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Efficiency of Animal (Cow, Donkey, Chicken and Horse) Bones, in Removal of Hexavalent Chromium from Aqueous Solution as a Low Cost Adsorbent

Nworu Jerome Sunday[1, *], Enemose Edith Ajirioghene[1], Osideru Oluwatobi Omotayo[2], Emmanuel Okon Asukwo[3]

[1]Department of Chemistry, Nigeria Maritime University, Delta, Nigeria

[2]Department of Chemistry, University of Ibadan, Uyo, Nigeria

[3]Department of Mechanical Engineering, Nigeria Maritime University, Delta, Nigeria

Email address:

Jeromenworu102@gmail.com (N. J. Sunday)

[*]Corresponding author

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Abstract: As a low cost adsorbent source, a mixture of activated animal bones has been investigated on their efficiency in chromium ion removal from aqueous solution. Adsorption parameters such as contact time, biosorbent size, pH, biosorbent dosage, temperature and concentrations were investigated. Maximum adsorption of hexavalent chromium occurred at 35minutes, 53µm size of adsorbent, pH = 6, 70mg/L of chromium ion, 3g of adsorbent dosage and 303K. The experimental data from the adsorption processes were all tested with Langmuir and Freundlich isotherms. Both isotherms showed good correlations. The higher value of R^2 = 0.9938 from Freundlich isotherm over the R^2 = 0.99 value of Langmuir isotherm showed a better fitness of the adsorption process to Freundlich isotherm over Langmuir model. It can be concluded that any activated carbon from the bones of Cow, Donkey, Chicken and Horse are effective and can be used in industries for removal of hexavalent chromium.

Keywords: Biosorption, Activated Carbon, Adsorption, Chromium, Animal Bones

1. Introduction

Heavy metals such as chromium are present in water effluents from several chemical industries. These metals are environmentally hazardous and will accumulate in the food chain and could cause much side effects. The environmental regulations and monitoring which are related to the discharge of these heavy metals makes it possible to establish processes for enhance removal from waste water. Activated carbons because of their high surface area to volume ratio, chemical nature of their surface and microporous character have been explored for this purpose [9, 10]. The applications of activated carbons are vast, which led to the current research on the usefulness of animal bones as an efficient adsorbent for heavy metal removal from liquid industrial wastes.

Several production industries such as mining, petroleum refining, electroplating, metal processing, tanneries, textiles, pesticides, paint manufacturing, photographic printing and industries and battery manufacturing releases plenty of heavy metals and are normally found in industrial waste-waters [1, 2, 7, 12, 21]. Heavy metals at high concentrations from industries can easily pollute a given environment, affecting the entire ecosystem since soil and water serves as a reservoir for heavy metals [6, 21]. These heavy metals are environmental pollutants which have high negative impacts and have the ability to modify the chemical and physical properties of water and soils [8, 9, 12, 17, 21]. Also, high concentration of heavy metal in drinking water, irrigation water, industrial waste-water has direct negative effects on human health. Heavy metals on soils are easily absorbed through the roots of plants and are highly chronic to the

health of the consumers [4, 21]. Purification of waste-water contaminated by heavy metals are carried out by several processes such as ion exchange membranes [9, 10], flocculation by coagulation [14, 16, 20], electrochemical processes [9, 11], chemical precipitation [4, 18] and through adsorption processes [3, 5, 13, 18, 19]. However, among these methods, adsorption process is a very cost free technique making use of environmental wastes as an adsorbent, thereby keeping the environment clean from these wastes. There are many known substances that has the ability of adsorbing ions when exposed on their surfaces such as silica gel, alumina, activated charcoal, earth fullers, clays etc [29, 32].

1.1. Adsorption Processes

When a solid surface is brought in contact with a liquid or gas molecules from the gas or liquid tends to collect at the surface of the solid. This process of a collection of gas or liquid molecules on the surface of the solid is known as adsorption. Adsorption is a surface phenomenon which involves the aggregation of molecular species onto an interface or a surface. The aggregated molecular species that gets adsorbed on the interface are termed the adsorbate and the interface on which the adsorption takes place is called the adsorbent [25, 28, 30-32].

