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Optimum Conditions for the Removal of Lead from Aqueous Solution Using Paw-paw Trunk Activated Carbon

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Abstract

The study investigated the optimum conditions for the removal of lead from aqueous solution using chemically activated pawpaw trunk (UPTAC) with $ZnCl_2$. The design of experiment (DoE) was based on three variables, contact time, adsorbate concentration and adsorbate pH, and a total of 27 experimental runs were used to study the effects of the parameters using the response surface methodology (RSM). Batch adsorption studies on the effects of adsorbent dosage, initial adsorbate concentration, contact time and adsorbate pH were used as variables to obtain the optimum conditions. Results showed that the amount of leads adsorbed was found to vary with adsorbent doses, initial adsorbate concentration, stirring time and adsorbate pH. However, the rate of lead removal increased with smaller adsorbent dosage while the amount adsorbed per unit mass increased with increase in initial lead concentrations. Generally, UPTAC achieved optimum % removal of 99.51% at initial lead concentration of 50mg/l and its removal was pH dependent (pH 6) tending towards neutral. Also, there was increase in adsorption of lead ions with increase in stirring time due to increase in kinetic energy of the metal and UPTAC attained equilibrium in 60mins. Thus, UPTAC could effectively remove lead from aqueous medium using the above optimum conditions.

Keywords: Adsorption; pawpaw trunk activated carbon; chemical activation; lead; optimum conditions.

1. Introduction

Lead is one of the major toxic pollutants which can enter water streams through various industrial operations such as battery manufacturing, metal plating and finishing, petroleum refining and many others. Lead poisoning can cause severe toxic damage to the human system including neuronal system, reproductive system, liver, kidney, brain and many other environmental damage [1,2]. Since lead do not degrade in the environment, it's safe and effective disposal is important.

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Various treatment options used to remove heavy metals from aqueous solution include chemical precipitation, electrochemical reduction, ion exchange, reverse osmosis, membrane separation and adsorption. Compared with other treatment method, adsorption appears to be an attractive process due to its simplicity, effectiveness and economical in the removal of heavy metals from aqueous solution. Activated carbon is widely used in adsorption process but its use is restricted due to high cost of commercial activated carbon. Thus, studies have been geared toward the use of agricultural waste to produce low-cost adsorbents. The production of activated carbon from agricultural waste has economic and environmental impacts as it converts unwanted waste materials into high-value adsorbents which increases its use in wastewater treatment. Also, it will reduce the importation of activated carbon thereby increasing the economic base of the country. Thus, waste materials like rice husk and corn-cob [3], coconut shell [4], groundnut shell [5], pawpaw seed [6] has been converted into low-cost adsorbents. This study investigated the optimum conditions for the removal of lead from aqueous solution using pawpaw trunk activated carbon.

2. Materials and methods

2.1 Preparation and Activation of Pawpaw Trunk Carbon

Activated carbon was prepared from pawpaw trunk sourced from Lubara in Khana LGA of River State. The Pawpaw trunk was cut into smaller sizes, washed and sun dried to reduce the moisture content. It was then activated with $ZnCl_2$ at impregnation ratio of 1:2 ($ZnCl_2$/Pawpaw) and carbonized at 400^oC for one hour and cooled and crushed to powder. This was named Unwashed Pawpaw Trunk Activated Carbon (UPTAC).

2.2. Design of Experiment (DoE) for Process Parameter Optimization

Three variables, contact time, adsorbate concentration and adsorbate pH, were selected for optimum condition for equilibrium adsorption and kinetic studies while the response variable was adsorbate removal efficiency. The above parameters were studied using the response surface methodology (RSM), based on design of experiment (DoE) and a total of 27 experimental runs were used to study the effects of three variables, namely adsorbate concentration, contact time and pH.

2.3. Batch Adsorption Studies

Batch adsorption studies were used to investigate the removal of lead (II) ions from the simulated solution using the pawpaw trunk activated carbon. The stock solution was prepared by mixing lead nitrate salt ($Pb(NO_3)_2$) in distilled water to obtain the desired initial concentrations. All the chemicals used were of analytical grade. Batch adsorption studies were conducted to obtain the effect of adsorbent concentration, adsorbate pH and contact time. Experimental procedure was carried out in accordance with the experimental design. The adsorbate concentration used were 5, 27.5 and 50mg/l; the pH used were 2, 7 and 12 while the contact time used were 30, 105 and 180mins. The adsorption efficiency of UPTAC, as expressed in Equation 1, was used as criterion for determining optimum conditions for lead removal.

$$\% R = \frac{C_i - C_e}{C_i} \times 100\% \quad (1)$$

Where: R= adsorption efficiency (%)

C_e = equilibrium concentration of the adsorbate (mg/l).

