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REMOVAL OF HEAVY METALS BY ADSORBENT PRODUCED FROM *KHAYA SENEGALENSIS*

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ABSTRACT

Quest for better life by mankind has led to advancements in modern technologies which include a number of manufacturing processes and methodologies. Some of these processes and methodologies often release harmful substances into the environment including heavy metals which could lead to pollution. These heavy metals are non-biodegradable and therefore need to be removed. Attention has been devoted to emerging technologies such as adsorption, which are relatively cheap, for the removal of heavy metal ions from contaminated waters. This study reports the adsorption of Cr(VI), Cd (II), Zn (II) and Ni(II) from synthetic solution by activated carbon produced from *Khaya senegalensis* in a batch experiment as a function of pH, metal concentration, adsorbent dose and contact time. Solutions after the batch experiments were analyzed using atomic absorption spectrophotometer. The result revealed dependency of adsorption process on pH. The optimal metal removal occurred at pH 6 for Cd (II), Zn (II) and Ni (II) and 3 for Cr (VI). Maximum adsorption of 82.2 %, 78.9 %, 87.2 % and 83.3 % was attained for Cr (VI), Cd (II), Zn (II) and Ni (II) respectively. Adsorption capacity of the adsorbent improved with initial metal concentration. The data collected were modelled by the Langmuir isotherm over the entire concentration range, suggesting a monolayer coverage. The result showed that, sulphurised *Khaya senegalensis* is effective in removing the selected heavy metal ions from aqueous solution. The prepared adsorbent is efficient and can be used as a low cost alternative in treating heavy metal-bearing effluents.

Keywords: *Khaya senegalesis*, batch experiment, heavy metal, adsorption, efficiency

INTRODUCTION

The need to remove or reduce the concentration of some dissolved metal ions from aqueous medium is a challenge for scientists due to their health impacts on humans and other living creatures (Chen *et al*., 2014). Due to the demands for better life, excessive amounts of heavy metals are released into the environment through a number of industrial processes (Hegazi, 2013). The aqueous wastes of many industries such as textile, mining operations and tanneries are contaminated with heavy metals. The heavy metals usually traced to these industries include: cobalt, lead, zinc, nickel, cadmium, copper, chromium, iron, mercury (Simon, *et al*., 2022). These metals get to the environment through the discharge of the waste waters into water bodies and their subsequent use for irrigations.

Heavy metal ions are not susceptible to biodegradations but rather bio-accumulate in the environment leading to environmental toxicity (Hegazi, 2013; Abdullahi *et al*.,2020). Hence their removal is necessary. Some of these heavy metals such as Cu^{2+} Ni $^{2+}$ and Zn^{2+} are essential for some plant biochemical functions, while others such as Pb and Cd have no biological functions (Condurache, *et al*., 2022; Simon, *et al*., 2022). A number of health issues have been attributed to some of these metals when they come in contact with humans and other living creatures, even in low concentrations. Cadmium for example, is a human carcinogen even at small dose and cause kidney problems, hypertension among others. Chromium VI causes kidney and liver damage as well as respiratory problems and other related issues.

Techniques currently in use for the removal or reduction of these heavy metal ions from aqueous medium include extraction, precipitation, crystallization, ion exchange and carbon adsorption (Lesmana, *et al*., 2009; Tang, *et al*., 2014). Most of these methods are prohibitively expensive and are less effective at low metal ion concentration (Sayqal and Ahmed, 2021). Studies have revealed that, adsorption process using activated carbon is one of the most effective and commonly applied technique for the treatment of heavy metal-bearing effluents (Hegazi, 2013).

In recent times, the metal adsorption capacity of many agro based adsorbent materials have been studied. These materials include rice husk and fly ash (Hegazi, 2013), wool fibers (Condurache, *et al*., 2022); pine sawdust, sunflower seed hulls and corn residues (Simon *et al*., 2022); defatted rice bran, rice hulls, soybeans hulls and cotton seed hulls (Teixeria and Zezzi, 2002); among others.

In line with efforts to identify more agro based, cheap, efficient and readily available materials for wastewater treatment, the current study investigates the adsorption capacity of adsorbent prepared from *Khaya senegalensis*, in a batch experiment with metal concentration, adsorbent dose, solution pH and contact time as the variables.

