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Adsorption study of Cr (VI) and Pb (II) from aqueous solution using animal charcoal derived from cow bone

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ABSTRACT

Cow bones (femur and humerus) obtained from Zango abattoir village, Zaria, Nigeria were washed, rinsed with de-ionized water and sundried for a week. The cow bones were further dried in the oven at 105^{0}C for 72 hours, after which the bones were crushed and calcined in a muffle furnace (model GLM-3+PD/ IND) at 500^{0}C for 30 minutes. The carbonized bone samples were sieved into particle size 355µm using an Endecott's sieve. Adsorption experiments were carried out at a temperature 30^{0}C , three different timings viz: 5, 10 and 20 minutes, and five different initial metal ion concentrations viz: 10ppm, 20ppm, 30ppm, 40ppm and 50ppm of lead and chromium ions were prepared from the standard stock of each metal ion solutions respectively. The adsorbent (cow bone charcoal) was used to investigate the adsorption of lead and chromium from aqueous solution. The effect of initial concentration and adsorption isotherms were studied. The cow bone charcoal exhibited good sorption capacity, and the adsorption data fitted the Langmuir and Freundlich isotherm; and on the basis of the Langmuir constants, the maximum adsorption capacity was observed for lead (1.42) at 30^{0}C and 10 minutes, while that of chromium (2.49) was observed at 30^{0}C and 10 minutes.

Keywords: Adsorption isotherm; Cow bone charcoal; Effect; Heavy metal ions.

INTRODUCTION

The increasing awareness of the environmental consequences arising from heavy metal contamination of the aquatic environment has led to the demand for the treatment of industrial wastewater before discharge into the aquatic environment [1]. A conventional method for removing metals from industrial effluents includes chemical precipitation, coagulation, solvent extraction, electrolysis, membrane separation, ion-exchange and carbon adsorption. Most of these methods suffer with high capital and regeneration costs of the materials [2]. Therefore, there is currently a need for new, innovative and cost effective methods for the removal of toxic substances from wastewaters. Bone char as an adsorbent is an effective and versatile means and can be easily adopted in low cost to remove heavy metals from large amount of industrial wastewaters. Recent studies have shown that heavy metals can be removed using plant materials such as palm pressed fibers and coconut husk [3], water fern: *Azolla filiculoids* [4], peat moss [5], lignocellulosic substrate extracted from wheat bran [6], *Rhizopus nigricans* [7], cork and yohimbe bark wastes [8]and leaves of indigenous biomaterials, s *Tridax procumben* [9]. Apart from the plant based materials, chemical modification of various adsorbents, phenol formaldehyde cationic matrices [10], polyethyloamide modified wood [11], sulphur containing modified silica gels [9] and commercial activated charcoals are also employed [12].

MATERIALS AND METHODS

CHEMICALS AND REAGENTS

The metal ion solutions: Pb^{2+} and Cr (VI) ions were prepared from analar grade (BDH) Pb $(NO_3)_2$ and $K_2Cr_2O_7$ respectively. De-ionised water was used for the preparation of all solutions and adsorption experiments.

SAMPLE COLLECTION AND PREPARATION

The cow bones (Femur and Humerus) were collected from Zango abattoir village, Zaria, Nigeria. The bones were thoroughly washed to rid them of adhering dirts, rinsed thoroughly with de-ionised water and sun-dried for a week. Afterwards, the bones were taken to the laboratory and further oven-dried for 72 hours at 105^0C [13]. The dried cow bones were broken into smaller pieces, ground into powder using mortar and pestle and sieved into particle size of 355µm using an Endecott's sieve.

PRELIMINARY WORK

The physical characteristics carried out on the raw adsorbent were: Bulk density, carbonization, moisture content, dry matter, total Ash content, total surface area, volatile content, fixed carbon and pH.

CARBONISATION

Carbonization of the sized cow bone (Femur and Humerus) powder was carried out at 500^0C for 30 minutes in a muffle furnace (Model GLM-3+PD/IND) manufactured by carbolite, Bramford, Sheffield, England [14]. 6g each of the raw cow bone powder were measured in batches into 5 large nickel crucibles and calcined at 500^0C in an enclosed environment for a resident time of 30 minutes; this task was repeated until all sample were calcined. Carbonised products from the raw bone sample were aerated and pooled together in a plastic container.

