inorganic substances as suggested by Mohan *et al.* [12]. Organic substances include phenolics, dyes, pesticides, polynuclear aromatics and antibiotics while inorganic substances include cations (such as Cu^{2+} , Fe^{2+} , Ni^{2+} , Mg^{2+} etc.) and anions (such as SO_4^{2-} , PO_4^{3-} , Cl^- etc.).

3.1 Production of biochar

Bio-char can be produced from several materials such as feedstock materials such as residues from agricultural and forest materials, by-products of industrial processes and their wastes, municipal solid waste materials, waste tyres, papers and even bones [13]. Nevertheless, most bio-chars are produced from agricultural and forest residues due to their abundance and their low-cost. A research by Duku *et al.* [14] shows that the worldwide production of agricultural residues annually is estimated to be around 500 million tons, which presents a large availability of these materials. For instance, about 4159×10^3 tonnes of crop residues were produced in Ghana in 2008, with major residues from maize and sorghum plantations. From the same research, coconut residues mainly husk and shells, oil palm empty fruit bunch and sugarcane also formed potential feedstock for biochar production. Traditionally, these residues were scarcely used due to lack of knowledge on their capabilities. Due to their ease of processing, agricultural and forest residues such as wood and forest waste are attractive feedstocks for biochar development [15].

Bio-char is a solid product from thermochemical conversion of biomass in temperatures above 200°C in the absence of oxygen through a process known as pyrolysis. It is not a pure carbon material, but rather it consists of other elements such as oxygen, nitrogen, sulphur and ash. According to Wistara *et al.* [16], good quality biochars should have at least 75% fixed carbon content. The building blocks of biomass (cellulose, hemicellulose and lignin) undergo various processes during pyrolysis, such as depolymerisation, cross-linking and fragmentation at different temperatures to yield liquids (bio-oils), gases (carbon dioxide, carbon monoxide, hydrogen, hydrocarbons) and char [17]. The yields of biochar depend on several conditions including temperature, residence time, pressure, heating rate, nature and composition of biomass [18].

3.2 Adsorptive characteristics of biochars

Biochar produced from agricultural and forestry residues have a strong sorption ability that can be attributed to the surface properties of the feed materials. These surface properties include the high surface area, pore structures, surface functional groups, surface charges etc. The breaking and rearrangement of chemical bonds in biomass during pyrolysis results in the formation of numerous functional groups which brings forth the sorption abilities of biochar [14]. These functional groups include hydroxyl $-\text{OH}$, carboxyl $-(\text{C}=\text{O})\text{OH}$, aldehyde $-(\text{C}=\text{O})\text{H}$, ester $-(\text{C}=\text{O})\text{OR}$, amino $-\text{NH}_2$ which are found on the outer surface of the pores. To aid in the adsorption process, some of these acts as electron donors and acceptors hence attraction of ions during the treatment process. For instance, a study done by Aksu and Isoglu [19] states that pyrolysis of sugar beet tailings yielded electron donor functional groups (C-OH, C-O, C-O-R) due to the presence of heteropolysaccharides which contain arabinose, galactose and other several protein substances. It was further explained that the sorption of aqueous chromium Cr (VI) on biochar is promoted by the oxygenated groups which reduces it to Cr (III) [20]. The other vital property of biochars, is that the surface charge helps in gaining high cation exchange capacity (CEC). CEC refers to the number of exchangeable cations that are located on the surface of the biochars. Mohan *et al.* [21] revealed that the presence of some cations of Na, K and Mg in pine and oak wood feedstocks increases the CEC of their corresponding biochars after they

enhanced the sorption of Pb^{2+} by ion exchange under acidic conditions.