Adsorption is an exothermic process and the enthalpy change is always negative. Forces of attraction always exist between the adsorbent and the adsorbate and due to these forces of attraction, heat energy is released to the surrounding. So adsorption is an exothermic process. When the adsorbate molecules are adsorbed on the interface, there will be a restriction to the movement of the adsorbate and this leads to decrease in the entropy of adsorption [4, 12, 15].

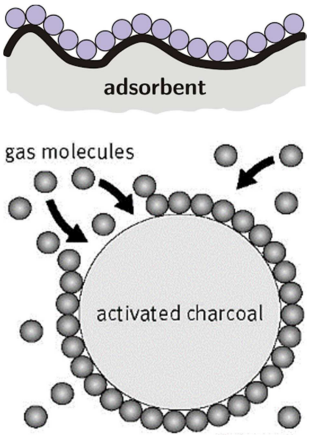

Figure 1. *Adsorption processess.*

Adsorption is a spontaneous process occurring at non-uniform rate and the rate always increase at the initial stage and gradually decreases as time of adsorption increases. During adsorption, the concentration at the interface of the adsorbent is different from that in the bulk solution. For reaction or process to be spontaneous, there must be decreases in free energy of the system i.e. ΔG of the system must have negative value [10, 15, 17].

$$\Delta G = \Delta H - T\Delta S$$

Positive result of this research work could suggest the huge economic benefits of these animal bones which could be beneficial to the developing countries where these animals are largely reared and could be easily incorporated in the development of appropriate processes and technologies.

1.2. A Review on Hexavalent Chromium Adsorption

In waste water treatment, chromium is one of the major heavy metals in consideration. The environmental toxicity level of chromium is high, which accounts for the priority given to it for environmental regulation. The removal of these hexavalent chromium has best been achieved by adsorption processes. So many adsorbents have been used for this purpose, such as fly ash, polymer, carbon nanotubes, clays, silica gel, zeolites, peat moss, chitosan, biosorbent, food waste, etc. At the recent time, many adsorbents have been developed by researchers, which can be impregnated or modified for improved capacity of their adsorption. The river sand has been used for adsorption of hexavalent chromium which recorded 0.15 mg/g adsorption capacity with 74.30% removal capacity [40]. Lee *et al*. (2010) have also prepared Manganese-coated sand by wet coating method and reported improvement in adsorption capacity up to 6.27 mg/g [41]. Silica gel, alumina, and magnetite were explored as adsorbents for adsorption of hexavalent chromium. The removal capacity for hexavalent chromium was observed to be more than 80% [42]. A cross-linked graft copolymer of [2-(metha-cryloyloxy)ethyl] trimethylammonium chloride on poly(vinyl alcohol) has been reported and it is cross-linked by glutaraldehyde for the adsorption of hexavalent chromium, which shows adsorption efficiency of 6.69 mg/g from aqueous solution at 300K [43]. The literature survey shows several polymers with their good adsorption capacity such as, polyaniline/poly ethylene glycol with 109.9 and 68.97 mg/g respectively [44]. The Chromium (VI) percentage removal capacity was reported for quaternized cross-linked poly (4-vinylpyridines) [45] and aminated polyacrylonitrile fibers [46] as 97.4% and 96% respectively. The adsorbents reported with their adsorption capacity such as, condensed-tannin gels derived from a natural polymer with polyhydroxyphenyl group (287 mg/g) [47], short chain polyaniline (PANI), a polymer was synthesized on the surface of jute fiber (62.9 mg/g) [48], ethylene diamine-modified cross-linked magnetic chitosan resin (51.813 mg/g at 293 K) [49]. Adsorption using activated carbon is an attractive choice for chromium removal for efficiency removal and pollutant alteration. This has triggered the interest of researchers to source for any possible means for treatment of waste water which contains chromium through adsorption processes. This work is aimed at determination of the adsorption capacity of animal bone mixtures in chromium metal removal.

2. Materials and Methods

2.1. Sample Collection and Charcoal Preparation

The bone samples of cow, donkey, chicken and horse were collected from a local slaughter house in Ezzangbo, Abakaliki, Nigeria. Samples were washed and oven dried at 105°C. Accurately weighed and dried bone samples of cow, donkey, chicken and horse were carbonized in a closed crucible at 400°C, using Fisher Scientific Isotemp Muffle Furnace, for 1 hour.

