Original Research Article

Sugarcane bagasse based adsorbents and their adsorption efficacy on removal

of heavy metals from Nakuru industrial water: optimization, kinetic and

thermodynamic aspects

ABSTRACT:

KEYWORDS: Sugarcane bagasse, Adsorption, heavy metals, wastewater.

- **INTRODUCTION:**

Water is a source of life []. However, the quality of the world's water is increasingly threatened due to freshwater resources becoming heavily polluted by heavy metals, pathogens, turbidity, oil, and its derivatives from industries and agricultural effluents [and]. Heavy metal contaminated water is a real threat for agriculture, fishing and human consumption [and]. Among the heavy metals, Cu^{2+}, Cr^{6+}, $Mn^{2+,}$ Ni^{2+}, Fe^{3+}, Cd^{2+}, $Pb^{2+,}$ and Zn^{2+} ions are of primary concern in aquatic and terrestrial environments because of their high toxicity, high mobility, and solubility[]. These metals enter the human body either directly or through the food chain []. They tend to accumulate in the human body [ ] when ingested and cause serious health disorders []. For example, Pb2+ poisoning can lead to low intelligence quotient, concentration issues in children, axon degeneration, edema, infertility, menstrual problems, and stillbirths in adults[, and] while cadmium causes damage to the kidneys, lungs, and liver [].

Currently, numerous conventional physicochemical methods such as electrochemical treatment, ion-exchange, precipitation, reverse osmosis, evaporation, and oxidation/reduction [] have been used for the removal of heavy metal ions from wastewaters. However, these methods have had their limitations, the major ones being: initial high costs, not being eco-friendly as well as incomplete removal of large quantities of toxic sludge produced, a huge amount of energy needed [3]. Adsorption has been used for centuries by Egyptians for the removal of odours and purification of drinking water []. Adsorption is a viable alternative treatment method because it is cost-effective, simple to operate [], requires low energy, offers good selectivity, allows for the recovery of heavy metals [], and provides options for adsorbent regeneration [and]. Adsorption using activated carbon has been found to be an attractive process for the removal of heavy metals from industtrial effluents and dyes from aqueous solutions []. However, the cost of activated carbon and the loss of adsorption efficiency after regeneration of the exhausted activated carbon have limited its use in effluent wastewater treatment.

Bio-adsorbents made from sugarcane bagasse are inexhaustible materials containing carbon-oxygen functional groups such as carboxyl, ketone, ester, aromatic rings, and hydroxyl groups []. These functional groups have capacity for adsorbing metal ions through mechanisms like chelation and electrostatic interactions [], which offer greater selectivity for bio-sorption studies on heavy metal ions, activation increases their efficiency and high adsorption capacity [] due to their large surface area [] and surface reactivity [], an essential property for removing heavy metal ions from contaminated water []. The effectiveness of removing these ions is influenced by experimental conditions such as temperature, concentration, contact time [24], pH, and particle size [, and].

There is need to investigate the kinetic and thermodynamic behaviour of sugarcane bio-sorbent to remove cadmium (Cd2+), chromium (Cr3+), copper (Cu2+), Nickel (Ni2+) and lead (Pb2+) ions from industrial wastewater under varying experimental conditions of pH, contact time [], particle size, initial concentration, adsorbent dosage and temperature [] in order to obtain a detailed understanding of the adsorption mechanism. This is of vital importance because sugarcane bagasse is a low-cost farm waste sorbent that can be regenerated for re-use and exhibits high efficiency in detoxifying extremely dilute effluents. To describe the interactions between liquid and solid phases [], numerous equations have been used to correlate experimental adsorption isotherm data so as to determine the best fit isotherms model []. The Freundlich isotherm has been shown to be suitable for multilayer adsorption caused by various functional groups on the surface of adsorbent. The Langmuir isotherm, on the other hand, is derived on the assumption of monolayer adsorption [].

In this study the adsorption mechanism and maximum adsorption capacity were studied through the application of these adsorption models after which thermodynamic parameters (were determined. The adsorption kinetics were investigated using pseudo-first and pseudo-second order rate equations. The adsorbents were subsequently explored for its efficacy in removing heavy metals from real wastewater samples.

2.0 MATERIALS AND METHODS:

2.1 Chemicals, reagents and preparation of metal ion solutions:

All the chemicals used throughout this study were analytical-grade reagents. Double-distilled water was used to prepare all solutions and reagents. Stock solutions of the heavy metal standards were prepared using analytical grade salts (($Cu(NO_3)_2$, $Pb(NO_3)_2$, $Cr(NO_3)_3$, $NiCl_2$, and $CdCl_2$ (purchased from Sigma Aldrich , Kobian Nairobi)) in distilled water to which 3.0 cm^3 concentrated HNO_3 acid had been added, and then diluted to 1.0 Litre. The working standard solutions of each metal were obtained by dilution of appropriate amounts of heavy metal solution using distilled water. A few drops of Caesium-lanthanum ($CsCl/LaCl_3$; 5:20 g/L) solution was added to each of the working standards as an interference suppressant. The initial pH of the solutions during the analyses was adjusted using 0.1 M HCl or 0.1 M NaOH.

