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A comparative study of Zinc (II) ions removal by a locally produced Granular activated carbon

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Abstract:
Physiochemical properties of wastewater effluent from the plants of a brewery in Lagos, Nigeria were analyzed. The adsorption capacity of Granular activated carbon from animal horns when compared with the available commercial Granulated Activated Carbon (GAC) has been presented. Kinetics of adsorption was also investigated. The adsorption isotherms could be well defined with Freundlich model instead of Langmuir model for both GAC studied. The experimental data, when applied to the first and second-order kinetic models, followed the first-order with $r^2 = 0.931$ for GAC from animal horns while commercial GAC followed the second-order with $r^2 = 0.936$. The results illustrated how animal horns, a solid waste disposal menace from the abattoir at the Oshodi market in Lagos metropolis, was used as an effective biosorbent for the removal of Zn^{2+} ions; offering a cheap option for primary treatment of the wastewater effluent.

Keywords**—** Biosorption, animal horns, Granulated Activated Carbon, wastewater, effluent

1. Introduction

Over the past century, the advent of industrialization has increased the demand on industries to find alternative means and cost effective methods of waste disposal thus leading to the use of water ways by industries to dispose of waste and in the process polluting these water ways with harmful and toxic substances. This pollution of our water ways has increased over 50% of water borne diseases like typhoid, cholera etc. To effectively check this trend, it has become imperative to make industries subject their wastewater to proper treatment before discharge into the environment and this is undertaken by the relevant environmental protection agencies with laws and regulation that are environment friendly [1]. These laws and regulations are used as pollution control measures to try and ensure that the discharge waste gets to the water ways in a form that is less harmful to the environment.

These pollution control measures are very necessary as virtually all industrial operations produce a certain amount of wastewater which must be returned to the environment. Wastewater depending on it's source is a mixture of natural organic and inorganic materials mixed up with man-made, substances which are by products of industrial processes. It is a combination of water borne waste removed from industries along with such ground and surface water that may be present [2].

Most wastewater discharge by industries apart from being serious pollutants contain a lot of toxic material which can be very deadly when exposed or allowed to come in contact with the human body. Toxic substances are poisonous and harmful to the human body. For instance, hepatic toxic substances attack and destroy the liver when this organ is exposed to them. Most water borne diseases are also caused as a result of indiscriminate discharge of poorly treated wastewater into the environment. Diseases like cholera, typhoid fever, dysentery etc can all be related to polluted water ways.

Also most industrial wastewater effluents contain heavy metals like lead (Pb), Mercury (Hg), Arsenic (As) etc. These metals have a neuro-toxic effect when absorbed into the body.

Most heavy metals are classified as priority pollutants. Excessive quantities of these metals due to their toxic nature may interfere with proper use of water. Also some heavy metals are necessary for the growth of biological life. It is therefore desirable to measure and control the concentration of these substances.

The adsorption process using activated carbon and ion exchange resin as adsorbents is widely applied in the advanced treatment of wastewater [3]. However, the high costs of adsorption restrict the extensive application of activated carbon and ion exchange resin. The main factors affecting the adsorption costs include adsorption rate and the capacity of the adsorbent. Therefore, improving the rate and capacity is an effective way to reduce the adsorption operating costs [4].

Granular activated carbon is irregular shaped particles with sizes ranging from 0.2 to 0.5mm. It is used in both liquid and gas phase applications. It is used in wastewater treatment to improve settle ability of activated sludge and remove toxic materials such as heavy metals.

The quality and quantity of brewery waste depends on the processes which the brewery undertakes e.g. raw materials handling, horst preparation, fermentation, filtration etc. The amount of wastewater produced is thus related to the specific water consumption (expressed as Hector litre (hl) for beer brewed). A portion is lost to evaporation thus usually the wastewater to the beer ratio is about 1.2 – 2hl less than the water to beer ratio.

The aim of this study is to show that the granular activated carbon obtained from animal horn can be an alternative for commercial activated carbon in the treatment of industrial wastewater.

2. METHODOLOGY

2.1 Sample Collection

The animal horns (from cattle) were collected from the Abattoir at the Oshodi market in Lagos metropolis.