2.2. Preparation of Activated Carbon

The carbonized bone was then activated by measuring 200g of each of the crushed samples into a beaker which was then made into sludge with 250ml of 2M hydrochloric acid. The resulting mixture was heated for one hour at 80°C, filtered off and washed with distilled water to remove the acid on the surface of the carbons and then dried in an oven at 105°C for 24 hours. The dried sample was sieved to 2 mm size and kept in a small tray. This procedure was done for all carbonized bone sample.

2.3. Adsorbate Preparation

Chemicals reagents used were of analytical reagent grade. A stock of chromium solution was prepared by dissolving 2.83g of potassium dichromate ($K_2Cr_2O_7$) in a one litre flask, with a distilled water and further diluted to desired concentrations containing 20, 50, 70, 80, 100, 150, and 200 mg/L of chromium in aqueous phase standard solutions. The pH of the solutions was maintained using 0.5M HCl and 0.5M NaOH solutions.

2.3.1. Effect of Contact Time on % Biosorption of Chromium Biosorbent - A Mixture of Animal Bones

In a prepared standard solution of a Chromium metal (Co = 20 mg/L), 0.5 g (10 g/L) by weight of the adsorbent with a pore size of 53 µm was agitated in a mechanical shaker (250rpm) for 1, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60 minutes at Temperature, T = 303 K. The volume of the Chromium aqueous solution is 50 mL (pH = 6). Sample was then filtered with a Whatman filter paper, stored a white bottle and subjected to Atomic Absorption Spectrophotometer (Buck Scientific 210 VGP model).

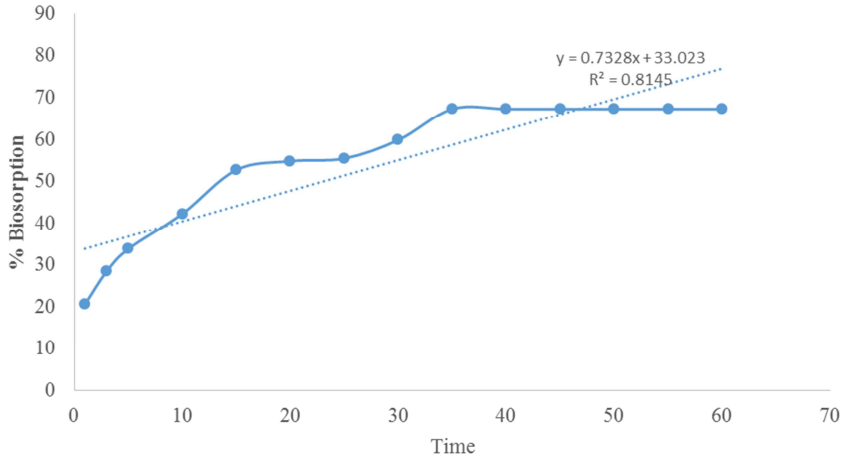

Figure 2. *Effect of contact time on % biosorption of Chromium Biosorbent-A mixture of animal bones. Agitation speed = 250rpm, Chromium concentration = 20 mg/L, pH = 6, Temperature = 303K, Adsorbent dosage = 10 g/L.*

Contact time plays a very significant role during Chromium adsorption. The contact time for the adsorption of chromium metal by the adsorbate (animal bone mixture) was studied at different time intervals. Figure 2 showed the effects of contact time on Biosorption of chromium metal. From figure 2, there is a progressive increase in the percentage of chromium metal Biosorption from 1-30 minutes. Figure 2 also showed that there is an equilibrium Biosorption of chromium metal at the surface of the adsorbent from 35-60 minutes, with chromium concentration of 20 mg/L at pH = 6. At lower time of contacts between the adsorbate and the adsorbent (1-30 minutes), Biosorption was lower because of decreased time of collision. Also, increased collision time enhances chemical reaction [28, 33, 38].