BULK DENSITY

The bulk density of the adsorbent (cow bone powder) was carried out in the laboratory; the method described in European standards, [15] was employed. This was done by measuring the volume of water displaced when a known weight of the raw sample was dropped into a graduated measuring cylinder.

ASH CONTENT DETERMINATION

Ash content determination was determined using the method employed by [16] and [17]. 2g of the sorbent was placed in a preweighed porcelain crucible and transferred into a preheated muffle furnace at a temperature of 500^0C for 2 hours, subsequently; the crucible and its content were cooled in a dessicator. The crucible and its content were reweighed and the new weight was noted. The percentage ash content was calculated with the formula below:

A_c (%) = W_a / W_0 x 100%

W_a = weight of ash after cooling
W_0 = original weight of dry sorbent

VOLATILE CONTENT DETERMINATION

2g of the sample was heated to about 300^0C for 10 minutes in a partially closed porcelain crucible placed in a muffle furnace. The crucible and its content were retrieved and cooled in a dessicator. The difference in weight was recorded and the volatile content determined thus.

V_c (%) = $[W_0 – W_a]$ x 100%

Where, V_c = volatile component in percentage
W_0 = original weight of dry sorbent
W_a = weight of matter after cooling

PREPARATION OF STANDARD SOLUTIONS

De-ionised water obtained from the Chemistry Department of Ahmadu Bello University, Zaria, was used in the preparation of all solutions. Stock solutions of the following metal ions were prepared as described below: 1000ppm of Pb^{2+} was prepared by dissolving 1.5985g of lead nitrate, Pb $(NO_3)_2$ in de-ionised water and the volume was made to the mark in a 1000cm^3 volumetric flask using de-ionised water.

1000ppm of Cr (VI) ion was prepared by dissolving 2.8289g of potassium dichromate, $(K_2Cr_2O_7)$ in de-ionised water and the volume was made to the mark in a 1000cm^3 volumetric flask using de-ionised water.

PREPARATION OF METAL ION SOLUTIONS

Metal ion (Pb^{2+} and Cr (VI) ions) solution of varying concentrations 10ppm, 20ppm, 30ppm, 40ppm and 50ppm were prepared using a serial dilution from the standard stock of each metal ion.

ADSORPTION EXPERIMENTS

The experiment was carried out in a batch mode for the measurement of adsorption capabilities. 1.00g of the adsorbent (bone charcoal) was placed into each of five dry 100ml conical flasks. Different initial metal ion concentrations of 10, 20, 30, 40, and 50mg/l of lead and chromium ions measured from the standard stock of each metal ion were added to each conical flask and made up to the 100ml mark with de-ionized water. The conical flasks were tightly stoppered, then shaken periodically at room temperature on an end-over-end shaker for one hour; after which the reaction mixture was allowed to equilibrate at different contact time of 5, 10, and 20 minutes in a thermostatic water bath maintained at a temperature of 30^0C.

At the end of each contact time, the mixture in each conical flask was filtered through Whatman (No 1) filter paper into 120ml plastic bottles. The residual (equilibrium) concentrations of lead and chromium ions in the filtrate were determined by Atomic Absorption Spectrophotometer (AAS). Differences between the initial and final (residual) concentrations were recorded as the amount of each lead and chromium ions removed from solution. In order to obtain the sorption characteristics of the adsorbent with respect to lead and chromium, the Langmuir and Freundlich expressions were used in analyzing the data obtained from the adsorption experiments [18].

RESULTS AND DISCUSSION

PRELIMINARY INVESTIGATION

Table 1: Physical characterization of cow bone charcoal (femur & humerus)

Solubility	Insoluble in cold & hot water
Bulk density	1.05g/l
Ash content	66%
Volatile content	22%

On investigation, it was observed that the cow bone charcoal had a high bulk density of $1.05g/cm^3$ which is an indication of good filterability. That is, it would be able to filter more liquid volume before available cake space is filled. The 66% ash content value obtained for the cow bone charcoal is an affirmation that the cow bone charcoal is rich in inorganic constituents. The 22% low volatile content of the cow bone charcoal showed that this biological material is stable for adsorption experiment.