2.2 Instrumentation:

Flame Atomic Absorption Spectrophotometer (AA model S11 from Thermo Jarell Ash Cooperation of Waltham, MA, USA) with an air acetylene flame was used to analyse heavy metals. pH meter used was Jenway pH meter model 3505, grinding was done using a blender (Heavy duty blender model 24CB10C), muffle furnace (Gallenkamp muffle furnace size 2 tactical 308), water bath shaker used (American optical model 406016 NY142). Sieving done using supertek standard sieves. FTIR analyses done using ATR FTIR JASCO 4700 WITH ATR PRO ONE head. Number of scans 40/s. Range 500-4000cm^{-1}. Resolution 4.0cm^{-1}. Detector – TGS

2.3 Sampling sites and wastewater collection:

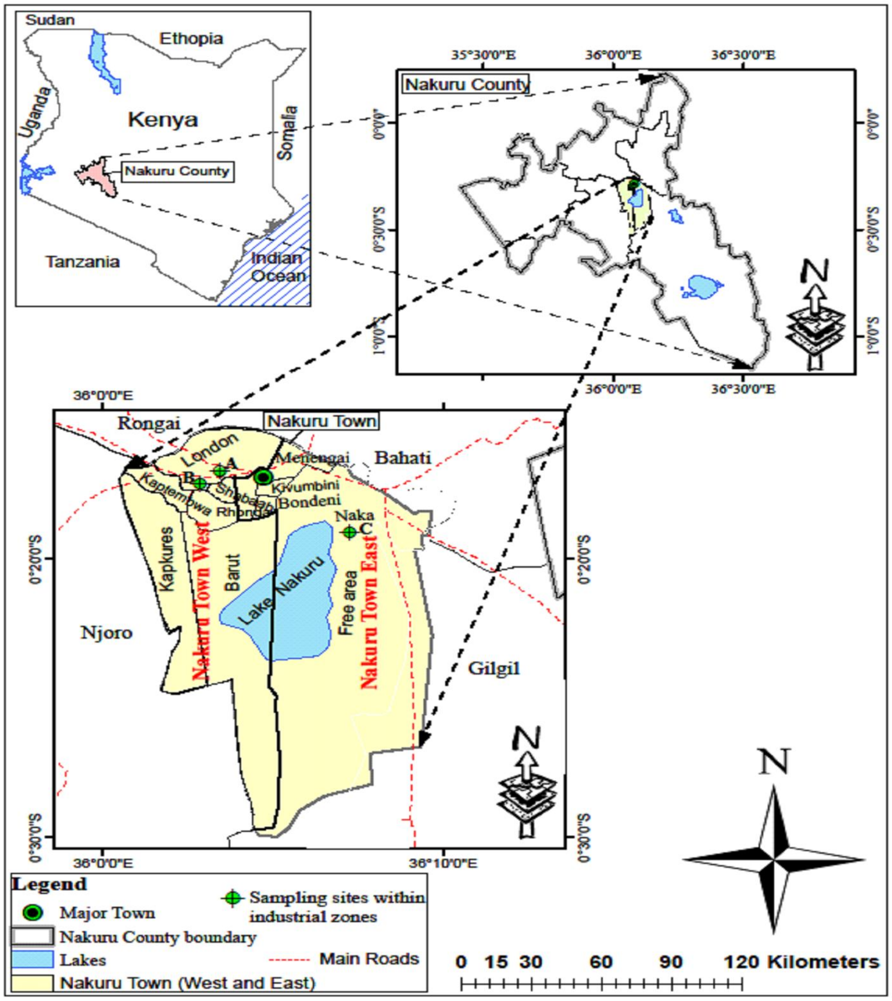

Figure1: Showing the study area and the sampling sites in Nakuru city in Nakuru County, Kenya

Waste water Samples were collected from Nakuru City, Nakuru County in Kenya from three different sampling sites that were coded **A** to **C**. Figure 1 shows the sites which included Jua Kali (Open air) garage (**A**), Tannery effluent (**B**), and Potable water refilling plant (**C**). Wastewater samples were collected in triplicate using pre-cleaned one litre plastic bottles then acidified with 1.0 ml concentrated HNO_3 and stored in a refrigerator for subsequent analysis.

2.4 Sampling and sample pre-treatment:

Sugarcane bagasse was collected from the Nzoia sugar factory in Western Kenya. Sugarcane bagasse was cut into small pieces (about 2 cm) then washed thoroughly with tap water and rinsed three times with distilled water, dried in air then in an oven at 60 °C for 24 hours and finally ground into fine powder. It was sieved done using 50, 150, 250, 425, 500, 595µm, and 1mm-size standard sieves and labelled normal sugarcane bagasse (NSCB).

2.5 Preparation of Sugarcane bagasse and valorized bagasse:

The sugarcane bagasse sample was heated in a muffle furnace at 300 ^{o}C for three hours for valorisation to take place then left to cool and sieved to the required particle size. The labelled as valorised sugarcane bagasse (VSCB).

2.6 Optimisation experiments:

The experiments were done in 100mL polypropylene bottles at 20 □C using a rotary shaker at

65rpm. Optimized experimental conditions include particle size, contact time, pH, initial metal ion concentration and temperature. This was done by keeping all other parameters constant while varying the one under consideration. 0.1g of adsorbent was placed in polypropylene bottle followed by 100mL of desired metal ion concentration then placed in the shaker for 60 minutes. Effect of particle size (50-595 μm), contact time (1-60mins), pH (2-10), initial metal ion concentration (2-60mg/L) and temperature (25-40^{o}C) were studied respectively, with each of the shaken solution was filtered through Whatman filter paper No. 1 and the metal ion concentration in the filtrate determined using a flame atomic absorption spectrophotometer (AAS). All determinations were conducted in triplicate.