2.3.2. Effect of Biosorbent Size on % Biosorption of Chromium Biosorbent - A Mixture of Animal Bones

A 0.5 g (10 g/L) of the adsorbent with different sizes (53, 75, 105, 125, 152 (µm)) was agitated for 35 minutes (Optimum contact time) in a 50 mL of Chromium salt solution whose initial concentration was Co = 20 mg/L at Temperature, T = 303 K. The pH of the aqueous solution = 6. Samples were filtered with a whatman filter paper and filtrate was analyzed using Atomic Absorption Spectrophotometer (Buck Scientific 210 VGP model).

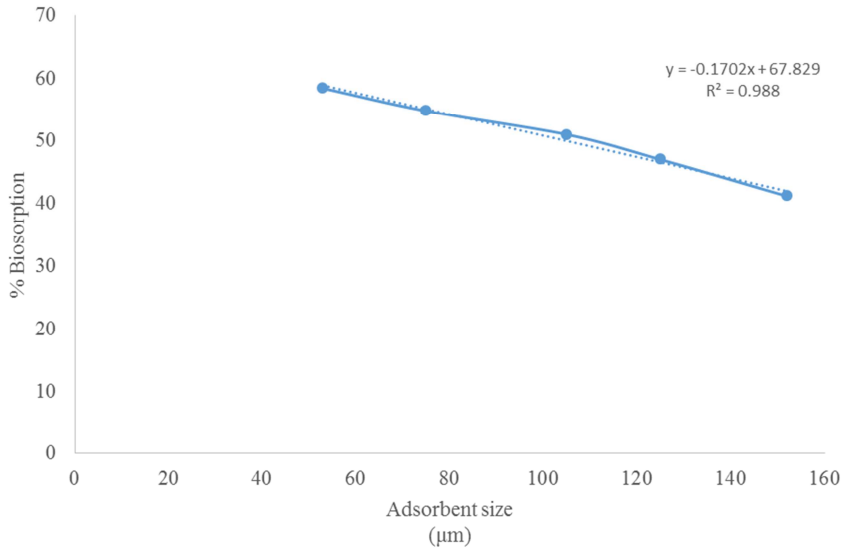

Figure 3. *Effect of biosorbent size on % biosorption of Chromium Biosorbent- A mixture of animal bones. Agitation speed = 250rpm, Chromium concentration = 20 mg/L, pH = 6, Temperature = 303K, Adsorbent dosage = 10 g/L.*

The effect of biosorbent size on percentage sorption of chromium metal is represented figure 3. From the graph, higher adsorbent sizes showed lower adsorption of chromium metal. Higher percentage removal and chromium metal uptake was noticed when adsorbent size of 53µm was used for chromium metal adsorption.

2.3.3. Effect of pH on % Biosorption of Chromium Biosorbent - A Mixture of Animal Bones

A 0.5 g (10 g/L) of the adsorbent with pH (2, 3, 4, 5, 6, 7, 8) was agitated for 35 minutes in a 50 mL of Chromium salt solution whose initial concentration was Co = 20 mg/L at Temperature, T = 303 K. Acids and bases were used in the pH regulation. Samples were filtered with a whatman filter paper and filtrate was analyzed using Atomic Absorption Spectrophotometer (Buck Scientific 210 VGP model).

pH is one of the factors that influences adsorption processes. Figure 4 represents the effects of pH on percentage Biosorption of chromium metal on the adsorbent. From the graph, there is a linearity and progressive increase in the percentage of Biosorption of chromium metal from pH 2-6. From pH 7-8, showed a decrease in the percentage of adsorbate removal. Highest and lowest percentage of Biosorption was seen at pH 6 [69.15%] and pH 2 [47.80%] respectively. All other experiments were done at this optimum pH. The result, showed that biosorption of chromium metal with mixture of animal bones (adsorbent) is more efficient at fairly acidic pH region of 6. From the research work [38]; acid condition at pH 1 until 5, volcanic ash could remove methylene blue 76.59% till 100%. After pH 5 till pH 9, capability of volcanic ash to adsorb methylene blue stayed on better in 100%. It was mean that more alkaline condition of solution, methylene blue removed was many. Volcanic ash needed base surface condition to adsorb methylene blue compound. It indicated that base condition could take place hydroxide ion (-OH) of siloxane and silanol on adsorbent surface. This condition made its interaction up and could adsorb methylene blue.

