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Remediation and adsorption studies of Pb^{2+} and Cu^{2+} in fresh foundry wastewater using Activated Charcoal-250

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ABSTRACT

Application of adsorption process in the attenuation of heavy metals in industrial wastewater is becoming more embraced in recent times. This paper utilized a commercially-sourced Activated Charcoal-250 (AC-250) adsorbent to remediate Zn^{2+}, Cu^{2+}, Mg^{2+} and Pb^{2+} from fresh wastewater obtained from Lamina Foundry, Nitte Southern India. The adsorption study on Pb^{2+} and Cu^{2+} was carried out after the remediation experiment.The AC-250 samples were prepared by rinsing with distilled water and washing with 0.001 mol^{-1} of HCl solution and pH adjusted to between 6 and 7. The collected fresh samples of wastewater were filtered and stored in the room temperature while an equivalent volume of domestic sewage was also collected from the inlet of the NMAM Wastewater Treatment Plant Nitte to serve as control. Batch adsorption experiments with One Factor at A Time (OFAT) were conducted on the wastewater samples using factors which include adsorbent dosage, contact time, pH, and the shaking speed of rotary incubator. The adsorption isotherms and kinetics on the AC-250 were studied using Langmuir, Freundlich, Pseudo-first-order and pseudo-second-order models. Treated samples were centrifugated and the filtrates subjected to Atomic Absorption Spectroscopy (AAS) while the pellets obtained after centrifugation were analyzed with Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX) machines. Results from AAS analyses showed that AC-250 dosage of 0.2 to1.0g (at 0.2g intervals) gave % removal efficiencies of 96.4, 100, 58.5 and 100 respectively for Zn, Cu, Mg and Pb. With the contact times of 20 to120 mins (at 20mins intervals) the removal efficiencies of the studied heavy metals were 98.2, 100, 52.1 and 100 respectively. The pH variation from 2 to 6 resulted into respective % removal efficiencies of 90.9, 96.9, 77.4 and 100. Rotating speeds of 150 to 350 rpm facilitated % removal efficiencies which were 94.5, 100, 57.4 and 100 respectively for the metals. The optimum values of AC-250 dosage for treating the wastewater was 1.0g; contact time, 40mins; and pH, 6. The data of this study showed that only the Pb^{2+} adsorption is optimum and fits well with Langmuir isotherm. The kinetic studies indicate that adsorption behavior of both the Pb^{2+} and Cu^{2+} can be perfectly described by the pseudo-second-order kinetic model (R^2 = 1.000). The SEM and EDX analyses confirmed the presence of the adsorbed metals in the pellets, with traces of Al, Si and Fe. The study concludes that the AC-250 is very efficient in remediation of Pb and Cu from the fresh foundry effluent, efficient in Zn removal but fairly efficient in Mg remediation. It is therefore recommended as an adsorbent for treatment before discharging the foundry effluent into the larger water body.

Keywords: Remediation, Wastewater, Adsorbent, Heavy metal

Aims Research Journal Reference Format:
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1. INTRODUCTION

One of the negative consequences of industrialization and industrial production is the generation and emission of toxic wastes that are pollutant in nature. (Baysal et al., 2013; Bernard and Jimoh, 2013). Wastewater from numerous industries such as paints and pigments, glass production, mining operations, metal plating, and battery manufacturing processes are known to contain contaminants such as heavy metal. Heavy metals such as Pb, Cd, Cr, Ni, Zn, Cu and Fe are present in industrial wastewater. These heavy metals in wastewater are not biodegradable and their existence in receiving lakes and streams causes bioaccumulation in living organisms, which leads to several health problems in animals, plants and human beings such as cancer, kidney failure, metabolic acidosis, oral ulcer, renal failure and damage in stomach of the rodent (Bernard et al., 2013). In particular effluents from various processing industries such as electroplating industries and foundries are reported to contain high amounts of heavy metal ions, such as nickel, iron, lead, zinc, chromium, cadmium and copper (Konstantinos et al., 2011).