2.7 Data analysis:

The removal efficiency (%), amount of HMs adsorbed at a given time (q_t), amount of HMs adsorbed at equilibrium (q_e) given by (1,2 & 3, respectively):

(1)
(2)

(3)

Whereby Removal efficiency is the percentage removal of metal ions, C_o is the initial metal ion concentration (mg/L), C_t is the metal ion concentration at time t (mg/L), C_e is the equilibrium concentration (mg/L), V is the volume of solution and m is the mass of adsorbent (g) [].

2.8 Adsorption isotherms:

0.1g of adsorbent was weighed into a glass beaker then 100ml of 10mg/L solution of each heavy metal (Cu^{2+}, Pb^{2+}, Cr^{3+} , Ni^{2+}, and Cd^{2+}) ions solution was added. A contact time study was done at 1, 2, 3, 4, 5, 30 and 60 mins at pH 5 and at 25 °C in order to be representative of environmentally relevant condition, and at a shaking speed of 65 rpm to ensure that equilibrium was reached. The study on isotherms was conducted so as to understand interaction between the adsorbent and the heavy metal ions occurs as a monolayer or multilayer. Langmuir isotherm model assumes monolayer coverage [] while Freudlich assumes multilayer coverage []. Langmuir isotherm model is given by equation (4)

(4)

Where q_e is the amount of heavy metal ions adsorbed at equilibrium, q_{max} is is the maximum adsorption capacity (mg/g), K_L is the Langmuir constant and Ce is the heavy metal ion concentration at equilibrium (mg/L).

Freundlich isotherm model is given by equation (5)

log (5)

Where q_e is the amount of heavy metal ions adsorbed at equilibrium, K_F is the Freundlich constant and C_e is the heavy metal ion concentration at equilibrium (mg/L).

2.9 Thermodynamic data modelling:

This was done in order to determine thermodynamic parameters Gibbs energy (ΔG), entropy (ΔS), and enthalpy (ΔH) of the reaction []. Thermodynamic data was obtained by varying the temperature(25-40^{o}C). A plot of ln vs $\frac{1}{T}$ was plotted to estimate the thermodynamic parameters ΔG, ΔS, and ΔH from the Van't Hoff's plot which gives the relationship between the thermodynamic parameters:

+ (6)

2.10 Kinetic data modelling:

Kinetic studies were done by varying the contact time (1-60mins) and the obtained data was regressed against two equations: the Lagergren pseudo first-order (equation 7), and also against a pseudo-second-order kinetic equations (equation 8).

(7)

(8)

Where q_t is the metal uptake per unit weight of adsorbent (mg g^{-1}) at time t, while q_e is the metal uptake per unit weight of adsorbent (mg $g-1$) at equilibrium. k_1 (min $^{-1}$) and k_2 (mg g^{-1} min $^{-1}$) are the rate constants of the first-order kinetics and second order kinetics respectively (min^{-1}). The slopes and intercepts are used to determine the values of k_1 and k_2 as well as the equilibrium capacity (q_e) []. It is the plot that has the higher regression coefficient, R^2, that gives the best fit.

2.11 FTIR analyses:

NSCB and VSCB were dried in an oven at 105°C for 7 hours to remove moisture. Each of the adsorbents was left to cool to room temperature in a dessicator overnight and then put in sample vials. NSCB and VSCB were soaked in 500 mg L^{-1} metal ion solution overnight and then filtered. The adsorbent /adsorbate product was dried in an oven at 105 ^oC in an oven for 7 hours. This sample was left to cool in a dessicator. The samples were then put in sample vials.FTIR spectra were obtained for the adsorbents and for adsorbents treated with metal ions as powder in excess dry KBr solvent.

3.0 RESULTS AND DISCUSSION:

3.1 Concentration of Heavy metals in wastewater:

The results of concentration of the heavy metals in the wastewater samples at sites **A**, **B** and **C** are provided in Table1. It is noted that the lead, cadmium, nickel, and chromium contents of the wastewaters, coming out of the Jua Kali garage, tanning industry and potable water plant, were significantly higher than the permissible limits of the World health organization (WHO, 2011) and Kenya (National Environment Management Authority (NEMA,2011) and Kenya Bureau of Standards (KEBS), and maximum permissible level according to WHO guidelines for drinking water []. The concentrations of copper (Cu) were below the detection limit in all the sampling sites. The high amounts of heavy metals observed in these wastewaters are capable of causing significantly high corresponding increase in the receiving water- bodies, thereby affecting humans, wildlife, the environment and aquatic life that directly/ or indirectly depends on it [].

Table 1. Concentration (mg/l) of heavy metals in wastewater

Site	Heavy metal concentration (mg/l)				
	Pb	**Cu**	**Cd**	**Ni**	**Cr**
A	1.15 ± 0.00	0.81 ± 0.01	0.10 ± 0.01	0.67 ± 0.01	0.66 ± 0.05
B	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.20 ± 0.02	9.94 ± 1.93
C	0.10 ± 0.01	nd	0.02 ± 0.00	0.32 ± 0.00	nd
NEMA (Maximum Allowable effluent discharge Limits)	0.01	1.0	0.003	0.02	0.05

A = Jua Kali garage wastewater, B = Tannery effluent, C = Potable water refilling plant wastewater; nd = not detected, NEMA= National environmental management authority (Kenya)

3.2 Experimental conditions for adsorption:

Table 2: Experimental conditions for adsorption.