MATERIALS AND METHODS

All reagents used were of analytical grade. Stock solutions of 1000 ppm of the individual metal ions (Cr VI, Cd II, Ni II, and Zn II) were prepared by dissolving appropriate amounts of their salts $K_2Cr_2O_7$, $CdSO_4.8H_2O$; $NiSO_4.6H_2O$, $ZnCl_2$, respectively in deionized water. From these stock solutions, working solutions of varying concentrations (75, 50, 35, 25, and 20 ppm) were prepared by the appropriate dilutions. Metal ion concentration in the supernatant was determined using atomic absorption spectrophotometry (AAS) after each of the experiments.

Adsorbent preparation

Khaya senegalensis was collected from Kano Nigeria (latitude 12^{o} 0 0.0000` N and longitude 8^{o} 51 6667' E), and was identified at the Herbarium of the Department of Biological Sciences, Ahmadu Bello University, Zaria in February, 2022. The collected sample was air dried for a week then pounded in a wooden mortar and sieved before activation.

The method described in Demirbas *et al*., (2004) was modified and used for the preparation of adsorbent in this study.

The sieved plant sample was weighed and soaked in concentrated sulphuric acid in a 1:1 ratio for 24 hours, after which it was heated at 200^{o}C and left for 24 hours. After cooling to room temperature, the sample was washed several times with distilled/ deionized water and then soaked again in 1 % $NaHCO_3$ solution to remove excess acid in the activated carbon.

The sample was again washed with distilled/deionized water until the pH was 6, after which it was dried at 105^o C for 5 hours, sieved to obtain 1.00 mm diameter using analytical sieve and stored in plastic container for later use.

Adsorption studies

Batch experiments were conducted to study the effects of the various chosen parameters on the adsorption of the selected metal ions from solutions by the prepared adsorbent. For the contact time, 50 cm^3 solution of a 100 ppm of a metal ion concentration, with 0.5 g of adsorbent at a pH of 4 was shaken on a mechanical shaker. Samples (20 cm^3) were taken at time range of 15 – 180 minutes; and then taken for AAS analysis. This established the equilibration time to be between 130 – 180 minutes so 180 min was retained and 50 cm^3 solution for the rest of the study. For the adsorbent dose, the quantity of the adsorbent was varied between 0.1 – 1.0 g using initial metal ion concentration of 20 ppm at pH 3. For the pH study, the solution pH was varied between 1 – 6, with 20 ppm metal ion concentration, adsorbent dose of 0.6 g and 180 min contact time. The adsorption of these metal ions by the prepared adsorbent as a function of their initial concentrations was investigated by varying the metal ion concentration from 20 ppm to 75 ppm, at pH of 4, 0.6 g adsorbent dose and 180 minutes as contact time. All the mixtures were filtered after the batch experiment using Whatman no 1filter paper before AAS analysis.

The amount of metal ion adsorbed in mg/g at time t was calculated using the equation

$$q_t = \frac{(C_o - C_t)V}{X}$$

The percentage of removed metal ions from solution was calculated using the equation:

$$R(\%) = \frac{(C_o - C_t)100}{C_o}$$

Where C_o and C_t are the initial and final metal ion concentration in mg/g, v is the volume of the metal ion solution in cm^3, x is the weight of adsorbent in g.

RESULTS AND DISCUSSION

Effect of contact time

The effect of contact time on the adsorption of the studied metals is as depicted in Figure 1. The result indicated that, removal efficiency of the adsorbent increased with increase in contact time before equilibrium was established. It is also evident from Figure 1 that 60 – 80 % of metal removal was achieved in the first 15 minutes and adsorption became gradual afterwards. The rapid rate of adsorption in the early stages of the process could be as a result of surface accumulation, because all the adsorption sites on the adsorbent was not occupied initially and more time was required for internal diffusion. A similar observation was made in the study by Okoli and Ezuma (2014). It can also be inferred from Figure 1 that, adsorption was relatively constant after 130 minutes for some of the metal ions, perhaps due to desorption as a result of surface saturation of the adsorbent or attainment of equilibrium. In general, the sequestration of these metal ions in this study was influenced by the contact time of the process.