The wastewater samples were collected from the reservoir of effluent from the plants of a brewery in Lagos, Nigeria and physiochemical analysis was carried out using AOAC method of analysis [5]. Atomic adsorption spectrometer (AAS) was used to determine the concentration of Zn^{2+} ions present in the brewery wastewater studied.

2.2 Preparation of Granular activated carbon

The animal horns were cut to sizes of about 5 mm to l0 mm, washed to remove dirt and then sorted. It was then dried in an oven at about 100°C. The sample was then charred by carbonizing in a furnace at a temperature of about 560°C for three (3) hours then cooled at ambient temperatures in a desiccator.

2 kg of the sample was mixed with 250 ml of 5.5M HCl solution and refluxed by boiling for 3 hours. After slight cooling, the slurry is filtered and washed using distilled water with pH near neutrality. The product is later dried at 120°C for an hour.

2.3 Determination of best adsorbent dose

The studies were conducted by varying the amount of adsorbent. A known volume of the wastewater sample was treated with different doses of activated carbon ranging from 30g/L to 240g/L. The samples were agitated for 60 minutes, filtered then analyzed for residual parameters.

2.4 Determination of contact time

The study for the contact time was carried out by agitating the best adsorbent Concentrations, 90 g /L for animal horn and 30g/L for commercial activated carbon for the ranges of 30 to 300 minutes.

2.5 Determination of metal (Zinc) concentrations

The metal concentrations were determined using the spectrometric method of atomic adsorption spectrophotometer (AAS).

3. RESULTS AND DISCUSSION

Langmuir and Freundlich are general mathematical relationships that were developed to describe the equilibrium distribution of a solute between the dissolved (liquid) and adsorbed (solid) phases.

3.1 Langmuir isotherm

The Langmuir adsorption isotherm equation (6) was derived and is defined as

$$\frac{x}{m} = \frac{Q_0 b C_e}{1 + bC_e} \qquad \text{(1)}$$

And the linearized Langmuir model is given by;

$$\frac{c_e}{x/m} = \frac{1}{Q_0} b + c_e/Q_0 \qquad \text{(2)}$$

where;

$\frac{x}{m} = q$ is the amount adsorbed per unit weight/mass of adsorbent Q_o, b are the Langmuir constants related to maximum adsorption capacity and energy of adsorption respectively.

C_e is the equilibrium concentration of adsorbate in solution after adsorption.

The constants in the Langmuir isotherm can be determined by plotting $\frac{c_e}{q}$ versus C_e adsorption.

3.2 Freundlich isotherm

The empirically derived equation proposed by Freundlich is given as follows [7].

$$\frac{x}{m} = k_f C^{1/n} \qquad \text{(3)}$$

where;

k_f and n are the Freundlich constants that incorporate all factors affecting the adsorption process such as adsorption capacity and intensity.

$\frac{x}{m}$ = Cs' is the amount of adsorbate/weight adsorbed (solute) per unit weight of adsorbent C is the concentration in fluid (adsorbate in solution after adsorption is complete at

equilibrium) mg/l

Taking logs on both sides of equation 3 and rearranging;

$$\log Cs' \log k_f + \frac{1}{n} \log c^* \qquad \text{(4)}$$

The coefficient k_f and n can be estimated from slopes and by substituting values from a line fitted to a graph of log Cs' versus log C*; log k_f is the intercept; the sorption capacity and the slope $\frac{1}{n}$ is the function of the strength of adsorption. It agrees with Langmuir equation over a moderate range of concentrations.