C_i = the initial conc. of adsorbate (mg/l).

Also, the amount of adsorbate adsorbed per unit mass of adsorbent at time t (q_t mg/g), and the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (q_e mg/g), were calculated from Equations 2 and 3:

$$q_t = V \times C_i - C_t M_s \quad (2)$$

$$q_e = V \times C_i - C_e M_s \quad (3)$$

where C_i and C_e (mg/L) are the initial and the final concentrations of adsorbates respectively, C_t (mg/L) is the concentrations of adsorbates at time t, V is the volume of the solution (L) and M_s is the mass of dry adsorbent used (g).

2.3.1 Effects of Adsorbent dose

The effect of adsorbent dose was investigated by mixing 50ml of simulated wastewater samples of pH 7 and a fixed initial adsorbate conc. of 50mg/l stock solution of lead with different adsorbent doses of 0.5, 1, 1.5, 2, 2.5 and 5g and then stirred for 30 mins using a magnetic stirrer at 500rpm and 30^{o}C. The mixture was then filtered using Whatman filter paper and the filtrates analyzed for residual concentration of lead using Atomic Adsorption Spectrometer (AAS). The optimum adsorbent dosage for lead removal was noted and adopted for the next experiment.

2.3.2 Effect of Initial Adsorbate Concentration

Effect of different initial concentration of lead (5, 10, 20, 30, 40 and 50mg/l) were investigated by adjusting the initial concentration of lead via dilution of the simulated wastewater sample while the optimum condition of adsorbent dosage was adopted. The experimental procedure remained the same and the residual concentration of lead was analyzed. The optimum initial lead concentration was noted.

2.3.3 Effect of Contact Time

The effect of different contact time (5, 30, 45, 60, 75 and 90mins) on the adsorption of lead was conducted by varying the stirring time but adopting the optimum adsorbent dose and optimum initial concentrations. The experimental procedure and other test conditions remained the same except that the flasks were removed from the magnetic stirring at specified time intervals of 30, 60, 90, 105, 150 and 180mins. The residual concentration of lead was analyzed and their optimum contact time for adsorption was noted.

2.3.4 Effect of Adsorbate pH

To investigate the effect of adsorbate pH on the adsorption of lead, the pH of the stock solution was adjusted to 2, 4, 6, 8, 10 and 12 by adding 0.1M (NaOH) or HCl solutions as the case may be. The optimum adsorbent dosage, initial concentration and agitation time were adopted while other test conditions and experimental procedure remained same. The optimum adsorbate pH for the adsorption was noted.

3. Results and discussion

3.1 Results of Batch Adsorption Studies

Table 1: Result of Batch Adsorption Study of Lead with UPTAC Based on DoE

Obs.	Run order	Repetition	C_i (mg/l)	Contact Time (Min)	pH	Ce (mg/l)	Amt Adsorbed qt (mg/l)	% Removal
1	30	1	5	30	2	0.850	4.150	83.0
2	30	1	27.5	30	2	0.953	26.547	96.5
3	30	1	50	30	2	1.565	48.435	96.9
4	105	1	5	105	2	0.975	4.025	80.5
5	105	1	27.5	105	2	0.786	26.714	97.1
6	105	1	50	105	2	1.310	48.690	97.4
7	180	1	5	180	2	0.622	4.378	87.6
8	180	1	27.5	180	2	0.225	27.275	99.2
9	180	1	50	180	2	1.166	48.834	97.7
10	30	1	5	30	7	0.001	4.999	99.9
11	30	1	27.5	30	7	0.543	26.957	98.0
12	30	1	50	30	7	0.836	49.164	98.3
13	105	1	5	105	7	0.205	4.795	95.9
14	105	1	27.5	105	7	0.520	26.980	98.1
15	105	1	50	105	7	0.215	49.785	99.6
16	180	1	5	180	7	0.229	4.771	95.4
17	180	1	27.5	180	7	0.857	26.643	96.9
18	180	1	50	180	7	0.220	49.780	99.6
19	30	1	5	30	12	0.249	4.751	95.0
20	30	1	27.5	30	12	0.258	27.242	99.1
21	30	1	50	30	12	0.266	49.734	99.5
22	105	1	5	105	12	0.045	4.955	99.1
23	105	1	27.5	105	12	0.230	27.270	99.2
24	105	1	50	105	12	0.245	49.755	99.5
25	180	1	5	180	12	0.551	4.449	89.0
26	180	1	27.5	180	12	0.399	27.101	98.5
27	180	1	50	180	12	0.315	49.685	99.4