ADSORPTION ISOTHERM AND EFFECT OF INITIAL CONCENTRATION

The results obtained on the adsorption of Pb^{2+} and Cr (VI) ions with particle size 355µm and at different temperatures, initial concentrations and times were analyzed by using the models given by Langmuir and Freundlich which correspond to homogenous and heterogeneous adsorbent surfaces, respectively. The effect of initial concentration was also considered to observe the trend of adsorption. The Langmuir isotherm model assumes uniform energies of adsorption on to the surface and no migration of adsorbate in the plane of the surface [19].

Table 2: Adsorption constants for Langmuir and Freundlich isotherms at particle Size 355µm, 30^oC and 5min

	Langmuir constants			**Freundlich constants**		
Metal ion	Q_M (mg/g)	K_a	R^2	K_F(mg/g)	n	R^2
Pb^{2+}	0.31	0.06	0.984	0.03	0.78	poor
Cr (VI)	0.53	0.11	0.583	$1.72x10^{-3}$	0.28	0.844

A linearised plot of Langmuir and Freundlich isotherm and effect of concentration for Pb^{2+} and Cr (VI) at particle size of 355µm, 30^0C and 5 minutes are shown in Fig. 1--5.

Where Q_M = maximum adsorption capacity
K_a = affinity between the adsorbent and the metal ions
R^2 = rank correlation coefficient
n = adsorption intensity

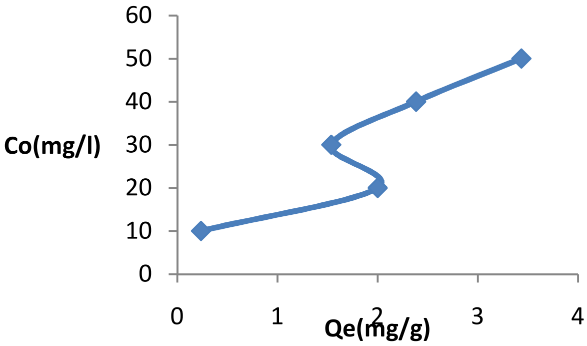


Fig.1 Effect of concentration on the adsorption of Pb^{2+} at 355µm, 30°C and 5min

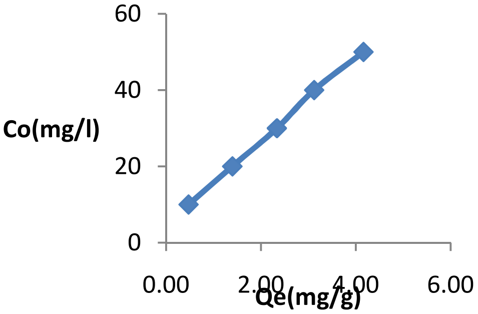
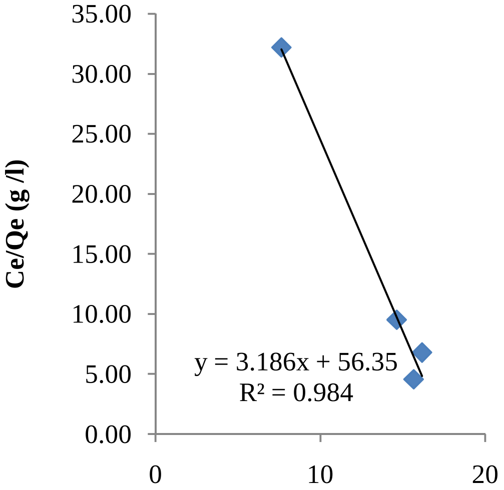


Fig. 2 .Effect of concentration on the adsorption of Cr (VI) at 355µm, 30°C and 5min



Ce (mg/l)

Fig. 3.Langmuir isotherm for the adsorption of Pb^{2+}at particle size 355µm,30^{0}C and5 min