Surface area and porosity play a major role in metal sorption of biochars because mesopores in biochars develop due to loss of water during dehydration by pyrolysis and these pores can be nano (<0.9nm), micro (<2nm) and macro pores (>50nm) [22]. Chars with small pores cannot trap large adsorbent particles therefore, larger pores are required. It was found by Chiang and You [23] that a municipal sewage sludge biochar was characterised to have a relatively high surface area of 100-200 m^2/g by physical activation and up to 400 m^2/g upon chemical activation. A study by Li *et al.* [24] shows that the surface area and porosity differ with pyrolysis temperature, Fig. 1 shows the surface area of biochars at different pyrolytic temperatures while **Error! Reference source not found.** presents the structure of biochar obtained from poultry waste. It can be shown that the increase in pyrolysis temperature increases the surface area of the agricultural waste biochars. The highest temperature which resulted in the largest surface area for most of these biochars was 700 °C for pine needle, wheat straw, wastewater sludge and municipal bio-solids.

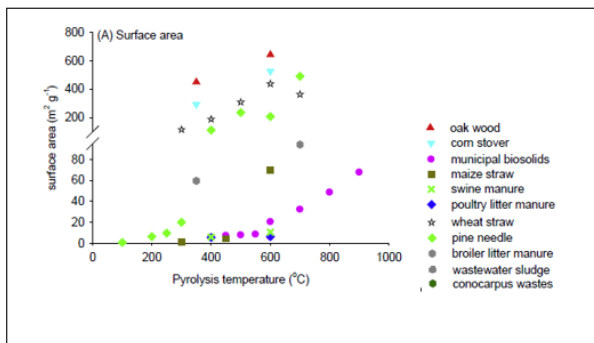


Fig. 1. Surface area of biochars and their pyrolysis temperature [24].

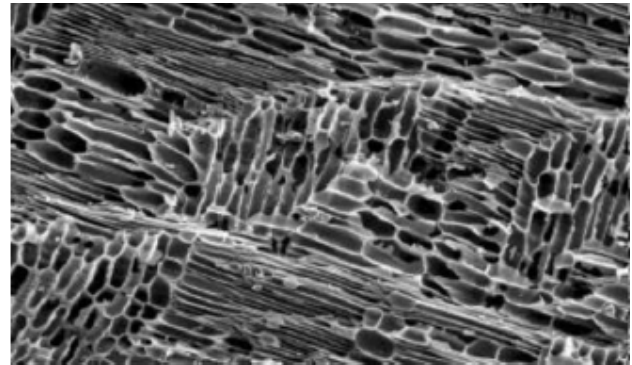


Fig. 2. Structure of biochar obtained from poultry waste [18]

4. Performance of Bio-char as an adsorbent

Several experiments as carried out by different researchers were compiled to analyse the effectiveness of different biochars on the adsorption process to remove different organic and inorganic pollutants as illustrated in Table 1.

Table 1. Performance of different bio-chars in removal of water contaminants

Type of biochar	Surface Area (m^2/g)	Contaminant removed	Adsorption capacity (mg/g)	Percentage Removal (%)	Pyrolysis temperature(°C)	References
Rice straw	-	Malachite green dye	149	25mg/L-99.9 300mg/L-73.3	700	[25]
Canola straw						
Peanut straw (PS)			PS- 256			
Soybean straw (SS)	-	Methyl violet	SS-179	-	350	[26]
Rice hulls (RH)			RH-25			
Soya bean stover	SS300-6 SS700-420 PS300-3 PS700-448	Trichloroethylene TCE	SB700-25.38 PB700-30.74		300 700	[27]
Peanut shells						
Buffalo weed	300 °C -1.35 500 °C -4.83 700 °C-279.8	Pb^{2+} Cd^{2+}	BWC700-333.3 BWC700-11.63	Pb^{2+} 5 50 98 Cd^{2+} 3 14 50	300 500 700	[28]
Dairy manure	1.9 5.61	Cu^{2+} Zn^{2+} Cd^{2+} Cu^{2+} Zn^{2+}	48.4 31.6 31.9 54.4 32.8	Cu^{2+} 54.6 Zn^{2+} 40.0 Cd^{2+} 31.9 Cu^{2+} 62.4 Zn^{2+} 49.4	200 350	[29]