TABLE 1
PHYSICOCHEMICAL ANALYSIS OF WASTEWATER EFFLUENT

Parameters	Concentration	Maximum Permissible limit
pH	8.7	6.0-9.0
EC(m.h.c.g/cm	40.2	Not Applicable
Temperature (^oC)	31.0	42
Turbidity (NTU)	23.5	7 – 10
Total solids (TS)	96.0	30
T.S.S.	44.0	2000
T.D.S.	56.0	34
COD	692.57	13
TOC	724.49	14
BOD	112.49	32
Zn^{2+} ions	21.20	0.15

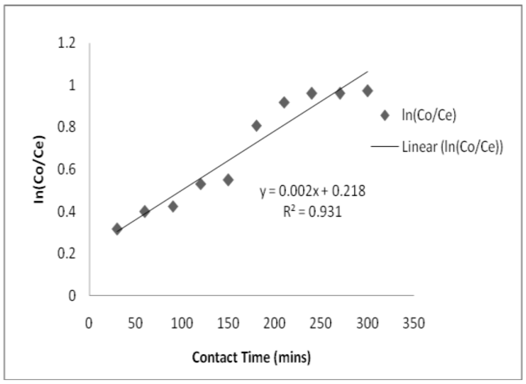

Fig. 1: 1st order adsorption kinetics of Zinc (Zn) ions using 90g/L of animal horn GAC

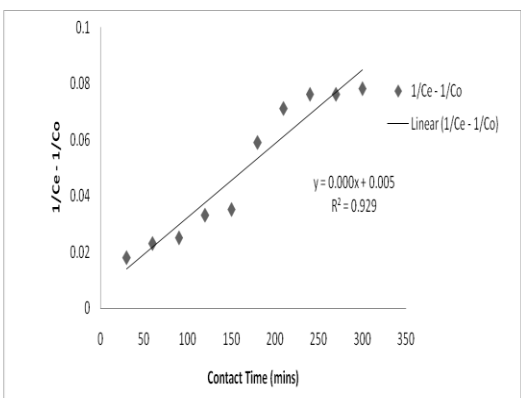

Fig. 2: 2nd order adsorption kinetics of Zinc (Zn) ions using 90g/L of animal horn GAC

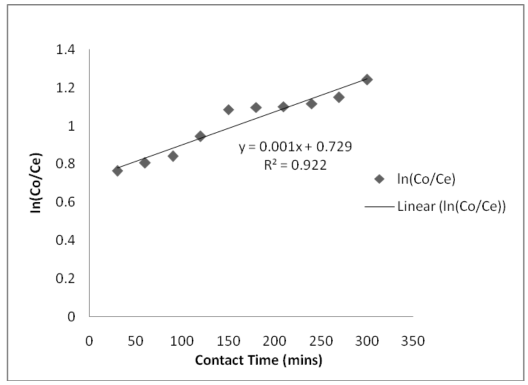

Fig. 3: 1st order adsorption kinetics of Zinc (Zn) ions using 30g/L of commercial GAC

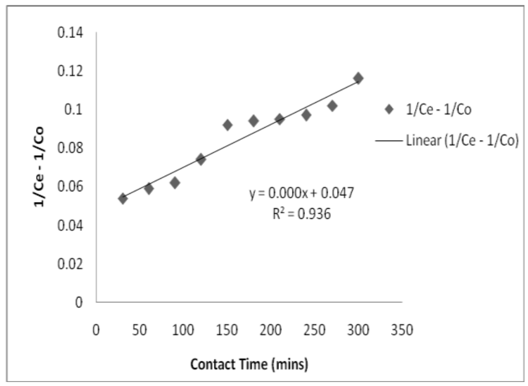

Fig. 4: 2nd order adsorption kinetics of Zinc (Zn) ions using 30g/L of commercial GAC