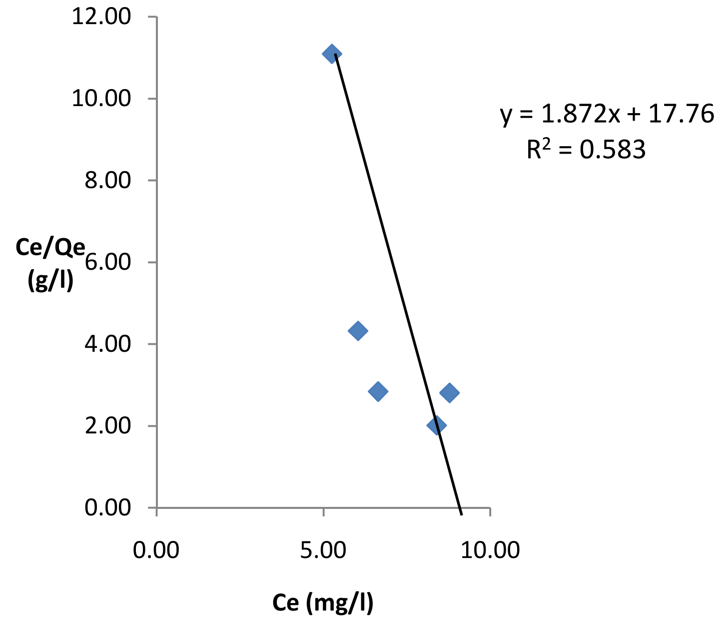


Fig.4. Langmuir isotherm for the adsorption of Cr (VI) at particle size 355µm,30°C and 5min

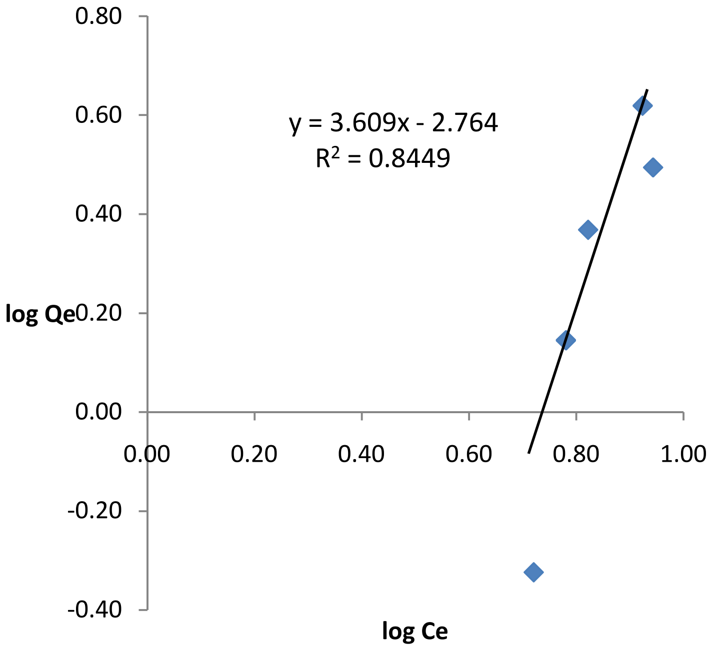


Fig.5. Freundlich isotherm for the adsorption of Cr (VI) at particle size 355µm, 30°Cand 5min

Fig.1-2 shows the effect of initial metal ion concentrations on the adsorption of lead and chromium with 355µm, 30^0C and 5 minutes. It can be observed that at 10mg/l for lead, adsorption increases steadily until there was a decrease at 30mg/l due to saturation of the binding sites. Afterwards, the amount of lead adsorbed became constant. In the case of chromium, as the initial metal ion concentration rises, adsorption increases, while the binding sites were not saturated. Fig..3--5 showed the linearity of the adsorption process with the Langmuir and Freundlich models. From Table 2, it was observed that the binding sites of chromium exceeded that of lead. However, the linear regression coefficient for lead R^2 value exceeded that of chromium with both models. Therefore, lead assumed homogenous adsorption with the Langmuir model at the specified parameters (30^0C and 5 minutes).