	Adsorbent dose (g)	pH	Particle size (µm)	Concentration ppm	Temperature ^{o}C	Time (mins)
Pb	0.1	5	150-250	2 - 60	25	60
Cu	0.1	5	150-250	2 - 60	25	60
Cr	0.1	5	150-250	2 - 60	25	60
Ni	0.1	5	150-250	2 - 60	25	60
Cd	0.1	5	150-250	2 - 60	25	60

3.3 Effect of adsorbent dosage:

To obtain the best adsorbent dosage, different amounts of adsorbent (0.05 g to 2.0 g) were added to individual heavy metal ion solutions (Lead, C o = 5.0 ppm, Chromium, C o = 2.5 ppm, Copper, C o = 2.0 ppm, Cadmium, C o = 1.5 ppm, and Nickel, C o = 3.0 ppm). It was observed from Figures (2a & 2b) that the higher the adsorbent dose the higher the removal efficiency [42]. This was attributed to the fact that a higher adsorbent dosage provides an increased number of adsorption sites available for metal adsorption [and] and also enhances the overall capacity of the adsorbent by providing more surface area for contaminants to adhere to []. Other studies also have shown that adsorbent dosage per se is a significant parameter that affects the ability of adsorption and the effectiveness of removal of a heavy metal [43].

Figure 2: Effect of adsorbent dose of (a) NSCB and (b) VSCB on the removal of Pb^{2+}, Cd^{2+}, Cu^{2+} , Ni^{2+} , and Cr^{3+} ions (particle size 150 µm, pH 5.0, adsorption time 60 minutes, and temperature 25 °C)

3.4 Effect of particle size of adsorbent:

It was observed from Figure 3 that smaller particle sized adsorbents (≤ 150µm) exhibited higher adsorption capabilities than larger size particles. Hence, a reduction of size from 595 to 150 microns led to an increase in the adsorption capacity or percentage removal effiffiency. This is so because smaller particles have a higher surface area-to-volume ratio compared to larger particles, and is supported by [and]. This is because a decrease in particle size leads to an increase in surface area to facilitate adsorption of metal ions [46] . Moreover, at large particle size, there is a slower adsorption kinetics []. Asimilar trend was observed for the other metal ions Pb^{2+} , Cd^{2+} and Cr^{3+} and the results are not shown in this paper.

Figure 3: Effect of particle size on the adsorption of Cu^{2+} and Ni^{2+} ions on sugarcane bagasse.

3.5 Effect of contact time on adsorption of metal ions:

The effect of contact time was determined by monitoring the uptake of the Pb (II), Cu(II, Cd(II) , Cr(III) and Ni (II) ions over a period of 60 min at room temperature. The results are shown in Figures 4 (a, &; b). Initially, metal ion uptake was high, likely due to the significant concentration gradient between the ions in the solution and the abundant vacant sites on the adsorbent surface []. Over time, adsorption onto the remaining sites becomes more challenging, primarily due to the repulsive forces between the adsorbed solute ions on the adsorbent surface and those in the bulk solution [] the maximum adsorption capacity order of the heavy metals in the single metal ion system was $Cr^{3+} \geq Cu^{2+} \approx Cd^{2+} \approx Ni^{2+} \geq Pb^{2+}$ for NSCB and $Cr^{3+} \geq Cd^{2+} \geq Ni^{2+} \geq Cu^{2+} \geq Pb^{2+}$ for VSCB and this could probably be because of the different affinities of NSCB and VSCB toward the metal ions. The maximum removal was be achieved within a period of 30 minutes. Therefore, the removal of the ions by the sugarcane bagasse and the valorized bagasse has revealed that adsorbent bagasse shows great adsorption potential towards heavy metals with higher electronegativity which has also been observed by other researcher who also observed that greater electronegativity leads to greater adsorption capacity []. Secondly this observation could also be explained in terms of hydrated ionic radii, Pb^{2+} has large ionic radii (119picometers) while Cr^{3+} will has the smallest (61picometers), the trend of hydrated ionic radii is $Cr^{3+} < Ni^{2+} \approx Cu^{2+} < Cd^{2+} < Pd^{2+}$ whereby the small ions will tend to be adsorbed better than larger ions [].