		Cd ²⁺	51.4	Cd ²⁺ 51.1		
Oak wood (OW)	OW- 2.73 OB- 1.88	Cr ⁶⁺	3.03 (25 °C)	-	400 450	[30]
Oak bark (OB)			4.08 (35 °C)			
Pine wood (PW)	PW- 2.73 PB- 1.88	F ⁻	4.61 (25 °C)	-	400 450	[31]
Pine bark (PB)			7.43 (35 °C)			
			7.66 (25 °C)			
			6.34 (35 °C)			
			4.46 (45 °C)			
			9.77 (25 °C)			
			10.53(35°C)			
			8.40 (45 °C)			

The performance of different bio-chars in removing different contaminants has been summarised in Table 1. Comparison of these experiments is very difficult since the bio-chars are produced at different conditions such as the pyrolysis temperature, particle size, surface areas and some are used for batch experiments while others are used for column tests, These biochars are used to remove different contaminants from wastewaters, industrial waters etc under different parameters such as pH, adsorbent loading and process temperatures. However, a review was done on each of these experiments in order to understand the theory behind adsorptive capabilities of bio-chars derived from different biomass materials.

From Table 1, Hameed and El-khaiary [25] used rice straws which were disposed as waste material in a food industry to remove malachite green (cationic dye) from aqueous solutions and the char was prepared in a vertical tubular reactor up to 700 °C with 2 hr of soaking time. The char was then washed with 0.1 M HCL until its pH reached 6-7. Two factors were varied in this experiment, i.e. solution pH and the concentration of malachite green in the solution. During this experiment, with dye concentration of 50 mg/L the pH was varied from 1-7, it was found that less sorption occurred at pH less than 3. This might have been due to excess H⁺ ions in the solution hence they compete for the negative active site of the char therefore less sorption. When increasing dye concentrations from 25 to 300 mg/L, the percentage removal decreased from 99.9 to 73.3%. Even though percentage removal decreases, the adsorptive capacity increased from 16.6 to 146.5mg/g for the same increase of dye concentration. This is because the biochar adsorptive sites are completely filled with the dye molecules (high adsorption capacity) therefore cannot hold any more of the dye (lower percentage removals). In comparison to an experiment carried out by Ahmad *et al.* (2012), they used soybean stover and peanut shell derived biochars to remove Trichloroethylene (TCE) an industrial solvent which is normally found in ground water near an industry in Wonju city in Korea. As already discussed, pyrolysis temperature plays a major role in biochar characteristics, hence a difference between the previous experiment and this one. Pyrolysis temperature plays a major role in biochar characteristics and Ahmad *et al* [27] produced biochar at 300 and 700°C and compared the results. One of the major property which differed was the surface area of the chars produced, those produced at 700 °C had higher surface areas of 420 m²/g and 448 m²/g for soybean stover and peanut shell respectively while those produced at 300 °C had the lowest which were less than 10 m²/g for both of them.

Novak *et al* [32] deduced that the removal of volatile matter during carbonization increased the micropore volume of the char hence increased surface area. It was also found that the removal of H and O from functional groups e.g. aliphatic alkyl -CH₂, esters C=O, phenols OH and aromatic CO greatly enlarged the surface area, this was from a study by Chen and Zhou [33], when removing polar and non-polar aromatics using pine needles char. The removal of these functional groups had a good effect in this adsorbent because their presence shielded the char surface hindering adsorbate particles to attach to the surface. Even though the increase in temperature resulted in a good effect of increasing the surface area of chars, Ahmad *et al* [27] also found that from 300 to 700 °C, the yield of biochars reduced from 37 to 22%, this was due to decomposition of lignin and cellulose in the feedstocks as stated by Kamara *et al* [34]. With the yield produced, the adsorption experiments showed that the chars produced at 700 °C had the highest adsorption capacity of 30.74 mg/g and 25.38 mg/g for peanut shells and soybean respectively. Another effect of pyrolysis temperature was demonstrated by Yakkala *et al* [28] when carrying out adsorption of Pb²⁺ and Cd²⁺ using buffalo weed based biochar. When determining the cation exchange capacity of chars produced at 300,500 and 700 °C, it was found that those produced at 700 °C had the highest CEC of 1268.7 cmol/kg, which indicate that the char can retain the adsorbed cations. Higher CEC is attributed to the increase in functional groups and oxidation of the aromatic carbon with temperature [35]. Moreover, these biochars also had more than 98% removal capacity for both metal ions as illustrated in Fig. 3.