Table 3: Adsorption constants for Langmuir and Freundlich isotherms at particle Size 355µm, 30°C and 10min

	Langmuir constants			**Freundlich Constants**		
Metal ion	Q_M (mg/g)	K_a	R^2	K_F(mg/g)	n	R^2
Pb^{2+}	1.42	0.02	0.876	1.70×10^{-2}	0.67	0.937
Cr (VI)	2.49	1.24	0.554	2.60×10^{-2}	0.45	0.910

A linearised plot of Langmuir and Freundlich isotherm and the effect of concentration for Pb^{2+} and Cr (VI) at particle size of 355 µm, 30°C and 10min are shown in Fig. 6-10.

Q_M = maximum adsorption capacity

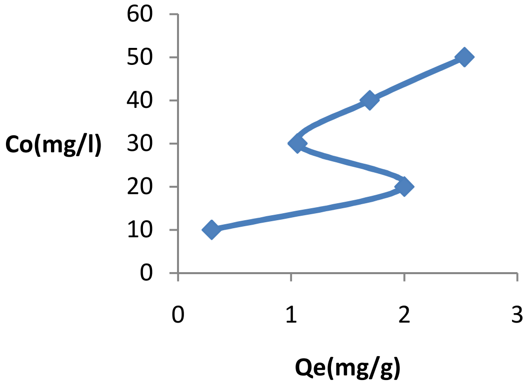


Fig.6.Effect of concentration on the adsorption of Pb^{2+} at 355µm, 30°C and 10min

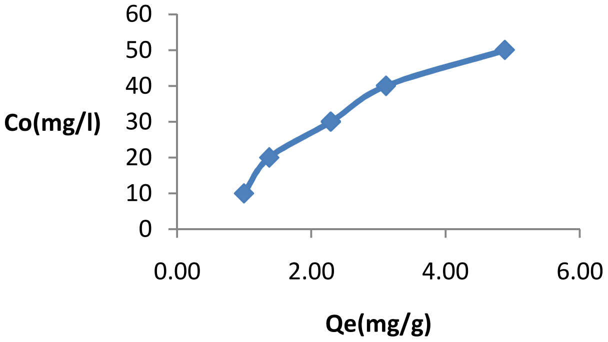


Fig.7.Effect of concentration on the adsorption of Cr (VI) at 355µm, 30°C and 10min

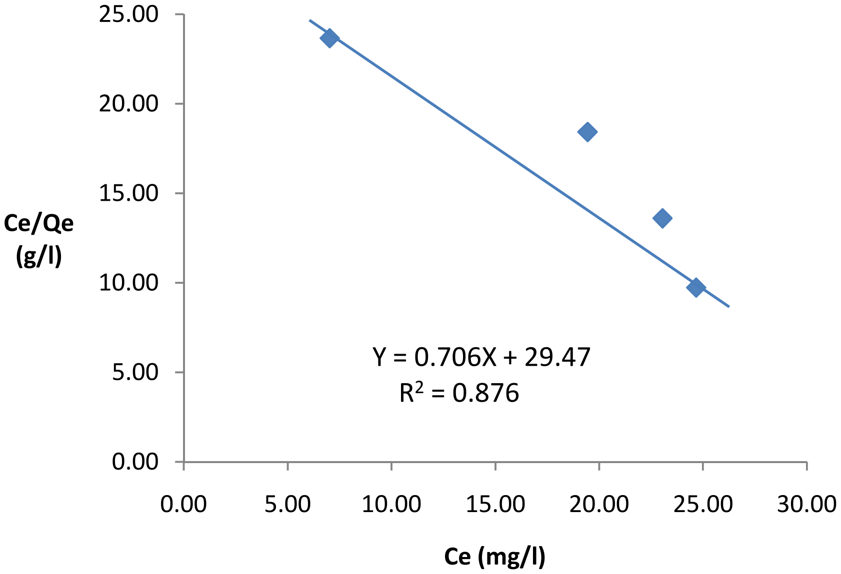


Fig. 8 Langmuir isotherm for the adsorption of Pb^{2+}at particle size355µm,30°C and 10min