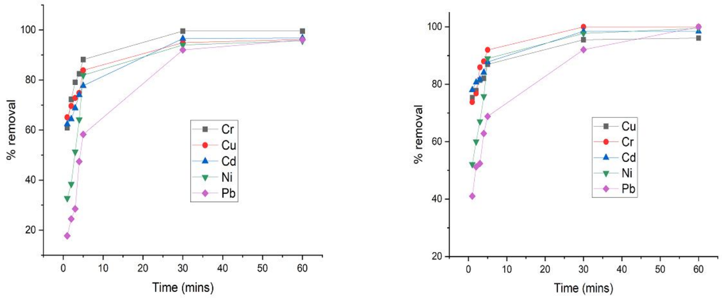

Figure 4: Effect of increasing contact time for (a) NSCB and (b) VSCB (Adsorbent dose 0.1 g, 100 mL of 10 mg/L metal ion solution, particle size ≤150 < 250 μm, at pH = 5.0 and temperature 25 °C

3.6 Effect of pH:

The result from figure 5 shows the effect of pH on the adsorption of Pb, Cr and Cd. At low pH ≤ 2.0, both the NSCB and VSCB (results not shown here for VSCB) showed very low tendency for uptake of all the investigated metal ions. This was as result of protonation of the varied functional groups on the active adsorbent sites, and the competition of H^+ ions with metal ions for the binding sites []. Increasing pH from 2 to 4 (i.e., fewer H_3O^+), the adsorbent surface active sites became more negatively charged, resulting in more active sites available for metal ion binding. As a resul, the removal efficiencies for Cr^{3+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, and Pb^{2+} increased. The binding capacities reached their maximum values around pH 4.0 then remaining nearly constant up to pH 6.0. After pH 6 there is a slight decrease in the amount of metal ions removed from the solution, whereas at high pH > 7.0, there is precipitation which leads to a decrease in the removal of metal ions [25]. Consequently, subsequent adsorption experiments were done under acidic conditions, at the optimum pH 5.0.

Figure 5: Removal efficiency of metal ions (Pb^{2+}, Cr^{3+} and Cd^{2+}) as function of pH using 0.1 g NSCB, 100 mL of 10 mg/L metal ion solution, particle size ≤150<250 µm, and at T = 25 °C.and at T = 25 °C.

3.7 Effect of initial concentration of metal ions:

Generally, there was an inverse relationship observed between the metal ion concentrations and the removal capabilities of the sugarcane bagasse (NSCB) for Cr +3 , Cd +2 , Cu 2+ , Ni 2+ and Pb 2+ ions (Figure 6). A similar trend was followed by the valorised bagasse ash (VSCB). At low concentrations (2 to 6 mg/L) the removal efficiency of Pb(II), Cd(II), CU(II), Ni(II) and Cr(III) was 100%. As a result of the low concentrations, there are enough active sites for adsorption and also less competition for the adsorption sites []. Lead (Pb) removal efficiency decreased gradually from 99.48 % to 61.62%, Cd (97.71% to 55.77%), Cr (99.55% to 64.70%), Cu (96.92% to 30.83%) and Ni (96.67% to 74.95%) with increasing metal ions concentration from 8 mg/L to 60 mg/L. A similar trend was described by [and], where the adsorption rate decreases as the initial concentration of the metal ion pollutants increases.

The overall reduction in metal ion removal with increasing ion concentration is attributed to the saturation of available active adsorption sites on the adsorbent surface [52] and to the repulsive forces between the adjacent adsorbed solute molecules in the solid phase and the ones in the bulk liquid phase [53]. Thus, the initial pollutant concentration provides the main driving force to overcome all mass transfer resistance between the aqueous and solid phases [54].

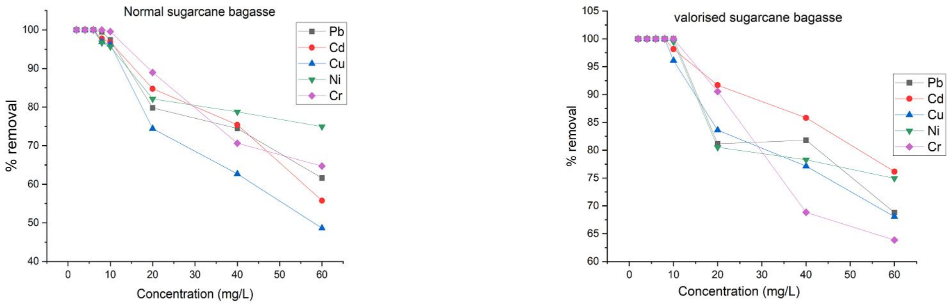

Figure 6: Removal of Cd(II), ,Cu(II), Ni(II), Pb(II) and Cr(III) from aqueous solution by (a) sugarcane bagasse (NSCB) and (b) valorised bagasse (VSCB), under different initial concentrations at 25 °C. (Adsorbent dose 0.1 g, particle size ≤ 150 µm, time 60 mins, and at pH 5

5).3.8 Effect of temperature:

The effect of temperature on the removal of Pb^{2+} and Cd^{2+} in aqueous solution by NSCB and

VSCB biomass was studied by varying the temperature between 20 and 60 ºC at the initial concentration of 20mg/L at pH 5.0, 0.1 g adsorbent dosage and contact time of 60 minutes. The data are presented in Table 3, and show that the adsorption of the metal ions by the NSCB adsorbent, increases with the increase in temperature from 20 °C to 60 °C, which is typical for the bio-sorption of most metal ions from their solution []. It is seen that at higher temperatures the percentage removal was also higher. This can be attributed to increased kinetic energy for the molecules. This indicates that an increase in temperature induces a positive effect on the adsorption process, which demonstrates that the adsorption of the metals studied is an endothermic process. However extreme temperatures can also change adsorbent structure lead to decrease in removal of metals. A similar trend was observed for VSCB.

Table 3: Percentage removal of metal ions at different temperatures for NSCB (0.1 g adsorbent, 100 mL of 10 mg/L metal ion solution, ≤ 150 µm adsorbent particle size and pH 5).

