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Adsorption of Pb (II) from Aqueous Solution by Activated Carbon Prepared from Cow Dung

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Abstract: The adsorption of lead (II) onto activated carbon prepared from cow dung was studied under various conditions such as temperature, contact time, pH, adsorbent dosage and concentration of adsorbate. Batch adsorption experiments were conducted and the result showed that the adsorption was pH, temperature, contact times and adsorbate concentration dependent but was partly dependent on the adsorbate dosage. It was rapid, stable and occurs in <100 min. This study showed that activated carbon prepared from cow dung is suitable for the adsorption of metal ions and as such could be used as a cost effective adsorbent in the treatment of the industrial wastewater.

Key words: Adsorption, activated carbon, cow dung, batch adsorption, Pb (II), Nigeria

INTRODUCTION

Industrial activities and mining operations have exposed man to the toxic effects of metals (Carrein and Becker, 1984). Heavy metals are present in the soil, natural water and air in various forms and may become contaminants in food and drinking water (Forsther, 1977). Some of them are constituents of pesticides, paints and fertilizers application. Hazards associated with the contamination of water have led to the development of various technologies for water purification namely filtration and ion-exchange, precipitation with carbonate or hydroxide (Arowolo, 2004).

Man's exposure to heavy metals comes from industrial activities such as mining, smelting, refining and manufacturing processes (Nriagu, 1996). Heavy metals constitute an important part of environmental pollutants and source of poisoning (Okieimen and Onyenkpa, 1989).

Due to the magnitude of the problem of heavy metal pollution, research into new and cheap methods of metal removal has been on the increase recently.

Several researchers have reported on the potential use of agricultural by-products as good substrates for the removal of metal ions from aqueous solutions and wastewaters. This process attempts to put into use the principle of using waste to treat waste and become even more efficient because these agricultural by-products are readily available and often pose waste disposal problems. Hence, they are available at little or no cost, since they are waste products. This makes the process of treating wastewaters with agricultural by-product adsorbents more cost effective than the use of conventional adsorbents like activated carbon. In addition, there is no need for complicated regeneration process when using agricultural by-products for wastewater treatment (Igwe and Abia, 2005).

The ability of some agricultural by-products to adsorb heavy metals from wastewater and aqueous metals solution has been reported in literature and these include: cow dung, cotton seed hulls, rice straw and sugarcane bagasse, cassava and yam peels, paper pulp and maize cobs.

MATERIALS AND METHODS

Chemical activation utilizes such as H_2SO_4, H_3PO_4, $ZnCl_2$, KOH and $CaCl_2$ which have dehydrating and oxidation characteristics (Kim *et al*., 2001). Carbonization and activation are usually carried out simultaneous in chemical activation process (Kobya *et al*., 2005).

The fresh cow dung was obtained from a cattle ranch at Sango along Jebba road, Ilorin, Kwara State, Nigeria. The fresh cow dung was sun dried and grinded and sieved to the desired size prior to activation. Chemical activation using H_2SO_4 at moderate temperatures produces a high surface area and high degree of micro porosity (Demirbas, 2003).

The method of Kobya *et al*. (2005) was adopted. About 100 g of the sieved material was mixed in a 1:1 wt. ratio with concentrated H_2SO_4 placed in an oven and heated to 200°C for 24 h. After this, the sample was allowed to cool to room temperature, washed with distilled water and soaked in 1% $NaHCO_3$ solution to neutralize any remaining acid. The sample was filtered and washed

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with distilled water until a pH of 7.0 was attained, dried at 105°C for 5 h and sieved to obtain the desired sample size (1.00-1.25 mm).

Batch experiments were conducted to investigate the effects of pH, adsorbent dosage, absorbate concentration, contact time and temperature on the adsorption of Pb^{2+} on the activated cow dung. All reagent used were of AR grade. Pb $(NO_3)_2$ salt was used in the preparation of the stock solutions by dissolving it at a known concentration in distilled water.

The initial concentration of metal ion and corresponding concentrations after fixed time periods were measured by atomic adsorption spectrophotometer (UNICAM 919). The metal concentration retained in the adsorbent phase (q_e, mg g^{-1}) was calculated by using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W_s}$$

Where:

C_o = The initial metal ion concentration in mg L^{-1}
C_e = The equilibrium concentration of metal ion in mg L^{-1}
V = The volume of the solution (l)
W_s = The mass of the adsorbent (g)

Each of the experiment was carried out in duplicate and the average of two values was used in the calculations.