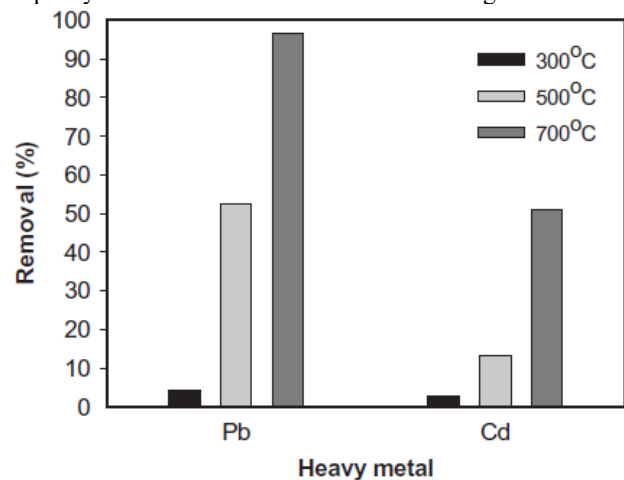


Fig. 3. Effect of pyrolysis temperature (300 °C,500 °C and 700 °C) on percentage removal of Pb²⁺ and Cd²⁺ using buffalo weed (biochar

dosage= 1g/L, contact time= 4h, solution pH=5, initial Pb²⁺ or Cd²⁺ concentration=10mg/L[28].

Hameed and El-khaiary [25] and Ahmad *et al* [27] agree that at lower pH values or acidic conditions there is lower adsorption of contaminants, because lower O contents in chars means low acidic functional groups hence increased hydrophobicity and in this way there is no competition between H molecules of water and the TCE for the active site of the char. On the contrary, Mohan *et al* [30] recorded the highest removal capacity when removing Cr⁶⁺ ions from aqueous solution using oak bark and wood char at acidic conditions (pH 2) as shown in Fig. 4. This was due to the interaction between the chromium ions and the complexes at the char surfaces, since chromium can exist as CrO₄²⁻, HCrO₄²⁻, Cr₂O₇²⁻ and HCr₂O₇²⁻ and biochar surfaces are positively charged at low pH ranges due to surface protonation thus electrostatic attraction occurs. When pH increases, the char becomes less positive due to deprotonation and this observation was also reported by Gupta *et al* [36] and Srivastava *et al* [37] for chromium sorption. Another parameter tested in this experiment was the temperature of adsorption which were carried out at 25, 35 and 45 °C and results revealed a high adsorption capacity of the biochar as temperature increased as shown in Table 1, indicating that the process was endothermic. On the other hand, another experiment which involved sorption of fluoride ions indicated that as temperature of adsorption increases the sorption capacity decreases indicating an exothermic process as presented in Table 1. For pH ranges, during this experiment it was found that a low pH aid in the removal processes in agreement with [30]. Mohan *et al* [31] used pine wood and pine bark chars produced from a fast pyrolysis auger reactor at 400 and 450 °C to remove fluoride ions in aqueous solution. When carrying out the tests at pH ranges from 2-10, results showed that higher removal percentages were observed at lower pH specifically pH 2. The observations were due to the high concentrations of hydronium ions at low pH which protonate basic functional groups in the char hence creating counter ion sites to bind with fluoride ions. It was further observed that presence of ash in the char might have induced the sorption process due to formation of strong metal fluoride bonds (CaF₂ and TiF₂) which have lower solubility in water hence greater stability.