Temp (°C)	20	25	30	35	40	60
% removal Cr	86	89	93	95	96	98
%removal Cd	87	89	90	92	93	99
% removal Pb	79	82	87	91	93	99
% removal Ni	79	81	89	91	93	97
% removal Cu	74	81	87	89	93	95

3.9 Characterization: FTIR analysis:

Fourier transform infrared (FTIR) spectroscopy analysis was carried out to determine the surface functional groups of the biochar samples using FTIR – 6100 JASCO spectrometer in the range 4000–400cm $^{-1}$ and the results are presented in Figure 7.The broad absorption band at 3860–338 cm^{-1} can be attributed to Si-OH, –OH (water, carboxylic acid and Phenol) stretching vibrations. The band at 1702 cm^{-1} was assigned to carbonyl (C=O) groups, and at 1600-1536 cm^{-1} represents C=C for alkene groups. The absorption bands at 1029 and 1034 cm^{-1} was attributed to C–O stretching vibration of cellulose, lignin and hemicelluloses. After interaction with metal ions, the absorption band of –OH [] in the NSCB and VSCB shifted 3334 cm^{-1} to 3346 cm^{-1}; and from 3796 to 3800 cm^{-1} in VSCB only due to Si-OH stretch obtained as a result of combustion of the bagasse. Absorption band at 1702 represents representing the carbonyl group. Band at 1590, 1509 is attributed to alkene group. This indicates that on adsorption the metal ion are attached to NSCB and VSCB through O-H or carboxylate, carbonyl and C=C aromatic groups.

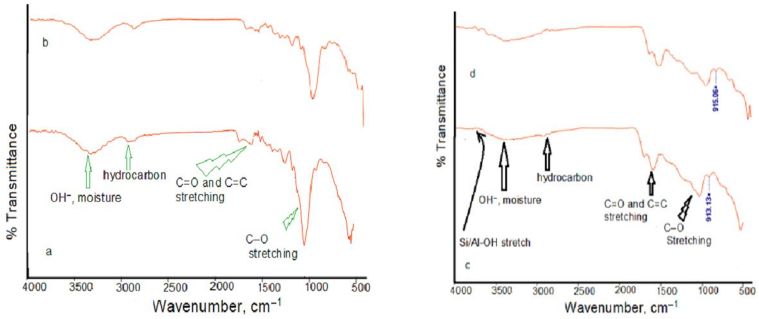

Figure 7: FTIR spectra of NSCB (a) prior to adsorption and (b) following adsorption on Left; VSCB (c) before adsorption and (d) after adsorption on Right.

3.10 Adsorption isotherms and adsorption capacity:

From this study (Table 4), the data fitted well the Langmuir (R^2 = 96.9–99.4%) and Freundlich

(R^2 = 95.6– 99.9%) adsorption isotherms models for Cr $^{3+}$, Cd $^{2+}$, Cu $^{2+}$, Ni $^{2+}$ and Pb $^{2+}$ ions onto NSCB and VSCB adsorbent surfaces. The Langmuir isotherm model provided a better fit for chromium, cadmium, and copper, by forming a well-defined monolayer on the NSCB adsorbent surfaces which showed that each adsorption site can hold one metal ion at a time [and]

From Langmuir adsorption isotherm the parameter R_L (separation factor) was in the range of 0.144–0.260, which justify the adsorption processes for Cr $^{3+}$ is 78.740 which was higher than that of Ni^{2+} (56.818), Pb^{2+} (44.053) Cd^{2+}(35.845) and Cu^{2+}(31.645); ions SCB and VSCB. The slope of the Freundlich isotherm (1/n), on the other hand, were found to lie in the range (0.206-0.513); and was Cr^{3+} (38.02) which was lower than that of Ni^{2+} (51.282), Pb^{2+} (45.871), Cd^{2+} (51.020) and Cu^{2+} (47.393mg/g), onto th sugarcane bagasse and its valorised ash, respectively. From these results, the affinity of the adsorption sites on the sugarcane bagasse (NSCB) to chromium ions is stronger compared to that of nickel, lead, cadmium and copper. The plausible reason is that the higher oxidation state of +3 on chromium imparts a higher charge density and higher attractive force to adsorbent sites compared to the +2 charge on nickel, lead, cadmium and copper ions. And on changing the adsorbent to valorised bagasse, the order of the adsorption affinity changed with order decreasing as Ni^{2+} > Cd^{2+} > Cu^{2+} > Pb^{2+} > Cr $^{3+}$. The amount of adsorbed Ni(II) is larger than that of Cd(II).

This trend is in accordance to the increasing size of the metal ions, typified by: Ni(II) (1.62 ˚A) > Cd(II) (1.71 ˚A); where smaller sized metal ions have more accessibility to the surface and pores than bigger sized metal ions, resulting in the higher adsorption of the smaller sized Nickel ion. Also, based on the Freundlich isotherm that is suitable for heterogeneous surfaces such as valorised adsorbents which often have various active sites and functional groups, a strong correlation between the VSCB and metals like lead, cadmium, copper, and nickel was observed.