Effect of contact time: About 100 mL each of stock solution of the metal was transferred into different 250 cm^3 Erlenmeyer flask, corked and labeled.

About 1.0 g each of the adsorbent was weighed into the different labeled flasks and agitated in a shaker for different contact times (20, 40, 60, 80 and 100 min). After each agitated time, the content of each flask was then filtered. The equilibrium concentration of the metal in each of the filtrate was determined. The results obtained are shown in Table 1.

Effect of temperature: About 100 mL each of stock solution was transferred into various 250 cm^3 flask containing 1.0 g each of the adsorbent, corked and labeled for different temperatures 40, 50, 60, 70 and 80°C, respectively and heated and shake to the appropriate temperature in a water bath. At the right temperature, the content of the each of the flask was removed, filtered and analyzed (Table 2).

Effect of pH: About 1.0 g of the adsorbent was used to adsorb Pb^{2+} at different pH values by adding 1.0 g each of the adsorbent to 100 mL of the stock solution in different 250 cm^3 flask and then agitated for 1 h. The pH was adjusted from 2-9 using HCl or NaOH as the case may be. The content of each flask was filtered and analyzed (Table 3).

Effect of adsorbate concentration: Several stock solution with concentration (20, 30, 40, 50 and 60 mg L^{-1}) were prepared. Each solution was added to 1.0 g of the adsorbent in different 250 mL flasks and agitated using a mechanical agitator for 1 h each. At the end of the time, the contents of the flasks were filtered and analyzed (Table 4).

Effect of adsorbent dosage: About 100 mL each of the metal ions solutions were added to various amount of the adsorbent (1.0-5.0 g) in different 250 mL flasks, flasks were

Table 1: Effects of contact time

Time (min)	Initial concentration of Pb^{2+}(mg L^{-1})	Lead concentration) at equilibrium (mg L^{-1})	Amount adsorbed (mg g^{-1})	Sorbed % (Qe)
20	625.40	10.48	614.92	98.32
40	625.40	14.79	610.61	97.64
60	625.40	8.34	617.06	98.67
80	625.40	8.19	617.20	98.69
100	625.40	8.74	616.66	98.60

Table 2: Effects of temperature

Temperature (°C)	Initial concentration of Pb^{2+}(mg L^{-1})	Lead concentration (mg L^{-1})	Amount adsorbed (mg g^{-1})	Sorbed % (Qe)
40	625.4	3.94	621.46	99.37
50	625.4	0.52	624.99	99.90
60	625.4	0.30	625.10	99.95
70	625.4	0.25	625.15	99.96
80	625.4	0.32	625.08	99.95

Table 3: Effects of pH

pH	Initial concentration (mg L^{-1})	Lead concentration (mg L^{-1})	Amount adsorbed (mg g^{-1})	Sorbed % (Qe)
2	625.4	1.04	624.36	99.83
3	625.4	4.55	620.85	99.27
4	625.4	5.91	619.49	99.05
5	625.4	5.72	619.68	99.08
6	625.4	5.05	620.35	99.19
7.	625.4	4.73	620.67	99.24
8	625.4	4.55	620.85	99.27
9	625.4	4.98	620.42	99.20

Table 4: Effects of adsorbate concentration

Concentration of adsorbate (mg L^{-1})	Initial concentration of Pb^{2+} (mg L^{-1})	Lead concentration mg L^{-1} at equilibrium	Amount adsorbed (mg g^{-1})	Sorbed % (Qe)
20	12.51	0.42	12.09	96.62
30	18.76	0.44	18.32	97.64
40	25.02	0.51	24.51	97.95
50	31.27	0.16	31.11	99.48
60	37.52	0.17	37.35	99.54

Table 5: Effects of adsorbent dosage

Adsorbent (g)	Initial concentration of Pb^{2+}mg L^{-1}	Lead concentration (mg L^{-1}) at equilibrium	Amount adsorbed (mg g^{-1})	Sorbed % (Qe)
1	625.4	0.15	625.25	99.98
2	625.4	0.16	625.24	99.97
3	625.4	0.08	625.32	99.99
4	625.4	0.17	625.23	99.97
5	625.4	0.14	625.26	99.98

corked and agitated for 1 h on a mechanical stirrer. The content of the flask was filtered and analyzed (Table 5).

RESULTS AND DISCUSSION

The result obtained from time-dependent experiments for the removal of Pb^{2+} by the activated cow dung was shown in Table 1. As the contact time was increased, the amount of metal ions removed also increased. This trend is consistent between 40 and 80 min contact time when equilibrium was attained. Further increase of contact time beyond 80 min generally results in decrease in the adsorption of Pb^{2+}. Mostly or at times, the observable time for maximum adsorption is between 60-100 min. Further contact time may be time wasting. This is in line with what was observed by Shukl and Pai (2005).

The effect of temperature on the removal of Pb (II) from aqueous solution was investigated by varying the temperature of adsorption between 40 and 80°C (Table 2). The data showed Pb^{2+} removal from aqueous solution increases initially until equilibrium was attained and then decreased.

The attractive forces between the adsorbent and the adsorbate ion may have been weakened making the sorption to decrease. An increase in temperature between 70 and 80°C caused a proportional decrease in the amount of metal ion adsorbed onto the surface of the adsorbent. At high temperature, the thickness of the boundary layer is expected to decrease due to the increased tendency of the metal ion to escape from the surface of the adsorbent to the solution phase (due to the increase in kinetic energy of the ions) hence there is bound to be weak adsorption interactions between the adsorbent and the adsorbate. The pH dependent data for the adsorption of Pb^{2+} is as shown in Table 3. From the data it was observed that at pH of 2.0 we had the highest percentage removal of Pb^{2+} which later decreased when the pH was increased to 3.0.

It was also observed that there was a steady increase between pH 4.0 and pH 8.0. This trend is not far from what Kobya *et al.* (2005) reported that the optimum pH for the removal of Cr (VI) is 1 while that for other metals is between 3-6. Binding behaviour may suggest that to some extent, COOH groups may be responsible for the binding of the Pb^{2+}, since the ionization constant for a number of COOH groups range between 4.0 and 6.0 (Horsefall and Spiff, 2004).

At lower pH the COOH groups retain their protons which reduce the probability of binding a positively charged ion. At pH>4, the ionized COO^- ligands attract the positively charged Pb^{2+} ions and binding occurs. The results thus indicate that binding follows an ion-exchange mechanism that involves electrostatic interaction between the negatively charged groups in the walls of the substrate and metallic cations.

The concentration-dependent data for the sorption of Pb^{2+} is shown in Table 4. It is generally expected that as the concentration of the adsorbate increases the metal ions removed should increase according to Okieimen and Onyenkpa (1989). From the Table 4, the trend is in agreement with the expected phenomenon.

It is believed that increase in concentration of the adsorbate bring about increase in competition of adsorbate molecules for few available binding sites on the surface of the adsorbent hence increase in the amount of metal ions removed.

It is shown in Table 4 that increase in adsorbate concentration result in an increase in adsorption process. This trend could also suggests that increase in adsorbate concentration results in increase in number of available molecules per binding site of the adsorbent thus, bringing about a higher probability of binding of molecules to the adsorbent (i.e, the probability of chemical interaction between the adsorbent and the adsorbate is enhanced by reason of the high availability of molecules of adsorbate in solution). The overall trend is consistent with the observed phenomenon.

The effect of the adsorbent dosage on the removal of Pb^{2+} from aqueous solution was investigated by varying the dosage of the adsorbent from 1.0-5.0 g. It is expected that an increase in the dosage of adsorbent should yield a corresponding increase in the amount of metal ion adsorbed onto the surface of the adsorbent since there will be more sites for the adsorbate to be adsorbed. Therefore, competition for bonding sites between molecules of the adsorbate should decrease with increase in dosage of the adsorbent. From Table 5 this trend was inconsistent and therefore suggests that the use of modified cow dung as adsorbent partly depend on its dosage in aqueous solution.

CONCLUSION

This study showed that a good adsorbent for the removal of Pb (II) from aqueous solution can be obtained

from activated carbon prepared from cow dung. Batch experiments were conducted and showed that the adsorption of Pb (II) is temperature dependent, pH dependent, time dependent and also dependent on the concentration of adsorbate but partly on the adsorbent dosage, rapid, stable and occurred in <100 min. Cow dung (a waste) is inexpensive and readily available, thus this study provide a cost effective means for removing metal ions from contaminated water or effluents.

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