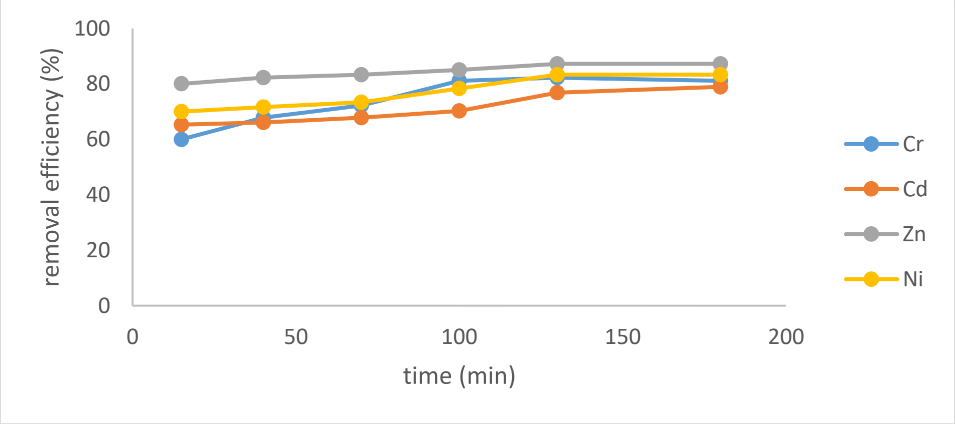

Figure 1: Removal efficiency Vs time

Effect of adsorbent dose

The relationship between metal ion adsorption and the quantity of adsorbent used by varying the amounts of the adsorbent from 0.1 g to 1.0 g is as shown in Figure 2. The Figure reveals a depreciating pattern in metal ion sequestration at a quicker rate, when the dose of adsorbent was increased. For example, 0.3 g of adsorbent was enough to remove 83 % Cr whereas 1.0 g adsorbent removed only 90 % of the same metal ion. This could be as a results of the fact that, at a lower adsorbent dose the metal ions could be readily accessible and adsorption per unit mass increases.

The general increase in adsorption of metal ion on increase in adsorbent dose was expected due to increase in the number of exchangeable sites. In almost all the batches, 0.6 g quantity of the substrate was sufficient for maximum adsorption of the metal ions.

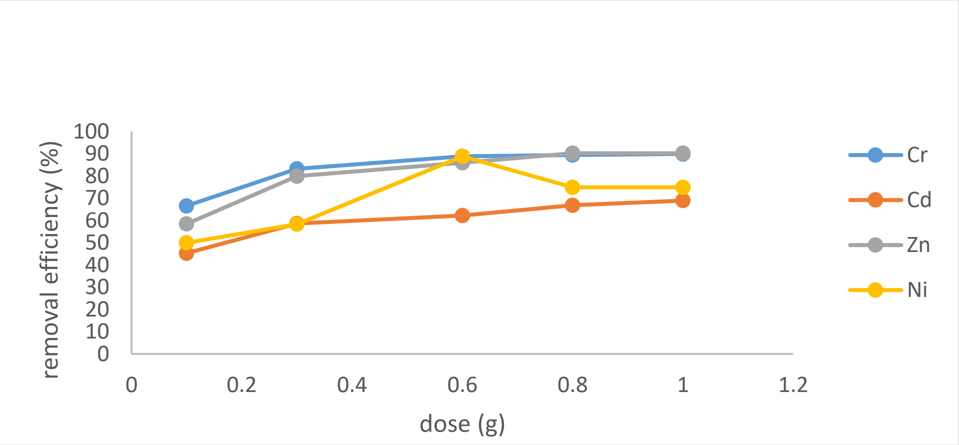

Figure 2: Removal efficiency vs adsorbent dose

Effect of pH

pH is an important factor in the adsorption of metal ions from solution due to the fact that it regulates the availability of both the metal ions in solution and counter ions on the adsorbent. Figure 3 presents the relationship pattern between pH and metal ion adsorption, for solution pH 1to 6. From the graph, it is obvious that, these metal ions with the exception of Cr were effectively adsorbed in the pH range of 4 – 6. There was a decrease in the pH of the solutions after adsorption for all the metals except Cr (VI). This is likely the result of protons being released into the solution by ion exchange between ions in solution and ions on the surface of adsorbent (Demirbas *et al*., 2004).

Maximum Cr (VI) ion was adsorbed at pH 3 (88 %) compared to that at pH 6 (55 %). It is a general knowledge that Cr (VI) occurs in form of oxo- anions like CrO_4^{2-}, $Cr_2O_7^{2-}$; etc, so its adsorption at higher pH which is the territory for negatively charged groups, is very low. A similar observation was made in the study by Mohan and Pittman (2006). A decrease in pH was observed after the adsorption of Cr (vi) which could be as a result of ion exchange between the oxo-anions and OH^- ions. This is perhaps, an indication that the adsorption process was mainly through ion exchange mechanism.