The Langmuir adsorption isotherm parameter R_L (separation factor) was in the range of 0.144–0.260, which justified the adsorption processes occurring for Cr^{3+} , Cd^{2+} , Cu^{2+} , Ni^{2+} and Pb^{2+} onto NSCB and VSCB. The slope of the Freundlich isotherm (1/n), on the other hand, was found to lie in the range (0.206-0.513); showing that normal adsorption process took place [56]. The Freundlich constant (1/n) suggests that the adsorption process is more favorable in cooperative adsorption,that includes both physisorption and chemisorption [57], and that chemisorption takes place on the initial layer of active sites for all functional groups on the SCB surface [58]. However, only chromium fitted well to the Langmuir model on both the NSCB and valorised bagasse adsorbents, which is in agreement with results previously reported by []

Table 4 Fitting of the parameters of the experimental results to the Langmuir and Freundlich equation parameters (pH 5, C_0 = 10 mg/L, V = 100 mL, 25 °C)

Adsorbent	**Adsorbate**	**Langmiur isotherm** **q_{max} (mg/g)**	**K_L (L/mg)**	**R_L**	**R^2**	**Freundlich isotherm** **K_F**	**n**	**1/n**	**R^2**
NSCB	Pb^{2+}	44.053	0.234	0.230	0.9392	11.939	2.804	0.357	0.9529
	Cu^{2+}	31.645	0.307	0.197	0.9771	11.665	3.899	0.257	0.9461
	Cd^{2+}	35.845	0.496	0.144	0.9922	13.359	3.362	0.297	0.9693
	Ni^{2+}	56.818	0.184	0.260	0.8228	12.331	2.339	0.428	0.9322
	Cr^{3+}	78.740	0.485	0.146	0.9512	17.624	4.852	0.206	0.9435

Adsorbent	**Adsorbate**	**q_{max} (mg/g)**	**Langmiur isotherm** **K_L (L/mg)**	**R_L**	**R^2**	**Freundlich isotherm** **K_F**	**n**	**1/n**	**R^2**
VSCB	Pb^{2+}	45.871	0.459	0.152	0.9496	10.515	1.948	0.513	0.9810
	Cu^{2+}	47.393	0.257	0.219	0.9459	12.758	2.663	0.376	0.9669
	Cd^{2+}	51.020	0.490	0.145	0.9748	17.230	2.766	0.362	0.9850

Ni^{2+}	51.282	0.243	0.226	0.7549	17.976	4.272	0.234	0.7982
Cr^{3+}	38.022	0.595	0.126	0.9505	11.579	2.640	0.379	0.9279

3.11 Kinetics for NSCB and VSCB:

In order to determine the rate at which the sorption process occurs, the pseudo-first-order and pseudo-second-order models were applied to fit the experimental data. The parameters for pseudo-first-order and pseudo-second-order models that were used to evaluate the kinetic mechanism which controls the adsorption process [] are shown in table 5. The correlation coefficients for pseudo second-order-kinetics (in the range R^2= 0.9961 - 0.999) is higher than that for pseudo first order kinetics (in the range R^2=0.8801 – 0.9993), suggesting that pseudo second kinetic have a better fit for the experimental results for both SCB and VSCB, across various metal ions (Pb^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, and Cr^{3+}).

Table 5 Kinetic parameters for the adsorption of heavy metals by NSCB and VSCB.

NSCB	Pseudo-First-order model			Pseudo-Second-order model		
	k_1 (min^{-1})	q_1 (mg/g)	R^2	k_2 (mg g^{-1} min^{-1})	q_2 (mg/g)	R^2
Pb^{2+}	0.101	8.019	0.9833	0.016	10.638	0.9961
Cd^{2+}	0.176	4.509	0.9993	0.094	9.881	0.9998
Ni^{2+}	0.119	5.394	0.9179	0.045	9.960	0.9999
Cu^{2+}	0.107	3.047	0.9762	0.118	9.765	0.9999
Cr^3	0.298	5.131	0.9858	0.133	10.101	0.9999
VSCB	Pseudo-First-order model			Pseudo-Second-order model		
	k_1 (min^{-1})	q_1 (mg/g)	R^2	k_2 (mg g^{-1} min^{-1})	q_2 (mg/g)	R^2
Pb^{2+}	0.295	8.260	0.8990	0.061	10.320	0.9994
Cd^{2+}	0.153	2.426	0.9302	0.194	9.911	0.9999
Ni^{2+}	0.187	5.976	0.9464	0.083	10.152	0.9998
Cu^{2+}	0.208	5.821	0.8801	0.120	16.807	0.9999
Cr^3	0.267	10.342	0.8164	0.032	10.582	0.9984

3.12 Thermodynamic parameters of Adsorption:

In order to better understand the effect of rising temperature on the adsorption of the Ni(II), Cu (II), Cr(III), Pb(II), and Cd(II) ions onto the sugarcane bagasse (NSCB) and valorized ash (VSCB), three basic thermodynamic parameters: the Gibbs free energy of adsorption (ΔG), the enthalpy change (ΔH), and the entropy change (ΔS) were determined from the Van't Hoff equation. The corresponding values of thermodynamic parameters are summarized in Table 6. The results show that ΔH° and ΔS° are positive across all experiments, while ΔG° is negative in every case indicating the adsorption process was feasible. The positive values of ΔH° indicate that the adsorption process of Cr^{3+} , Cd^{2+} , Cu^{2+} , Ni^{2+} , and Pb^{2+} ions on sugarcane bagasse (NSCB) and valorized bagasse (VSCB) was endothermic in nature, which agrees, as early discussed, that the amount heavy metal adsorbed at equilibrium increased with increasing temperature. The positive value of ΔS° suggests increased randomness and an increase in the degrees of freedom at the bio-adsorbent-solution interface as heavy metal ions are immobilized on the adsorbent's active sites. Which means further liberation of water molecules (solvent molecules) from solvated-heavy metal ions occurs before adsorption, thus, enabling complete randomness and spontaneity in the system [and].