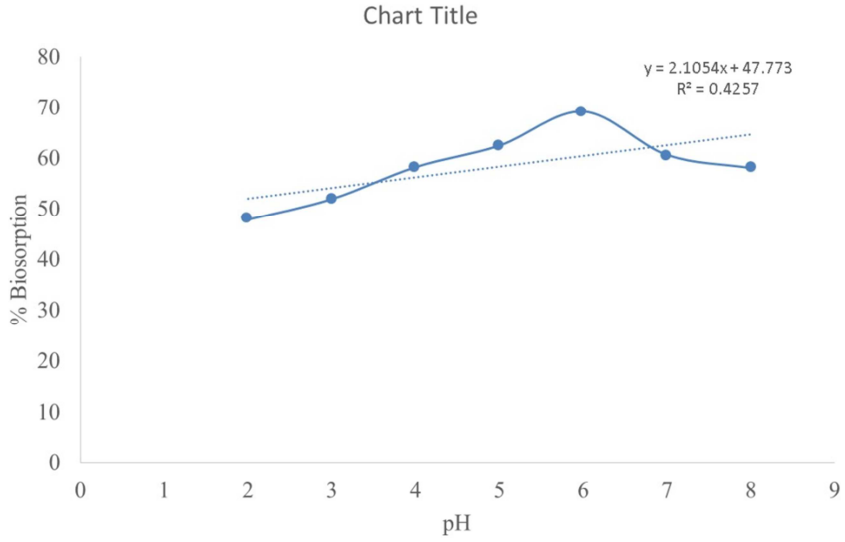

Figure 4. *Effect of pH on % biosorption of Chromium Biosorbent-A mixture of animal bones.*

2.3.4. Effect of Biosorbent Dosage on % Biosorption of Chromium Biosorbent - A Mixture of Animal Bones

The adsorbent dosage was varied (0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, 2.00, 2.50, 3.00). each dosage was agitated for 35 minutes in a 50 mL of Chromium salt solution whose initial concentration was Co = 20 mg/L at Temperature, T = 303 K. Samples were filtered with a whatman filter paper and filtrate was analyzed using Atomic Absorption Spectrophotometer (Buck Scientific 210 VGP model).

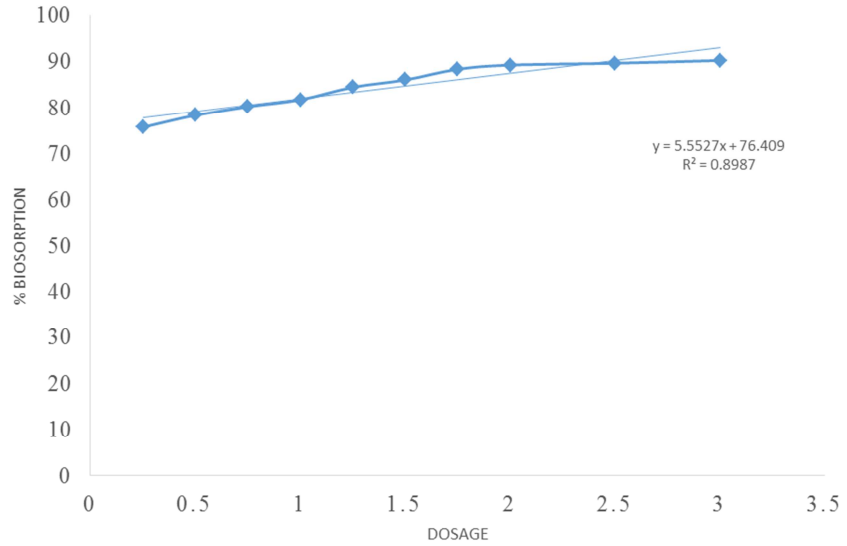

Figure 5. *Effect of biosorbent dosage on % biosorption of Chromium Biosorbent- A mixture of animal bones.*

The variation of the dosage of the adsorbent mixture as represented in figure 5, showed that, mass increase of the adsorbent dosage causes linear increase of the percentage Biosorption. High mass of the adsorbents would adsorbent higher adsorbate on to their active pore surfaces because of their increased surface area [39]. Maximum adsorption was observed to be 90.30% at 3.00g mass of the adsorbent. This indicates that, there will be an increase in adsorption of chromium with increased mass/dosage of the adsorbent. Adsorbent removal efficiency increases with increased in adsorbent dosage. This is as a result of increased availability of exchangeable sites for the adsorbate [39].