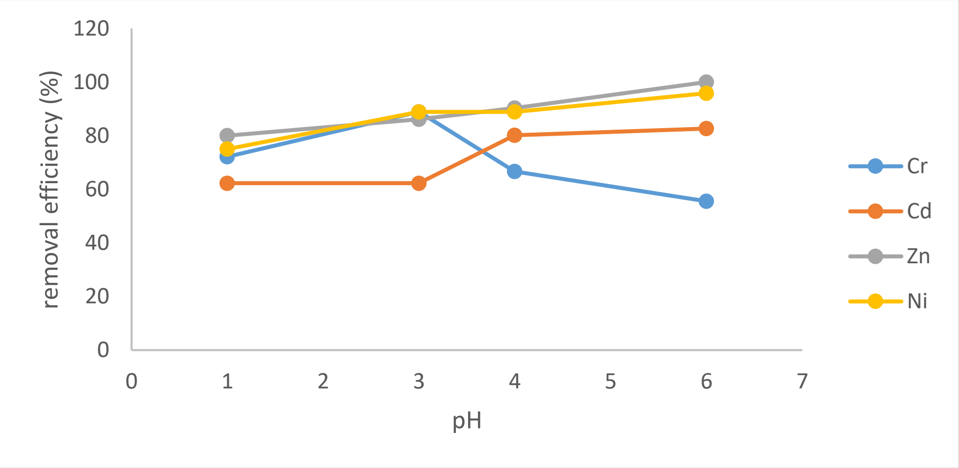

Figure 3: Removal efficiency vs pH

Effect of concentration

The quantity of both metal ions in solution and the adsorbent used is an important parameter to be considered for effective metal ion adsorption. As observed by Ramachandra *et al*., (2005), adsorption rate is a function of the quantity of the ions in solution. To evaluate the effect of the initial ion concentration on adsorption in a batch experiment, the solution concentration was varied between 20 ppm and 75 ppm and the result is as presented in Figure 4. From this Figure, the percentage metal ion adsorption for the studied metal ions decreased with increase in metal concentration. This phenomenon could be due to the fact that at lower metal ion concentration, the ratio between active sites/ surface area on adsorbent and ions in solution is low, therefore the amount adsorbed will not depend on initial concentration. Conversely, at higher ion concentration, the available active sites on the adsorbent become limited compared to metal ions in solution and adsorption will depend on initial concentration. This observation is in agreement with that observed in the study by Velan *et al.*, (2004).

The percentage adsorption decreased from 88.9 – 85.2 %, 82.65 – 79.07 %; 100 – 96 % and 95.85 – 91.11 % respectively for Cr (VI), Cd (II), Zn (II) and Ni (II), when the initial metal ion concentration increased from 20 ppm to 75 ppm. However, the adsorption capacity of the adsorbent (per gram) increased in all cases as the metal ion concentration increased from 20 ppm to 75 ppm. This is in agreement with the findings in a study by Hashem (2007). The adsorption capacity was between 27.6 mg/g – 120mg/g. This also indicates the dependency of the adsorption on the initial metal ion concentration in the solution.