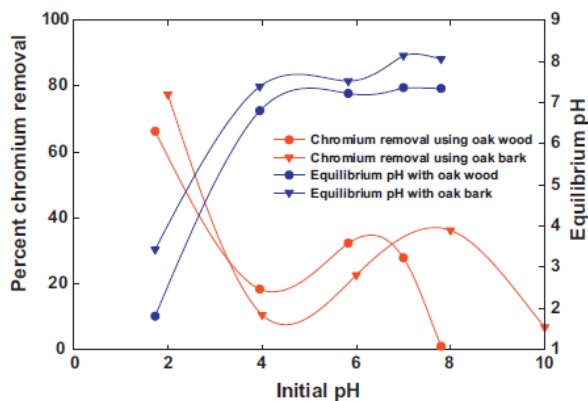


Fig. 4. Effect of pH on chromium removal using oak wood and oak bark. (initial chromium concentration of 10mg/L, adsorbent dosage= 10g/L and temperature of 25 °C [30].

Another experiment carried out by Xu *et al* [26] for the removal of methyl violet dye from aqueous solution using peanut straw, soybean straw and rice hulls derived biochars, a concept of zeta potential was highlighted behind the

adsorption capacities of this dye. The measurements of zeta potential indicated that biochars carry negative charges on their surfaces and they increased with increase in pH which favours adsorption. This was a result of the degree of phenolic -OH dissociation hence the electrostatic attraction of biochars to methyl violet as similar trends were observed by Doğan and Alkan [38] and Mall *et al* [39] using perlite and wood sawdust respectively. An experiment by Xu *et al* [29] revealed that sorption can be due to formation of precipitates. Cd, Zn and Cu were removed from solutions using dairy manure derived bio-char, of which the removal capacities in Table 1 were a result of formation of metal precipitates of phosphates and carbonates ions found in biochar. Dairy manure char was rich in mineral elements which were from the dairy cow diet for enhancement of milk production. It was found that from 200 to 350 °C, the carbon content reduced (31.1% to 25.2%) while Ca (6.09% to 8.89%), CaCO₃ (4.02% to 7.03%) increased. This led to reduced porosity and surface area which are the important adsorptive capabilities of bio-char. As a result, chances of adsorption were less hence precipitation occurred as a sorption mechanism. Removal percentages of the metals increased with the increase in pyrolysis temperature as shown in Table 1.

5. Adsorption Kinetics and Isotherm Studies

Mathematical modelling has been applied on adsorption processes using biochars to help in monitoring their efficiencies. The following are the commonly used kinetic and thermodynamic equations: Freundlich, Langmuir, Redlich–Peterson, Toth, Sips, and Radke. Kinetic models are also used to monitor the adsorption mechanisms that takes place during these surface reactions. Table 2 presents the equations for the kinetic isotherms and models.

Adsorption process is easily analysed and understood using kinetic models and isotherms listed in Table 3. The mostly used kinetic isotherms are Langmuir, Temkin and Freundlich. Comparisons between these were done using the correlation coefficients (R²). In an experiment using buffalo weed derived bio-char carried out by Yakkala *et al* [28], it was found that the experimental results correlated well with the Freundlich than the Langmuir isotherm. The correlation coefficients when using Freundlich isotherm were greater than 0.95. This showed that there is a heterogenous distribution of active sites on the biochar surface, furthermore the process occurred on a multi molecular layer. On the other hand, during adsorption of Trichloroethylene (TCE) using peanut shell and soybean stover the results showed that Langmuir isotherm well described the process based on the correlation coefficients (greater than 0.82) hence monolayer coverage of the solution adsorbate on a planar surfaces of the biochars [27]. For the removal of methyl violet from aqueous solutions, Xu *et al* [26] only used the Langmuir model to fit the adsorption of ions which fitted well with R²> 0.992 for crop residues (peanut straw, soybean straw and rice hull). Mohan *et al* [31] included Redlich–Peterson, Toth, Sips, Temkin, and Radke and Prausnitz and compared them to better analyse the process. It was found that the best fits of the isotherms for pine wood are as follows: Pine wood_{Langmuir} ≈ Pine wood_{Redlich-Peterson} > Pine wood_{Toth} > Pine wood_{Sips} > Pine wood_{Radke and Prausnitz} ≈ Pine wood_{Freundlich} > Pine wood_{Temkin} and for pine bark: Pine bark_{Toth} > Pine bark_{Radke and Prausnitz} ≈ Pine bark_{Freundlich} > Pine bark_{Redlich-Peterson} > Pine bark_{Langmuir} > Pine bark_{Sips} > Pine bark_{Temkin}. It was found that pine wood