2.3.5. Effect of Biosorbent Temperature on % Biosorption of Chromium Biosorbent - A Mixture of Animal Bones

A 0.5 g (10 g/L) of the adsorbent with pH (2, 3, 4, 5, 6, 7, 8) was agitated for 35 minutes in a 50 mL of Chromium salt solution whose initial concentration was Co = 20 mg/L at Temperature, T = 303 K. Samples were filtered with a whatman filter paper and filtrate was analyzed using Atomic Absorption Spectrophotometer (Buck Scientific 210 VGP model).

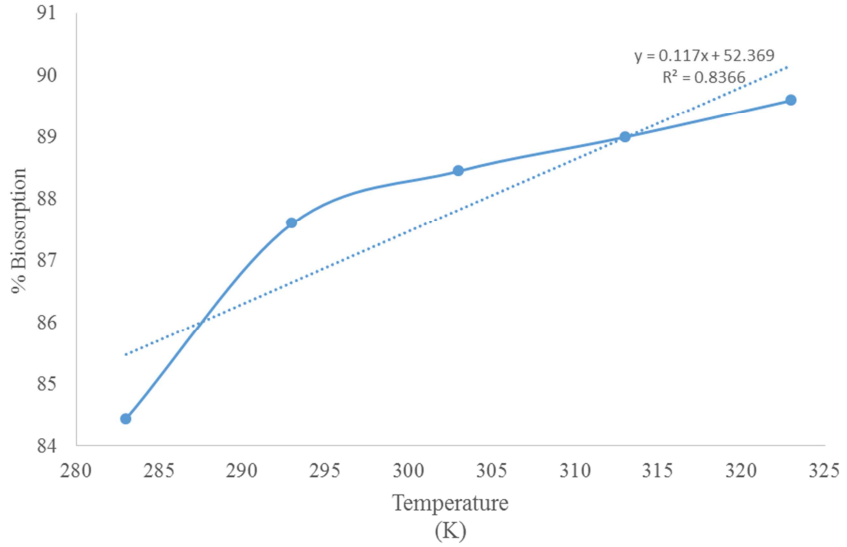

Figure 6. *Effect of biosorbent temperature on % biosorption of Chromium Biosorbent- A mixture of animal bones.*

Figure 6 showed the temperature effect on percentage adsorption of chromium by the adsorbent. Maximum

percentage adsorption occurred linearly with increasing temperature. At room temperature of 293K, chromium adsorption was very appreciable up to 87.60%. Generally, it was observed that increase in temperature favours chromium adsorption with a mixture of these adsorbents.

2.3.6. Effect of Initial Concentration of Aqueous Solution on % Biosorption of Chromium Biosorbent-A Mixture of Animal Bones

A 0.5 g (10 g/L) of the adsorbent was agitated with Chromium salt solution at varying initial concentrations (20, 50, 70, 80, 100, 150, 200) at Temperature, T = 303 K for 35 minutes (Optimum contact time). The volume of the Chromium aqueous solution is 50 mL. Samples were filtered with a whatman filter paper and filtrate was analyzed using Atomic Absorption Spectrophotometer (Buck Scientific 210 VGP model).

2.3.7. Adsorption Isotherms

The adsorption isotherm, which showed the amount of solute particle adsorbed per unit adsorbent was studied as a function of constant temperature and equilibrium concentration of the bulk solution (Figure 7). As stated in figure 7 for the adsorption isotherm for chromium adsorption. The isotherm has higher slope at low Ce and qt points because of the linear rise in the initial stage. This suggests that, at the initial stage of adsorption, accessible sites are numerous which defines the fitness of the isotherm to a monolayer coverage of chromium [50].