The results of batch adsorption study (based on the DoE shown in Table 1) to determine the optimum conditions for the removal of lead from aqueous solution with UPTAC showed that at adsorbate concentration of 5mg/l, a

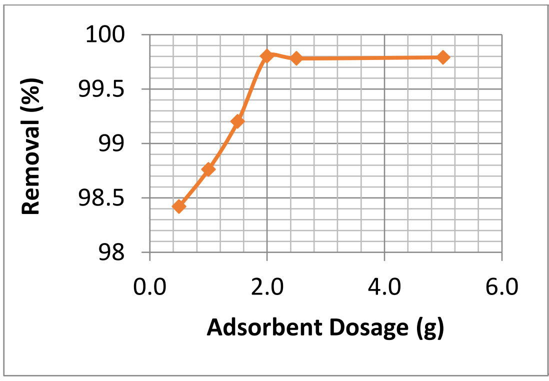
99.9% removal was achieved at pH 7 within 30mins. Also, a 99.6% removal of lead was achieved at 50mg/l adsorbate concentration within 105 mins at pH 7. Detailed results on the design matrix are shown in Table 1.

3.1.1 Effect of Adsorbent dose on Lead Removal

The effects of different adsorbent doses of UPTAC on lead removal from aqueous solution was investigated. Results showed an increase in % removal as the adsorbent dosage increased from 0.5g to 2g, but remained almost unchanged when adsorbent dosage was increased from 2g to 5g as shown in Figure 1. This increase in % removal may be due to the availability of larger surface area and more adsorption sites, but as the dosage increased, the % increase becomes very low as the surface metal ions concentration and solution metal ion concentration come to equilibrium with each other [7]. Thus, increased adsorbent dosage (greater than 2g) did not enhance the removal percentage of lead. This decrease in quantity adsorbed (q_e) with increase in the adsorbent dose may be due to the saturation of adsorption sites through the adsorption process. Another reason may be due to the particle interactions, such as aggregation, resulting from high sorbent concentration. Such aggregation would lead to a decrease in the total surface area of the adsorbent. Similar trends have been reported by [8,9,10,11]. Thus, the optimum adsorbent dosage for the removal of lead with UPTAC was 2g with removal efficiency of 99.8%.

3.1.2 Effect of adsorbate pH

Results on the effects of adsorbate pH on the removal of lead onto UPTAC is shown in Figure 2. The percentage removal efficiency for lead adsorption increased as the pH moves from the acidic pH 2 to pH 6 and then decreased as pH increased from 8 to 12. The low % removal observed at pH 2 could be due to the presence of excess hydrogen ions (H^+) at the surface of the adsorbent contending with lead ions at the binding sites [12]. As the pH increased to 6, the adsorbent acquired more negative charges for the attraction of lead and this resulted in higher removal at pH 6. However, the decreased observed from pH 8 to 12 could be caused by hydrolysis reaction. Such reaction often generates hydroxylated complex cations preventing the binding efficiency of the metal [13]. Similar trends have been reported by [14,10]. Thus, the optimum pH for the removal of lead with UPTAC was pH 6 with removal efficiency of 99.93%.