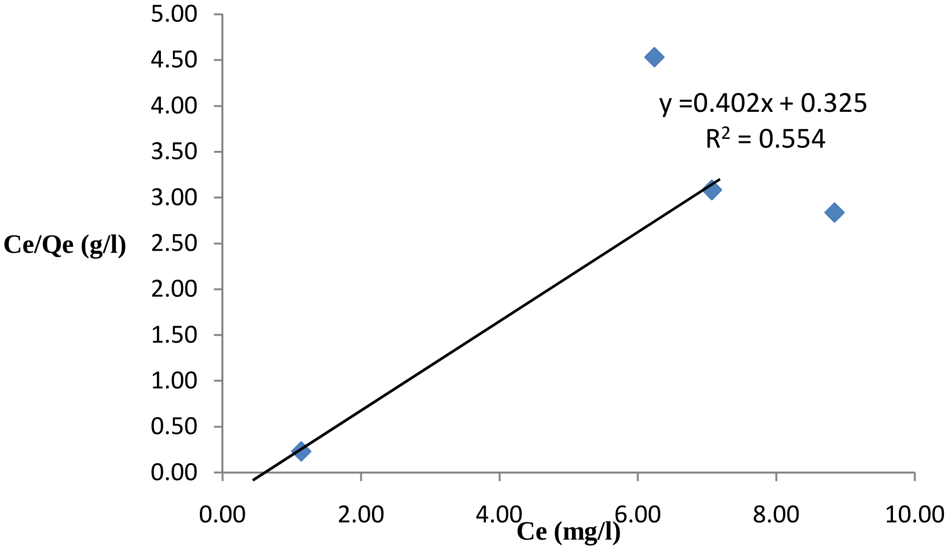


Fig. 9 Langmuir isotherm for the adsorption of Cr (VI) at particle size 355µm, 30°C and 10min.

Fig.6-7 shows that the effect of initial concentration on the amount of lead adsorbed at 10 minutes has similar trend with that of 5 minutes. While that of chromium maintained a steady rise at 10 minutes with no saturation. Fig. 8-10 shows the linearised form of the adsorption process with Langmuir and Freundlich model. From the Langmuir constants, the linear regression coefficient of lead and chromium indicates good linearity with the Freundlich model; but that of lead indicates better, with higher adsorption intensity. Therefore, the adsorption of lead fitted well with the Freundlich model.

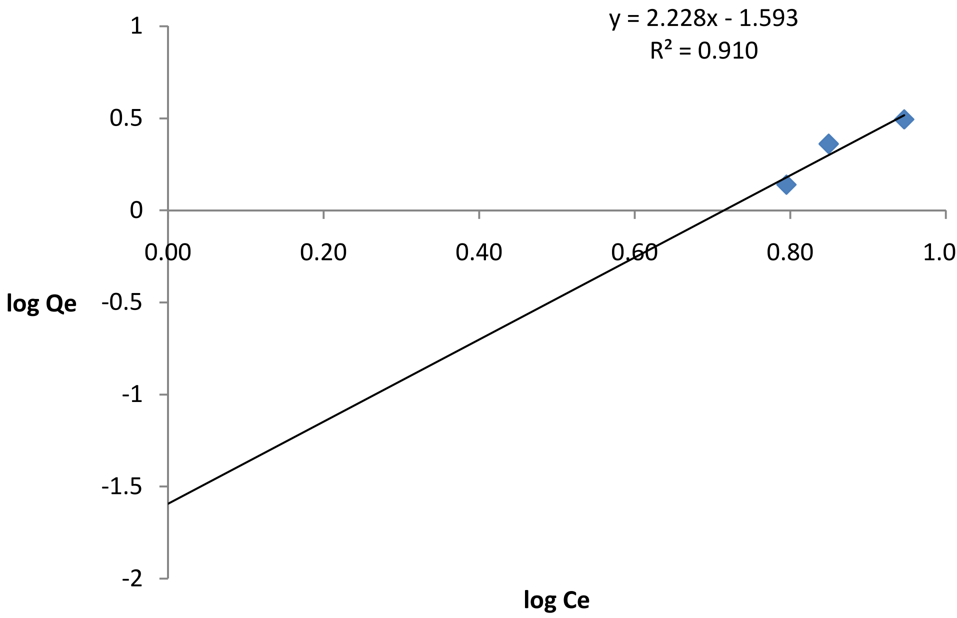


Fig.10. Freundlich isotherm for the adsorption of Cr (VI) at particle size 355µm, 30°C and 10min.