adsorption best fit the Langmuir and Redlich–Peterson, which indicate that monolayer adsorption occurred. Pine bark results indicate heterogeneity of the adsorptive sites since Toth model had the highest correlation. It can be shown that for both biochars, Temkin model gave the worst fit for the data. This model assumes that the heat energy of molecules increases linearly with coverage of the adsorbent surface. These isotherms were also used during adsorption of

chromium using oak wood and bark. In this experiment, it was found that Sips best fits the experimental data with the highest regression coefficients. This model is a combination of Langmuir and Freundlich thus it was concluded that the process was diffusion controlled at lower concentrations of chromium while monolayer diffusion occurred at higher concentrations [30].

Table 2. Equations of kinetic isotherms and kinetic models

Kinetic isotherm	Equation	Reference
Langmuir	$\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m}$	[26]
Freundlich	$\log q_e = \log K_f + \frac{1}{n} C_e$	[25]
Temkin	$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e$	[31]
Kinetic models		
Pseudo 1 st order	$\ln (q_t - q_e) = \ln q_e - k_1 t$	[25]
Pseudo 2 nd order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	[31]
Evolich	$q_t = \beta \ln \alpha \beta + \beta \ln t$	[40]
Intra particle diffusion	$q_t = K_p t^{0.5} + x_i$	[41]

Where;

q_m is the amount adsorbed at complete adsorption (mg/g)

q_e is the amount adsorbed at equilibrium (mg/g)

q_t is the amount adsorbed at time t (mg/g)

C_e is the solute concentration at equilibrium (mg/L)

K_L, K_f are the isotherm constants

k_1, k_2, K_p are the rate constants

α and β are the Evolich constants representing the initial adsorption rate and desorption rates.

K_T is the Temkin isotherm constant

b is the Temkin constant related to heat of sorption

Table 3. Kinetic models and adsorption isotherms studies

Type of biochar	Kinetic Models	Kinetic Isotherms	References
Rice straw	Pseudo 1 st order, ($R^2= 0.9750-0.9977$)	Langmuir $R^2 =0.9487$	[25]
	Pseudo 2 nd order, ($R^2=0.9538-0.9855$)	Freundlich $R^2 =0.9295$	
Canola straw Peanut straw Soybean straw Rice hulls	-	Langmuir PS $R^2 =0.996$ SS $R^2 =0.992$ RH $R^2 =0.999$	[26]
Soya bean stover	-	Langmuir $R^2 >0.92$	[27]
Peanut shells	Pseudo 1 st order	Freundlich	

Buffalo weed	Pseudo 2 nd order, R ² >0.97	Langmuir Freundlich, R ² >0.95	[28]
Dairy manure	-	Langmuir R ² (0.95-0.99)	[29]
Oak wood	Pseudo 1 st order	Freundlich R ² (0.74-0.94)	[30]
Oak bark	Pseudo 2 nd order	Sips (Langmuir-Freundlich)	
Pine wood	Pseudo 1 st order	PW-Langmuir and Redlich–Peterson	
Pine bark	Pseudo 2 nd order	PB- Toth	[31]