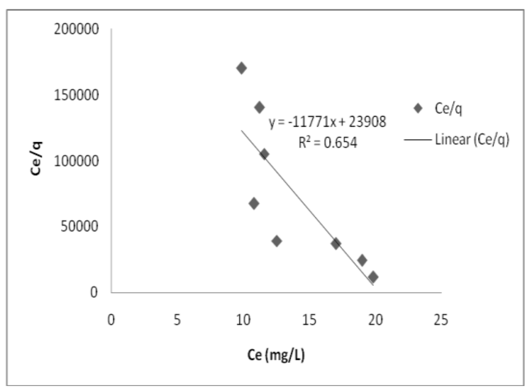

Fig. 5a: Langmuir isotherm for Zinc ions using animal horns GAC

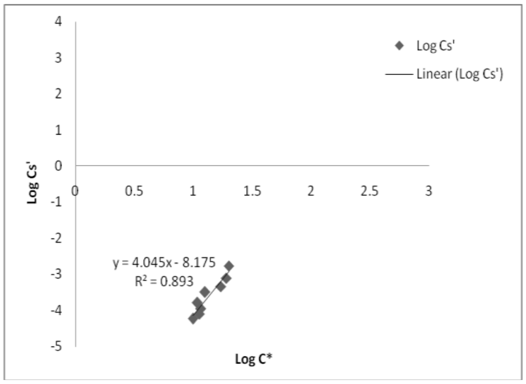

Fig. 5b: Freundlich adsorption for Zinc ions using animal horns GAC

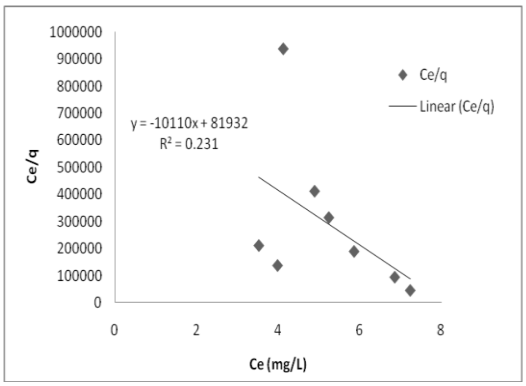

Fig. 6a: Langmuir isotherm for Lead ions using commercial GAC

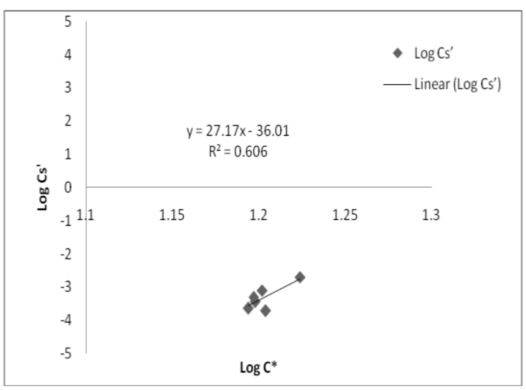

Fig. 6b: Freundlich adsorption for Zinc ions using commercial GAC

Table 1 showed the physicochemical parameters on analysis before the biosorption studies were carried out. The results obtained also indicated that the wastewater effluent obtained from the brewery was alkaline with pH 8.7.

Kinetics studies carried out showed that the adsorption reaction was first order. This was shown in figures 1 to 4. It was observed that for GAC obtained from animal horns, the regression value (R^2) for first order was 0.931(figure 1) which was higher than that for the second order which was 0.929 (figure 2) and as such the reaction was first order and followed Freundlich isotherm.

The kinetics studies for commercial GAC did not follow the pattern of GAC produced from animal horns. The coefficient of determination (R^2) for first order was 0.922 (figure 3) which was lower than that for the second order which was 0.936 (figure 4) and as such the reaction was second order and followed Freundlich isotherm.

Two different adsorption isotherms - Langmuir and Freundlich were studied. The data obtained for both models were represented graphically.

When Figure 5a was compared to Figure 5b for GAC prepared from animal horns it was observed that the adsorption adhered to the Freundlich isotherm with the coefficient of determination of 0.893 being greater than that of Langmuir with a coefficient of determination of 0.654. The same pattern was also observed with that for commercial GAC. The squared regression of Freundlich isotherm was 0.606 when compared to that of Langmuir of squared regression of 0.236 as shown in both figures 6a and 6b. Thus it can be concluded that adsorption using any of the two forms of activated carbon followed the Freundlich adsorption isotherm.

4. Conclusions

Analysis carried out on the GAC produced from animal horns gave results which suggested that it could be used in the biosorption of Zn^{2+} ions from industrial wastewater effluent and also as a viable substitute for commercial grade activated carbon in wastewater treatment processes.

The experimental results obtained showed that of the two adsorption isotherms studied, the Freundlich adsorption isotherm a higher coefficient of determination than that of Langmuir for the two types of activated carbon considered. For the kinetics in the adsorption of Zinc (II) ions for GAC from animal horns, it followed the first order while that for the commercial GAC followed that of the second order reaction.

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