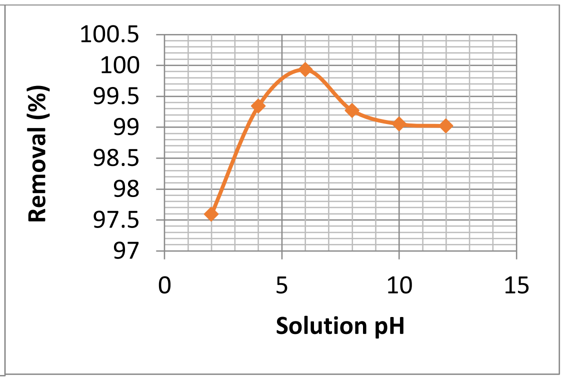


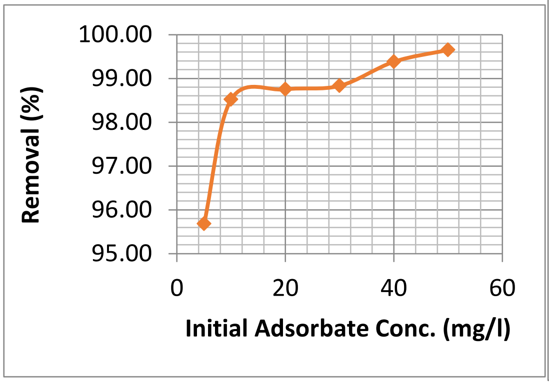
Figure1: Lead Removal as a function of Adsorbent Dosage. **Figure 2:** Lead Removal as a function of Solution pH.

3.1.3 Effect of Initial Adsorbate Concentration

Results on the effect of initial adsorbate concentration on the adsorption of lead onto UPTAC is presented in Figure 3. The results showed that percentage removal rate increased with increase in lead concentrations with a sharp increase in % removal from 5 to 10 mg/l and then a gradual increase as the concentration of the adsorbate increased. The trend may be attributed to adsorbent having more active sites relative to lower concentration of the adsorbate. Also, increasing the adsorbate concentration enabled the unfilled active sites on the adsorbent surface to be taken over by the metals ion thereby increases the amount adsorbed. Similar trends were reported by [15,16]. Hence, optimum removal efficiency of 99.6% was achieved with UPTAC at 50mg/l. Thus, lead removal was highly concentration dependent and this might also be due to high driving force for mass transfer (17).

3.1.4. Effect of Contact Time on lead Removal

The effect of contact time on the removal of lead (II) ions from aqueous solution using UPTAC is presented in Figure 4. It was observed that increased in contact time increased the % removal and optimum removal of 99.51% was recorded at 60 mins and thereafter, equilibrium was reached. This trend could be ascribed to the depletion of the metal ions at binding site available on the adsorbent. Similar observation was reported by [18].



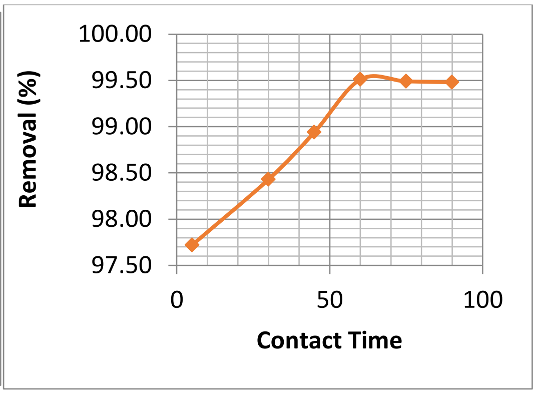


Figure 3: Lead Removal as a function of Adsorbate Conc. **Figure 4:** Lead Removal as a function of Contact Time.

4. Conclusions

This study revealed the optimum conditions for the removal of lead from aqueous solution using chemically activated unwashed pawpaw trunk with $ZnCl_2$. The amount of leads adsorbed was found to vary with adsorbent doses, initial adsorbate concentration, stirring time and adsorbate pH. The rate of removal increased with smaller adsorbent dosage while the amount adsorbed per unit mass increased with increase in initial lead concentrations. Generally, UPTAC achieved optimum % removal of 99.51% at initial lead concentration of 50mg/l and its removal was pH dependent (pH 6) tending towards neutral. There was also increase in adsorption of lead ions with increase in stirring time due to increase in kinetic energy of the metal and UPTAC attained equilibrium in 60mins.

In conclusion, chemically activated unwashed pawpaw trunk carbon can be used for the removal of lead from aqueous solution and it could effectively remove lead from aqueous medium. The optimum conditions for the adsorption of lead from aqueous solution using UPTAC is summarized in Table 2.

Table 2: Optimum Conditions for Adsorption of Lead from Aqueous Solution onto UPTAC

Parameters	Optimum Conditions
Adsorbent Dosage (g)	2
Adsorbate pH	6
Initial Adsorbate Conc. (mg/l)	50
Contact Time (Mins)	60
Temperature (^oC)	30
Stirring Speed (rpm)	500

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