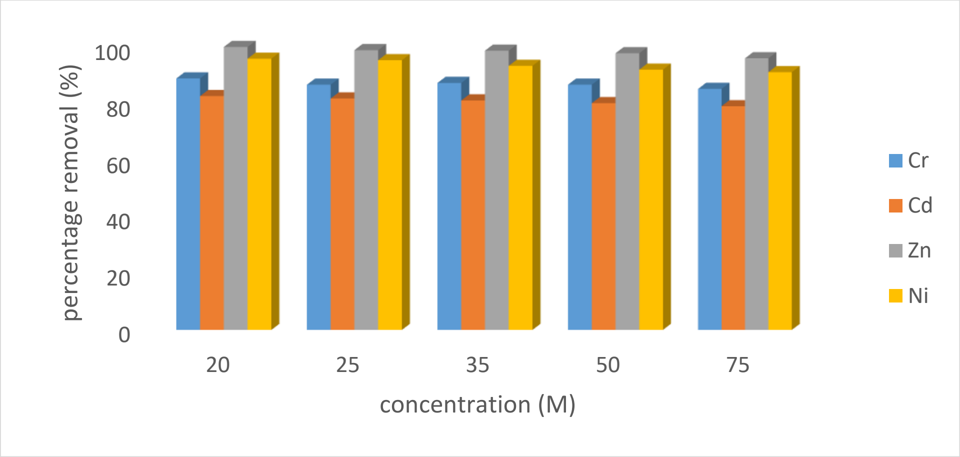

Figure 4: Percentage removal vs concentration

Adsorption isotherms

Equilibrium studies that reveal the adsorption capacity of the substrate and equilibrium correlations among sorbate and sorbent are often described using isotherms. Two common isotherm equations (Freundlich and Langmuir) were applied to the analytical data collected for correlation purpose.

Freundlich isotherm

The Freundlich isotherm is defined as $q_e = aC_e^b$ and the linear form is given as: $ln\, q_e = b\, ln\, C_e + \ln a$ where a and b are the Freundlich constants, q_e is the amount of metal ion adsorbed per unit mass of adsorbent.

A plot of ln q_e vs ln C_e should be linear for model applicability. A linear graph was not obtained for the gathered analytical data which implies non-applicability of the model.

Langmuir isotherm

The isotherm is commonly expressed as:

$$q_e = \frac{bC_e - q_o}{1 + bC_e}$$

and the linear form is

$$\frac{1}{q_e} = \frac{1}{q_o b C_o} + \frac{1}{q_o}$$

where q_e is the amount of metal ions adsorbed per unit mass of substrate (mg/g), c_e is the equilibrium solution phase concentration (mg/dm^3), q_o and b are Langmuir constants related to the maximum adsorption capacity and intensity of adsorption respectively.

According to Igwe and Abia (2007), the applicability of this model to the analytical data signifies a monolayer adsorption. The plot of $\frac{1}{q_e}$ vs $\frac{1}{C_e}$ (Figure 5) for the adsorption of the studied metal ions gave a straight line, signifying the applicability of the Langmuir model to the metal ions adsorption on the prepared adsorbent. Again, from Table 1 the r^2 and b values signify fairly intense adsorption on the monolayer coverage, further confirming the applicability of the Langmuir model to metal ion adsorption of the prepared adsorbent. The separation factor (R_L) gives insight into the favorability of the adsorption process or otherwise. According to Condurache, *et al.*, (2022), if R_L values are between 0 and 1, then the studied adsorption process is favorable. From Table 1, the R_L values are between 0.02 and 0.48 indicating favorable adsorption process.