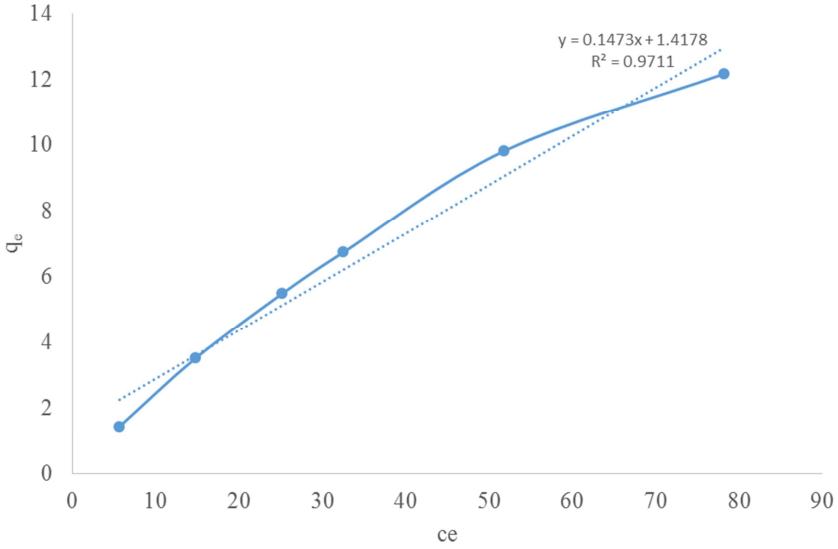

Figure 7. *Adsorption isotherm for Cr adsorption. T = 303K, Time = 35 minutes, pH = 6, Adsorbent dosage = 0.5g.*

Results from the analysis were tested with both Langmuir and Freundlich isotherms. The isotherms are represented in figure 6 and 7 respectively. The Langmuir and Freundlich isotherms showed good R-squared values of 0.99 and 0.9938 respectively, which are almost a unity value, indicating a good fitness of the adsorbent on chromium adsorption.

3. Langmuir Isotherm

According to Langmuir isotherm model, adsorption only occur at the active sites of the adsorbent surfaces and upon completely filling the active pore sites by the adsorbate, further adsorption quenches. In Langmuir model of isotherm, the surface of the adsorbent is uniform, that is, all the adsorption pore sites are equal, no interaction of the adsorbed molecules, adsorption occurs through the same process and at the point of maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other already adsorbed molecules of adsorbate, only on the free surface of the adsorbent. As shown in the Langmuir isotherm curve (Figure 8), the model showed a good fitness for the adsorption of chromium metal ion from aqueous solution with a good correlation coefficient R^2 value of 0.99.

The Langmuir isotherm model can be illustrated in the following Equation (1),

$$C_e / q_e = 1/q_m K_L + C_e/q_m \quad (1)$$

Where, C_e is the equilibrium concentration (mg/L), q_e is the amount of Cr(VI) adsorbed at equilibrium (mg/g) and q_m is q_e for a complete monolayer (mg/g); K_L is sorption equilibrium constant (L/mg). A plot of C_e/q_e versus C_e (Figure 8) is to indicate a straight line graph of slope $1/q_m$ and an intercept of $1/K_Lq_m$ [51]. Using the dimensionless separation factor, R_L, the Langmuir adsorption model can be used to predict the affinity between the adsorbent and adsorbate.

$$R_L=1 / (1+K_LC_e) \quad (2)$$

If the value of R_L lies between 0 - 1 the adsorption is said to be favorable, while R_L> 1 represents unfavorable adsorption, and R_L= 1 represents linear adsorption while the adsorption process is irreversible if R_L = 0. From the analysis, the sorption equilibrium constant K_L is 0.00903 L/mg. Chromium metal ion adsorption on the mixture of these animal bones follow the Langmuir adsorption model

and the dimensionless quantity R_L values for Ce (5.64, 14.81, 18.65, 25.15, 32.52, 51.81 and 78.26) are 0.9515, 0.8820, 0.8559, 0.8149, 0.7730, 0.6813 and 0.5859 respectively.