Kinetic models are used to predict the mechanisms that occur during the adsorption processes. The mostly used models include pseudo 1st and 2nd order, Evolich and intra particle diffusion models. Table 3 shows that during the removal of malachite green dye using rice straw, the correlation coefficients of the pseudo 1st order were higher than those of the pseudo 2nd order hence showing the predominance of the pseudo 1st order kinetic model. Comparisons between the amount adsorbed experimentally (q_{exp}) and the amount adsorbed using the kinetic formulas listed in Table 2 were made. A non-linear relationship between the increase in concentration of the adsorbate and the rate constants which indicated that several mechanisms were involved such as ion exchange, chelation and physical adsorption [25]. Experiments carried out by Yakkala *et al* [28], Mohan *et al* [30] and Mohan *et al* [31] showed that the pseudo 2nd order model fitted the data well in studying adsorption using biochars. It was further concluded that the results indicate that the rate controlling process is chemical adsorption involving the exchange of ions between biochar and the adsorbate. Another model suitable for modelling chemical adsorption processes is the Evolich model. This model was usually used for adsorption of gases on a solid surface but presently it was reported that it can be used to model liquid state sorption processes. It is mainly suited for chemisorption kinetics on a heterogeneous surface [4]. A plot of q_t vs $\ln t$ gives a straight line when the process is governed by the Evolich equation. In an experiment to remove heavy metals from acid mine drainage, it was found that the graphs had R² values of less than 0.99 for all metals which showed that the processes were not via chemisorption [40]. Diffusion models can also be used to analyse adsorption processes especially during the initial sorption process where diffusion is the limiting reaction mechanism. Intra particle diffusion has been used for the adsorption of heavy metals using biochars. This is modelled by plotting a graph of the amount of the solute adsorbed at any time vs the square root of time to give a straight line [4]. Furthermore, intra-particle diffusion model is more likely to occur for micro-porous than macro-porous adsorbents.

6. Conclusion

It can be concluded that the utilization of biochars in wastewater by adsorption is a promising low cost and clean

technology. Industrial waste materials especially those from agricultural by-products have proven to be reliable sources of biochar production. Several factors such as pyrolysis temperature, solution pH, adsorbent loading, contact time, temperature of adsorption and adsorbate concentration affect the process of adsorption. Among these; pyrolysis temperature, contact time, adsorbent loading increases the adsorption capacity and percentage removal of the contaminant while adsorption temperature and solution pH depends on other factors such as the type of biochar and the nature of the contaminant used. Higher pH ranges were observed to increase adsorption capacity for positively charged contaminants such as metal ions and some dyes whereas acidic conditions favoured adsorption of negatively charged contaminants such as anions as was seen by fluoride and chromium compound ions. Some researchers found that adsorption process is exothermic while others observed it to be endothermic by varying temperature during the tests. A summary of characteristics of biochars which induce adsorption have been identified. They include surface functional groups, cation exchange capacity (CEC), surface area, porosity, elemental composition, ash content, hydrophobicity, polarity, zeta potential and type of biochar precursor. Some of the oxygenated functional groups that exist on biochar surfaces include hydroxy, anhydride, carboxylic acid, ketone, quinone, ether, lactone, pyrone, catechol, hydroxyketone and others. Kinetic models and isotherms were used to further analyse the adsorption process to find out mechanisms which control the reactions. Some of the commonly used adsorption isotherms include Freundlich, Langmuir and Temkin and kinetic models include pseudo 1st and 2nd order, Evolich and intraparticle diffusion. It can be concluded that from several literature compiled, biochars are effective adsorbents and cost effective comparing to industrially manufactured activated carbons.

7. Future work

Further studies on biochar applications and properties should be prioritised in order to generate value out of these bio refinery by-products since they have been found to be environmentally friendly. Based on reviewed literature biochar capabilities have been recently developed even though this has been long discovered therefore knowledge on this should be updated. More research on different biochar

production methods should be undertaken because that is the root of good quality chars. In addition, type of feedstocks should also be analysed because its properties differ per biomass.

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