Table 4: Adsorption constants for Langmuir and Freundlich isotherms at particle size 355µm, 30°C and 20min

Langmuir Constants				**Freundlich Constants**		
Metal ion	Q_m(mg/g)	K_a	R^2	K_f(mg/g)	n	R^2
Pb^{2+}	-	-	-	$5.3x10^{-4}$	0.39	0.611
Cr(VI)	-	-	-	2.28	3.08	0.502

A linearised plot of Langmuir, Freundlich isotherm and effect of concentration for Pb^{2+} and Cr (VI) at particle size 355µm, 30°C and 20min are shown in Fig.11- 14.

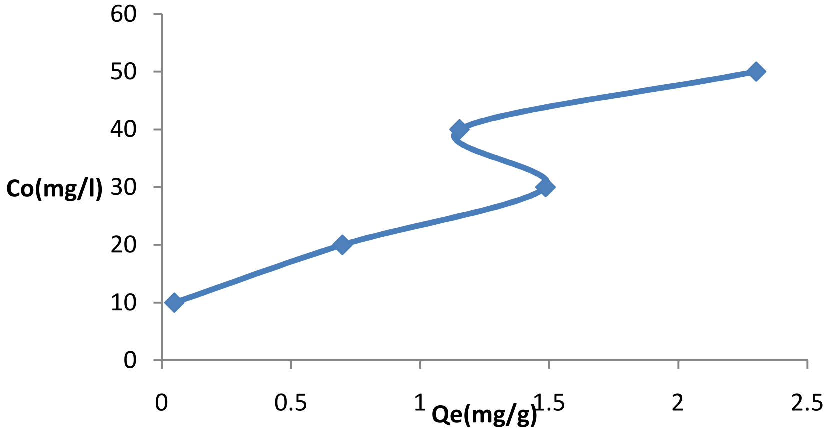


Fig.11.Effect of concentration on the adsorption of Pb^{2+} at 355µm, 30°C and 20min

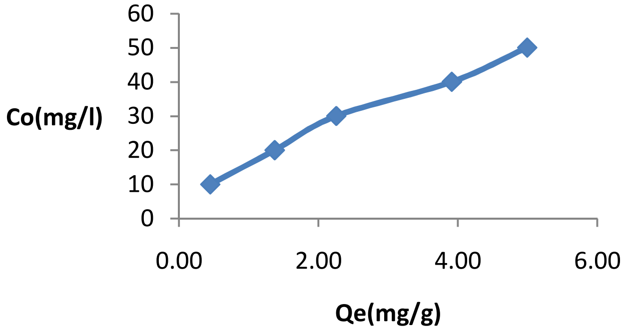


Fig.12.Effect of concentration on the adsorption of Cr (VI) at 355µm, 30°C and 20min

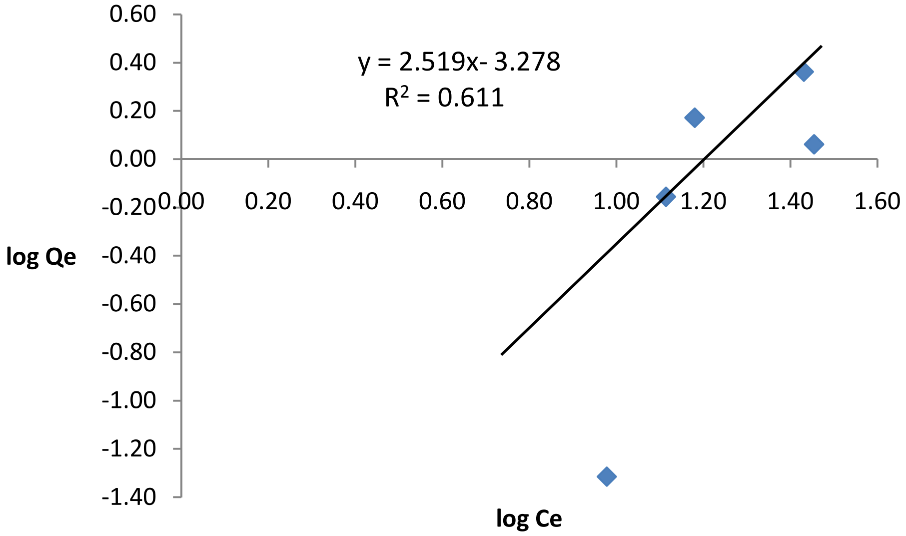


Fig.13. Freundlich isotherm for the adsorption of Pb^{2+} at particle size 355µm, 30°C and 20min.