Table 6: Thermodynamic parameters

	NSCB			VSCB		
	$\Delta G^{\#}$ $kJmol^{-1}K^{-1}$	$\Delta H^{\#}$ $kJmol^{-1}$	$\Delta S^{\#}$ $Jmol^{-1}K^{-1}$	$\Delta G^{\#}$ $kJmol^{-1}K^{-1}$	$\Delta H^{\#}$ $kJmol^{-1}$	$\Delta S^{\#}$ $Jmol^{-1}K^{-1}$
Cr^{2+}	-5.652	49.451	184.912	-6.300	74.840	272.284
Pb^{2+}	-3.802	76.562	269.681	-5.515	46.947	176.049
Ni^{2+}	-4.019	61.007	218.209	-5.210	48.117	178.950
Cd^{2+}	-4.758	57.867	210.153	-6.322	96.359	344.233
Cu^{2+}	-3.776	40.706	149.269	-4.946	28.340	111.698

3.13 Heavy metal removal studies on industrial effluents:

All the effluents were adjusted to the pH of 5, 0.1 g adsorbent dosage level for 60 minutes at room temperature (25 1 °C). The results of heavy metal removal efficiency by NSCB and VSCB on real industrial wastewater are shown in Table 7. The kinetic removal in batch experiment showed that the net uptake of Pb, Cd, Cu, Ni and Cr was 94.8%, 50.0%, 92.9%, 79.1 and 88.0%, respectively is the Jua Kali garage site (A) using NSCB, whereas using VSCB, it varied as 94.8%, 90.0%, 97.5%, 85.1% and 94.0% for the same dosages of VSCB. Therefore, it is concluded that as regards to NSCB, VSCB demonstrated higher potential to remove relatively all heavy metals in the Jua Kali garage wastewater. The order of concentration of heavy metals in industrilal wastewater was Jua Kali Site (**A**) > Tannery site (**B**) > Potable processing plant site (**C**).

From the data, the areas with high-degree of pollution, due to Cr, Cu, Ni, and Pb, are mostly concentrated near Jua Kali small-scale industrial garages, which is attributed to motor vehicle parts and paints containing heavy components of spare parts. The lower removal percentages observed, in some instances, can be attributed to the presence of competing metal ions in the wastewater, such as potassium (K), sodium (Na), magnesium (Mg), and calcium (Ca). These ions can interfere with the adsorption process by occupying active sites on the adsorbent materials, thereby reducing the availability of these sites for heavy metal ions.

Table 7: Effectiveness of optimal conditions for removing heavy metals from wastewater samples

Adsorbent	Adsorbate	Removal Efficiency (%) A	 B	 C
SCB	Pb	94.8 (1.09)	95.0 (0.02)*	60.0 (0.06)
	Cd	50.0 (0.01)	50.0 (0.01)	50.0 (0.01)
	Ni	79.1 (0.53)	nd	30.0 (0.06)
	Cu	92.6 (0.75)	nd	nd
	Cr	88.0 (0.58)	47.2 (4.69)	nd
VSCB	Pb	94.8 (1.09)	95.0 (0.02)	40.0 (0.04)
	Cd	90.0 (0.09)	50.0 (0.01)	50.0 (0.01)
	Ni	85.1(0.57)	35.0 (0.07)	68.8 (nd)
	Cu	97.5 (0.79)	nd	nd
	Cr	94.0 (0.62)	27.8 (2.76)	nd

A = Jua Kali garage wastewater, B = Tannery effluent, C = Potable water refilling plant wastewater;
nd = not detected. *Amount of heavy metal adsorbed (mg/g) are in parenthesis.

4.0 CONCLUSION

VSCB possess pollutant binding properties which can be extremely useful in water treatment. Sugarcane based can be extremely useful for removal of heavy metals from aqueous solutions. Valorising sugarcane bagasse significantly increased capacity of the groups on the surface of sugarcane bagasse. Adsorption of metals was dependent on the pH, initial concentration, particle size and temperature. Adsorption of heavy metals reached equilibrium at 1 hour. Adsorption followed pseudo second order kinetics. In NSCB Pb^{2+} and Ni^{2+} showed better fitting for Freundlich isotherm while Cd^{2+}, Cu^{2+} and Cr^{3+} showed better fit for Langmuir isotherm. For VSCB Freundlich isotherm had a better fitting for experimental results for all metals except Cr^{3+} showed better fit for Langmuir isotherm. Thermodynamic properties indicated that Gibbs free energy have negative values indicating a spontaneous process. The results from this study suggest carbonyl, hydroxyl and alkene functional groups are the main adsorption sites in sugarcane bagasse as well as in the valorised bagasse.

COMPETING INTERESTS:

Authors have declared that no competing interests exist.

ACKNOWLEDGEMENTS:

The authors would like to acknowledge Egerton University for providing laboratory space and equipment to enable this research.

Disclaimer (Artificial intelligence)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during the writing or editing of this manuscript.

REFERENCES