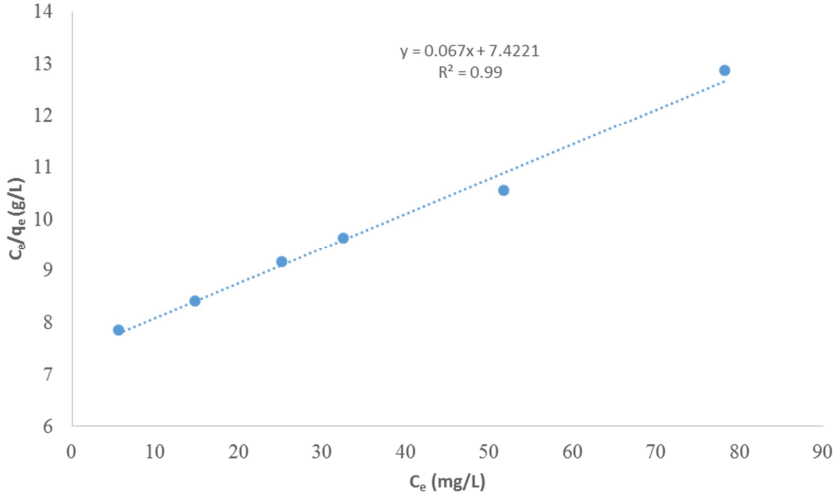

Figure 8. *Langmuir Isotherm.*

4. Freundlich Isotherm

Freundlich isotherm model has also been used to explain the results and validate the fitness of the results. The Freundlich isotherm is represented as follows.,

$$\log q_e = \log K_f + 1/n \log C_e \quad (3)$$

$$\ln qe = n \ln Ce + \ln Kf \quad (4)$$

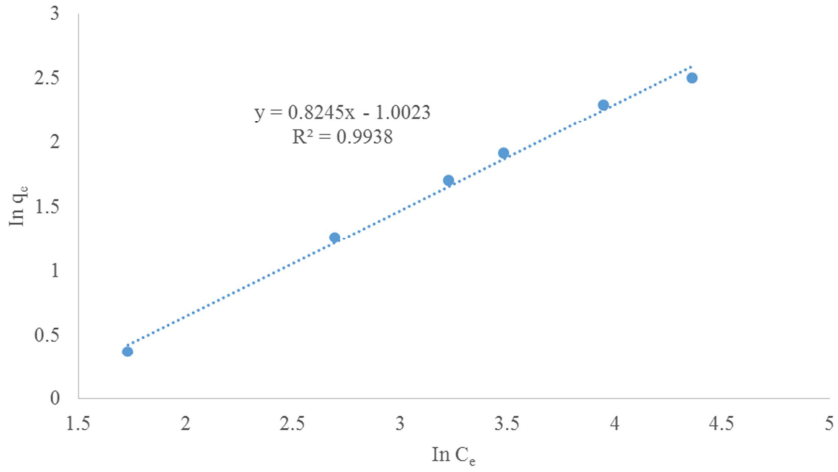

Figure 9. *Freundlich Isotherm.*

C_e represents the equilibrium concentration (mg/L), n and K_f represent constant incorporating all factors affecting the adsorption process such as intensity and adsorption capacity, respectively. A plot of In q_e vs In C_e (Figure 9) shows a linear graph with a slope of n and intercept of In K_f. The K_f value is related to the adsorption capacity; while the n value is related to the adsorption intensity (Equation 4). n values explain the type of isotherm to be irreversible (n = 0), favourable (0 < n < 1) and unfavorable (n >1) [52]. From the Freundlich isotherm (figure 9), the slope (n) and the intercept (In K_f) values are 0.8245 and -1.0023 respectively. The isotherm showed that the adsorption process is multilayer and apart from surface adsorption, parts of the adsorbate went into other layers on the surface of the adsorbent. The higher value of R^2 = 0.9938 over the R^2 value of Langmuir isotherm showed a better fitness of the adsorption process to Freundlich isotherm over Langmuir model.

5. Conclusion/Recommendation

The effectiveness of animal bone mixture as a low cost adsorbent in removal of chromium ion has been investigated. Best fit of linearity of concentration of chromium ion on the amount adsorbed by the adsorbent was pronounced evidently at 303K.

The regression data analysis showed good fitness to Langmuir isotherm and better fitness to Freundlich isotherm. Mixed animal bone charcoal can be evaluated as an alternative adsorbent to treat waste water containing chromium before discharge into the aquatic environment. It can be applied in developing countries due to low cost and availability of cow bones.

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