Several treatment methods have been suggested, developed and used to remove heavy metals from wastewaters. These methods include chemical precipitation, ion exchange, cementation, electro-winning, reverse osmosis/electrodialysis, membrane processes, electro-coagulation, precipitation, and membrane separation (Dean et al., 1972, Amuda et al., 2006, Aydiner et al., 2006; Kang et al. 2000; Sag and Kutsal, 2001; Wang and Tang, 2001; Ahalya et al. 2003; Wickramasingbe et al., 2004; Baysal et al. 2013). However, these techniques have been reported to be very expensive, making its adoption and application in most developing countries very unrealistic. For efficiency measurements, heavy metals removal processes in all respects are expected to be simple, effective and inexpensive.

In recent times, efforts have been made to employ cheaper and more effective organic materials, agricultural wastes, and related compounds as adsorbents. The use of activated carbon produced either commercially or from agricultural wastes like coconut shell, rice husk, orange peel, pine sawdust, peanut husk, Carica papaya etc to remove heavy metals from wastewater, is gaining fast recognition in this century (Kadirvelu et al., 2001; Abia and Igwe, 2005; Ahmad, 2005; Vaishnav et al., 2012; Bernard et al., 2013; Ojoawo and Udayakumar, 2016; Ojoawo et al. 2016).

Adsorption isotherms are used to describe how the reaction of adsorbing substance with adsorbent goes as well as optimizing the quantity of adsorbent application (Hameed, 2009). Langmuir model is based on the hypothesis that there is monolayer sorption between gas-solid phases and it is applicable to short sorption of a single heavy metal. The Freundlich model is a semi-empirical equation that may be used to describe surface sorption and multi-layer sorption under various non-ideal conditions (Davis et al, 2003; Dang et al, 2009; Farooq et al, 2010; Ding et al, 2012). Lagergren's first order kinetic model is based on the assumption that the sorption process is controlled by diffusion step and the sorption rate is proportional to the difference between equilibrium sorption capacity and adsorbed quantity at time t. A pseudo-second order kinetic model is also based on the assumption that the sorption rate is controlled by a chemical sorption mechanism involving electron sharing or electron transfer between adsorbent and adsorbate (Ho and McKay, 1999; Ding et al, 2012).

In this research, commercially sourced Activated Charcoal-250 (AC-250) was used as an adsorbent to treat heavy metals (Zn, Cu, Mg and Pb) present in foundry wastewater. Parameters that were investigated include pH, stirring speed, adsorbent dosage and contact time at 32^0C. The isotherms and kinetics adsorption studies of the remediation process were carried out. Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX) analysis were employed to study the pores structure of the bio-remediated and adsorbed substances.

2. Methodology

The study adopted the use of batch adsorption experiments with One Factor at A Time (OFAT) that were conducted on the wastewater samples varying the factors of adsorbent dosage, contact time, pH, and the shaking speed of rotary incubator.

(i) Preparation of adsorbent: Activated Charcoal/Carbon-250 was commercially sourced from Fisher Scientific Co, Product No: 22395, Cas No: 7440-44-0. The AC-250 samples were prepared in line with Bernard and Jimoh, 2013 and Gueu et al., 2006. They were rinsed several times with distilled water, then washed by 0.001 mol l^{-1} of HCl solution and the pH adjusted to between 6-7. These were centrifugated and the supernatant discarded while the AC-250 pellets were oven dried at 105^0C for 24hrs.

(ii) Collection of wastewater samples: Fresh industrial wastewater samples were collected from the Lamina Foundry, Nitte, India. They were filtered and kept in room temperature for immediate laboratory analysis. To serve as control, fresh domestic sewage samples were also collected from the inlet of the NMAM Wastewater Treatment Plant Nitte. These were carefully stocked in 2-l plastic bottles and taken to the laboratory for analysis.

(iii) