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HEAVY METAL ADSORPTION FROM AQUEOUS SOLUTION USING ACTIVATED CARBON FROM ORANGE AND BANANA PEELS.

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Abstract - In this study, liquid-phase adsorption removal of pb^{2+} and cd^{2+} in the concentration range of 30, 60, 90, 120mg/l using low-cost orange and banana peels was carried out in order to evaluate the effectiveness of the two adsorbents for the purpose of removing pb^{2+} and cd^{2+} from their prepared aqueous solutions. Orange and banana peels collected from Abakpa main market in Enugu East L.G.A of Enugu state were crushed into particle size of 2mm. The physico-chemical as well as the adsorption properties of the activated carbon orange peel (ACOP) and activated carbon banana peel (ACBP) were studied. The effects of the process factors ph,initial metal ion concentration and adsorbent dosages were also determined. Removal efficiency of pb^{2+} and cd^{2+} was found to decrease with increase in initialmetal concentration, and increase with increase in ph, adsorbent dosages and contact time. This study showed that orange and banana peel could be utilized as a low cost, ecofriendly and a sustainable activated carbon for the removal of pb^{2+} and cd^{2+} from their respective aqueous solutions.

KEYWORDS; Orange, banana, peels, adsorption, isotherms, heavy metals aqueous solutions

1. Introduction

Generally, Industrial waste water contains high concentration of pollutants such as organic materials, heavy metals and toxic compounds. The effects has always been environmental and health hazards and must be properly treated in order to meet the water quality standards for most countries before the ultimate disposal. Among different types of pollution, the industrial wastes constitute the major sources of metal pollution.

Sources of these heavy metals ranges from lead in petrol, industrial effluents, nuclear fuel preparation, purification of metals and electroplating (Barakat, 2010).

The conventional methods for metal removal from water include reduction, precipitation ion-exchange, electrochemical reduction, and reverse osmosis. These methods involve high capital cost with recurring expenses which are not suitable for small scale industries. (Juans, et al, 2003). Hence in order to a cheaper more effective and low cost methods that have metal binding capabilities, adsorption becomes the most useful of all those approaches for waste water treatment (Barakat, 2010).

The use of activated carbon for adsorption is expensive regardless of its extensive use in water and waste water treatment in the industries. Recently, interests have grown towards the production of alternatives that cost less compared to commercially available activated carbon due to the demand for secure and affordable means of eliminating heavy metals from polluted water. Hence, the immediate need to explore in details the feasibility of using all available sources of less cost adsorbents from agro materials, for the removal of heavy metals. (Hegazi etal, 2013).

This paper reports the potential of orange and banana peels as adsorbents for removal of pb^{2+} and cd^{2+} from their aqueous solution. The activated carbon produced from banana and orange peels can be processed and converted to be adsorbents due to they have large surface area, low ash and moisture content. They are highly convenient to use and have a high potential to adsorb pb^{2+} and cd^{2+} from aqueous solution.

2. Materials and Method.

Materials- To carry out the experiment, mortar pestle, standard sieves (2-3mm), muffle furnace (5302au) orbital sharker (scigenics biotech orbitech) ph meter, electronic weighing balance, electronic oven, atomic adsorption spectrophotometer (shimadzu AAS) are used. Others include test tube, crucible, measuring cylinders, conical flask, plastic container, polythene bags. Reactions were carried out using batch adsorption methods.

3. Sample Collection and Processing-

The samples of banana and orange peels were collected from Abakpa central market in Enugu East local Government Area of Enugu State. The banana and orange peels were washed exhaustively with deionized water to remove all traces of impurities, dirt particles, oil, dust and salts. This method was in accordance with the work done (Foo, et.al 2012). The samples were sundried until it tends to appear crispy. Thedried samples were ground and screened to the desired mesh size of 2mm using standard sieves.

Sample Analysis: Tests and analysis of samples (ACOP) and (ACBP) were carried out at Pymotech research institute, Enugu. National Research Institute for chemical technology laboratory Zaria. National Centre for energy research and development5. University of Nigeria Nsukka, Enugu state.

4. Activation and Carbonization of sample.

The carbonization process was performed by loading the precursors (banana and orange peels) into a muffle furnace, and the temperature was tamped from room temperature to the desired temperature of 800 ℃ for 2 hours. The char produced was soaked in 6M KOH (potassium hydroxide) solution with 1.5:1. Impregnation ratio defined as the dry weight of activating agent per weight of char (KOH: Char).

Similar carbonization procedure was used to carry out the conventional activation except that the final temperature and time were changed to 850℃ and 1 hour respectively. The activated carbon that resulted was washed continuously with 0.1m HCl and distilled water until a pH of 7 was achieved in the residual liquid.

5. Preparation Of Standard Solutions Of pb^{2+} and cd^{2+} (synthetic waste water).

Standard method for the examination of water and waste water (APHA,1998) was used. (1.599g) of lead nitrate ($Pb(No_3)_2$) was dissolved in 200ml of distilled water. 10ml of concentrated HNO_3 was then added and the resulting solution was diluted to 1000ml mark using deionized water. Working solution was then prepared from the stock solution by diluting 20ml of the stock solution to 1000ml with deionized water. Similarly, synthetic cadmium ion solution was prepared by dissolving a known mass of cadmium salt ($cdcl_2$) in distilled water. (1.599g) of cadmium chloride was dissolved in distilled water, 10ml of concentrated HNO_3 was then added and the solution diluted to 1000ml mark using deionized water. Working solution was then prepared as described in the procedure for lead.

6. Phy-sio-chemical characteristics of (ACOP) and (ACBP).

The following factors were determined; moisture, content, ash content, alkalinity, acidity, ph bulk density, iodine number surface area, volatile matters and fixed carbon.

7. **Verification Of Adsorption Potentials Of Activated Carbon from orange / banana Peels:**

The effects of adsorbent dose, ph and initial metal concentration on the removal efficiency of pb(ii) and cd(ii) was examined.

a. Effect of ph on the adsorption of pb(ii) and cd(ii) into adsorbents: The effect of ph on the removal efficiency of the pb^{2+} and cd^{2+} was investigated. The experiment was carried out at 120mg/l concentration at room temperature for 3hours equilibrium time. The solution was adjusted to pH of 2, 4, 6, 8 applying 0.1M HCl and 0.1M NaOH. At the end of the process, the suspension was centrifuged and the residual metal was analyzed using Shimadzu atomic adsorption spectrophotometeri.

b. Effect of adsorbent dosages on the adsorption of pb (ii) and cd (ii) onto adsorbents. The influence of the adsorbent dosage on equilibrium uptake of cadmium and lead was studied at initial concentration of 120mg/l at adsorbent dosage of 0.5g, 1.0g, 1.5g, 2.0g per 50ml of the solutions. The experiments were performed by shaking the different adsorbents concentration with the above different adsorbents dosage for 3 hours at 200 rpm. After centrifugation the residual concentration was analyzed using the Shimadzu atomic adsorption spectrophotometer.

c. Effects of initial metal ion concentration on the adsorption of pb(ii) and cd(ii) onto adsorbents- The effect of different initial concentration of cadmium and lead was analyzed using initial concentration of 30mg/l, 60mg/l, 90mg/l, 120mg/l at adsorbent dosage of 0.5g and pH of 7. The solution was equilibrated for 3 hours after which they were centrifuged at 200 rpm.

The residual concentration was analyzed the Shimadzu atomic adsorption spectrophotometer.

8. Batch Adsorption Analysis-

To determine the adsorption capacity of pb^{2+}. 20 ml of the working solution of lead ions containing 30mg/l, 60mg/l, 90mg/l, and 120mg/l of pb^{2+} each was taken into four different beakers and measured mass 0.5g of the adsorbent was added to the solution separately. The mixture was agitated at 200 revolutions per minute (rpm). For 3 hours equilibrium time. The resultant mixture was centrifuged and the filtrate was separated from the solution. The filtrate was analysed using atomic adsorption spectrophotometer to determine the pb^{2+} ion concentration. Similarly the batch isotherm studies were carried out in the same procedure but at a different temperatures of 303k, 313k, 323k, and 34k on an isothermal shaker. The same procedure was followed in the determination of the adsorptive capacity of the adsorbent for cd^{2+}. At the end of each experiment the amount of solute (pb^{2+} and cd^{2+}) removed (adsorbed) at equilibrium was calculated with the below equation.

$$q_e = \left(\frac{C_0 - C_e}{W}\right) V \quad \textbf{(1)}$$

C_0 = initial liquid-phase concentration of pb^{2+} and cd^{2+} (mg/l).

C_e = experimental concentration at equilibrium time $_{(e)}$ (mg/l).

V = the volume of the working solution (litre).

M = adsorbent mass (g).

Also the amount of solute pb^{2+} and cd^{2+} removed at a given time was calculated using equation 2

$$q_t = \left(\frac{C_0 - C_t}{W}\right) V \quad \textbf{(2)}$$

9. Results and Discussion

Results – The results of the adsorption studies of the two heavy metals ions (pb^{2+}, cd^{2+}) using activated carbon from orange and banana peels are presented and discussed below;

Description

SampleA: Activated Carbon Banana peel (ACBP)

SampleB: Activated Carbon Orange peel (ACOP)

Table:1.1:Physiochemical Characterization of Activated Banana and Orange peels.

S/N	PARAMETER	UNIT	A	B
1	Moisture content	%	1.85	1.56
2	Ash content	%	14.97	16.81
3	Bulk density	g/ml	0.2857	0.3076
4	PH	-	7.1	7.0
5	Iodine number	Mg/g	102.3683	139.5704
6	Surface area	M^2/g	224.8	347.2
7	Volatile matter	%	20.1	12.8
8	Acidity	Nmol/g	0.0173	0.0373
9	Alkalinity	Nmol/g	0.023	0.0200
10	Fixed carbon	%	63.05	68.83

Moisture content from table 1, the moisture content of ACOP and ACBP are shown to be 1.56% and 1.85% respectively. The moisture content plays a vital role in the quality of the activated carbon produced. The lower the (%) moisture content, the better the yield, quality and performance of the activated carbon (Adie et al, 2012).

Ash Content- Several work done on adsorption has suggested that the ash content gives an idea of the measure of mineral content of the samples. (Hegazi etal, 2012). The ash content were found to be 16.81% and 14.97% for ACOP and ACBP respectively. It can be said that the results are favorable and effective because the ash serves as an interference during the adsorption process. The lower the ash content, the better the material. (Adie et al, 2012).

Surface Area – From table 1, (ACOP) has 347.2m^2g^{-1} surface area where (ACBP) has 224.8m^2g^{-1} surface area. The higher the surface area the more adsorptive sites present at the surface and it yields a better adsorption. (Barakat et al, 2010), (Ejikeme et al, 2014).

Ph – Both (ACOP) and (ACBP) have a neutral ph of 7.0 and 7.1. these show a neutral ph value. The type of the activating process as well as the nature of the activating agents have significant effects on the ph of the activated carbon. (Abram 1973) noted that the ph can be modified by washing.

Iodine Number – Determining the iodine number is one of the proved methods to verify the adsorption capacity of activated carbons. It is a measure of the micro pore (0.20Ā) content of the activated carbon by adsorption of iodine from the solution. The iodine number for (ACOP) and (ACBP) are 139.5704mg/g and 102.3683mg/g respectively. The iodine adsorption of activated carbon increased with increasing a higher impregnation ratio. The micro pore content on the surface of the activated carbon increased with a higher impregnation ratio hence leading to a more extensive reaction between the 6m KOH and the surface carbon. (Mopoung etal, 2015).

10. Batch Adsorption Studies/Effect Of Process Parameters.

The Effect of ph on the adsorption of pb^{2+} and cd^{2+} onto (ACOP) and (ACBP) are represented below.

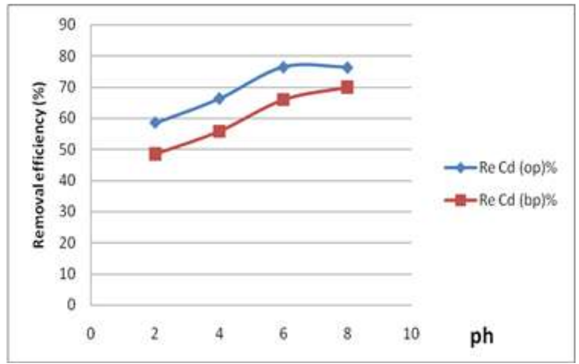

Fig: 1 Graph of Removal efficiency versus pH of solution for Pb(ii) onto banana and orange peel activated carbons

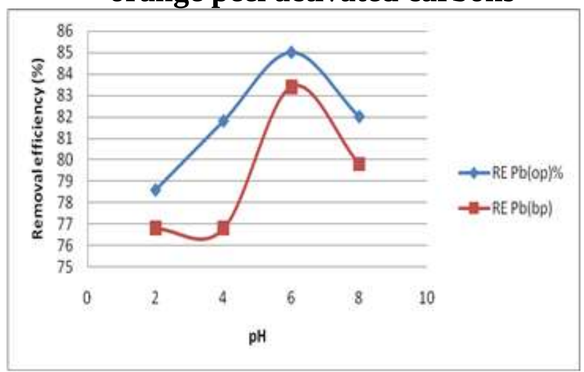

Fig: 2 Graph of Removal efficiency versus pH of solution for Cd (ii) and pb(ii) onto banana and orange peel activated carbons

The pH effect on the adsorption and removal efficiency of lead (ii) and cadmium (ii) ions onto banana and orange peel activated carbon is shown in Fig 1 to fig 2 It was observed that adsorption of lead (ii) and cadmium (ii) ions increase with increase in pH of solution; and was obtained for the two adsorbents using a pH range of 2-8. The low adsorption of all the metal at lower pH value is due to the fact that at lower Ph, more protons (H+) are present in solution and competes with the metals for the active sites. This usually results in lower adsorption of the metal ions at lower pH values. As the pH increases, the number of hydrogen ions in solution decreases thereby reducing the competition with the metals for the active sites of the two adsorbents (Kim,T.Y et al, 2004).This makes more sites to be available for the metal ions to bind, leading to a higher adsorption with increase in pH value. Since metal ion removal usually increase with increase in pH, it is a must check parameter in adsorption that has a significant impact on the uptake of heavy metal ions since it determines the surface charge of the adsorbent and the degree of ionization and specification of the adsorbate. (Oboh et al., 2009).

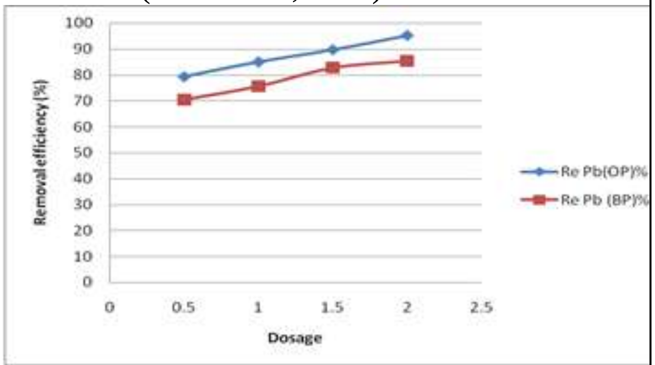

Fig:3 Graph of Removal efficiency versus adsorbent dosage for Pb(ii) onto activated orange and banana peel carbon.

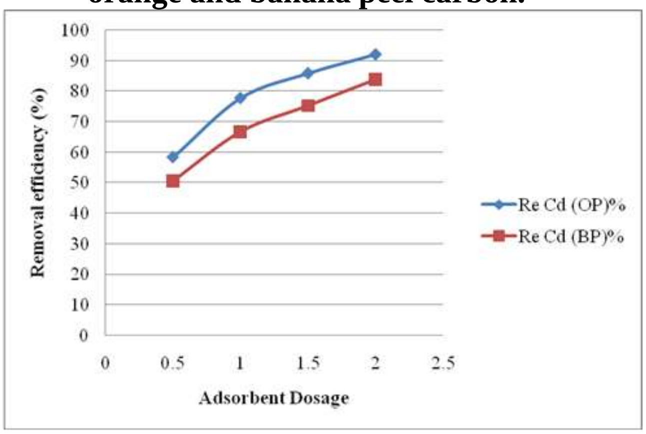

Fig:4 Graph of Removal efficiency versus dosage for Cd(ii) and pb(ii) onto acti5vated orange and banana peel carbon.

The effect of adsorbent dose on the adsorption capacity and removal efficiency (%) of the two metals ions are presented respectively in Fig 3 to Fig 4 above. It was observed that as the mass of the adsorbents was increased from 0.5 to 2.0g, there was a corresponding increase in the removal efficiencies for the two metal ions. According to Barakat (2010), the increase in the percentage adsorption is majorly attributed to the increase in the availability of the surface area of more active binding sites on the adsorbent surface with increase in the dose of the adsorbent.

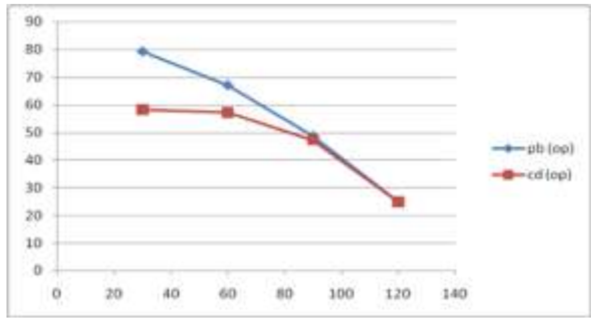

Fig: 5 Removal efficiency versus initial concentration for Pb (II) andcd (11) activated orange carbon.

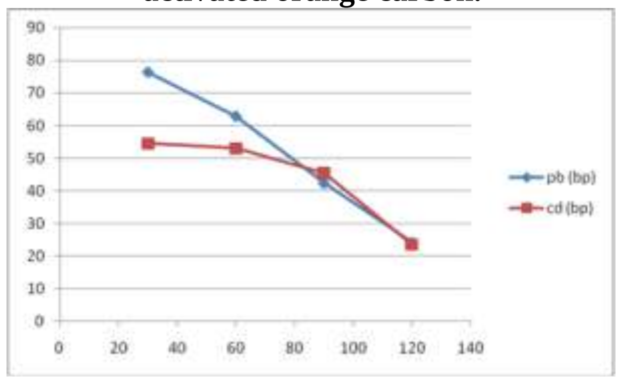

Fig: 6 removal efficiency versus initial concentration for Pb (II) activated orange and banana peel carbon.

The initial metal concentration effect on the Pb (ii) ion adsorption onto activated orange and banana peel carbon is shown in Fig 5to Fig6.The removal efficiency also decreased with increase in initial metal concentration from the above table

The removal efficiency and adsorptive capacity reduced as the initial concentration of the metals rises; and this is mainly due to the saturation of the active binding sites on the surface of the adsorbent at a higher (AOPC) and (AOBC) concentration. Most of the pb(11) and cd(11) ions are left unabsorbed due to saturation of the adsorptive sites at higher concentration. The ratio of sorptive surface to ion concentration decreased with increasing metal ion concentration and hence ion removal reduced. (Ejikeme et.al. 2014), Gupta and Mohapatra, (2002).

11. Conclusion

The removal of pb^{2+} and cd^{2+} from their aqueous solution using (ACOP) and (ACBP) were studied. This study (from experiment, observations and results) shows the suitability of using (ACOP) and (ACBP) for the removal of pb^{2+} and cd^{2+} in aqueous solution using batch adsorption studies. The process factors study shows that increase in ph, adsorbent dosages increases the removal efficiency whereas increase in initial metal ion concentration decrease removal efficiency. Ultimately, this work shows that locally available materials which is also an agricultural waste from end users, i.e. (orange and banana peel) could easily be used to produce activated carbon which can be used as efficient adsorbents for pb^{2+} and cd^{2+} ion removal from aqueous solution. This has also verified a very effective means to control environmental pollution using an agricultural waste.

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