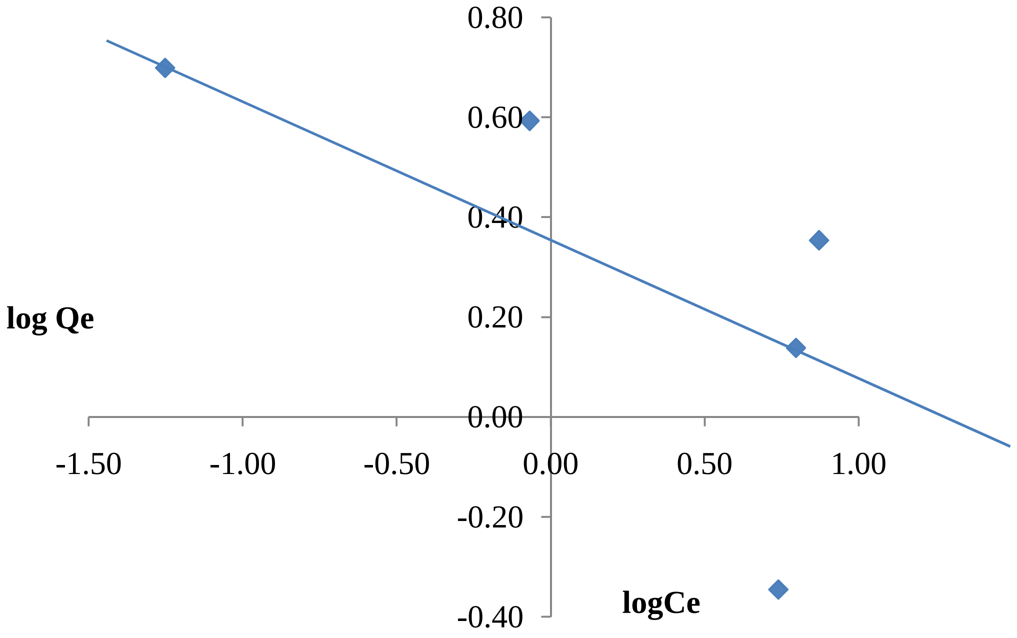


Fig.14. Freundlich isotherm for the adsorption of Cr (VI) at particle size 355µm, 30°C and 20min

Fig.11-14 shows that the effect of initial concentration on the amount of lead adsorbed at 20 minutes rose steadily without saturation from 10mg/l to 40mg/l from which saturation took effect. Afterwards, concentration became steady. While in the case of chromium, adsorption increases with the amount adsorbed. Table 4. indicates that the linear regression coefficient for lead with the Freundlich model was fairly higher than that of chromium. Therefore, the Freundlich model indicates better linearity for the adsorption of lead in heterogeneous condition.

CONCLUSION

The preliminary studies on bone charcoal obtained from the (femur and humerus) of cow showed the mineral enrichment and effectiveness of this biological material in the removal of lead and chromium from aqueous solutions. the regression analysis of the equilibrium data fitted the Langmuir and Freundlich adsorption isotherms. However, it was observed that the Langmuir isotherm plot for chromium was poor at (30^{0}C and 20 minutes) while the Langmuir and Freundlich isotherms plot for lead were poor at (30^{0}C and 20 minutes) respectively. The highest maximum adsorption capacity (Q_m) was observed for lead at 30^{0}C and 10 minutes; while that of chromium was observed at 30^{0}C and 10 minutes. As the temperature increases, the amount adsorbed increases as well, which indicates endothermic adsorption. The adsorbent, cow bone charcoal is cheap and readily available, therefore it will be useful in the treatment of lead and chromium contaminated wastewater before discharge into the aquatic environment under these observed conditions.

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