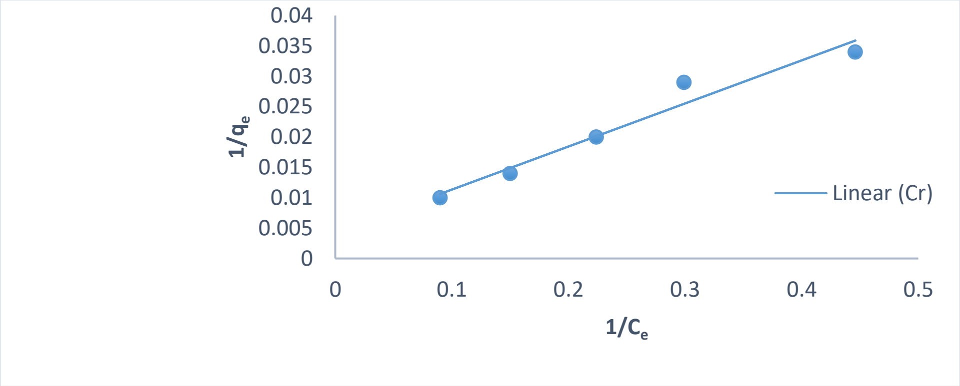

Figure 5a: Langmuir isotherm for Cr

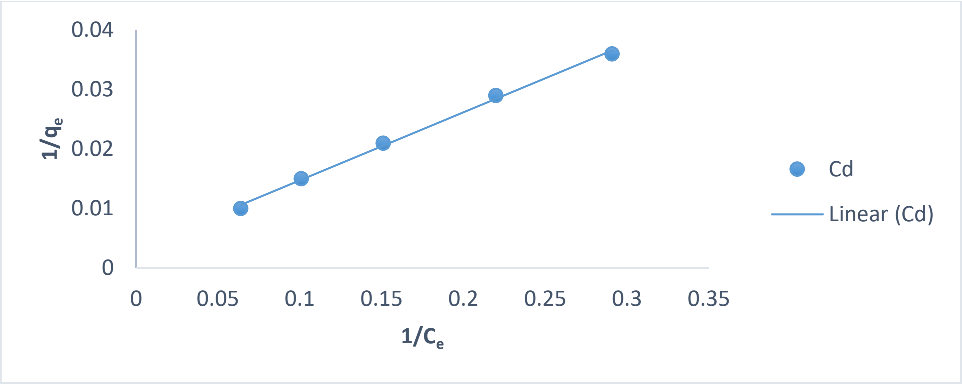

Figure 5b: Langmuir isotherm for Cd

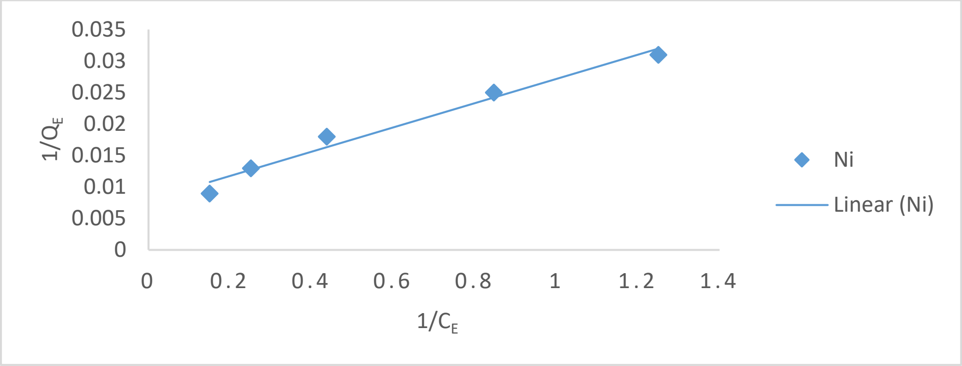

Figure 5c: Langmuir isotherm for Ni

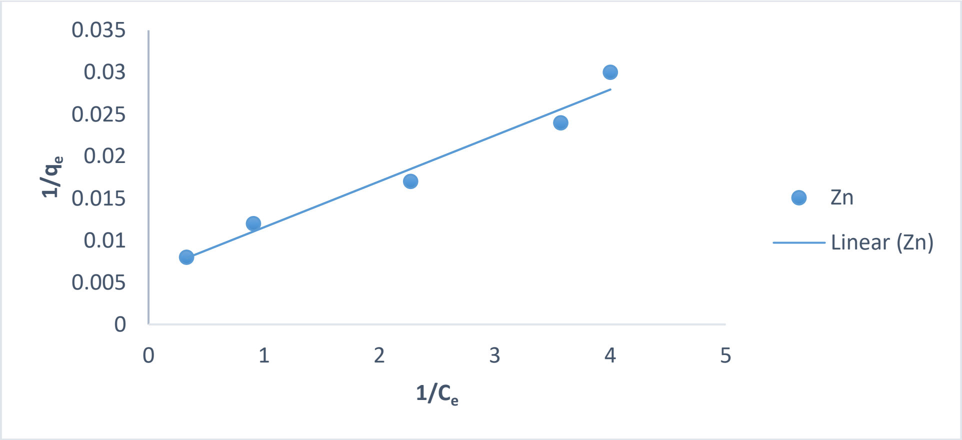

Figure 5d: Langmuir isotherm for Zn

Table 1: Langmuir constants.

Metal	q	b	r^2	R_L
Cr	227.8	0.07	0.96	0.36
Cd	322.6	0.11	0.99	0.48
Zn	144.9	0.01	0.97	0.02
Ni	129.9	0.02	0.98	0.07

CONCLUSION

The information gathered reveal that, the adsorbent from *Khaya senegalensis* has great potential and has proven to be adequate adsorbent for the removal of the studied metal ions from aqueous solution, as percentage metal ion removal range between 69 – 90 %. The removal of these metal ions was highly pH dependent and the optimum pH was between pH 3-6.

The adsorption capacity increased considerably with increase in the variables. The mechanism of the metal ion adsorption onto the prepared adsorbent is likely to involve ion exchange. Based on the percentage ion adsorbed, it is concluded that sulphurised activated carbon prepared from *Khaya senegalensis* is effective and can be used for their sequestration from aqueous solution

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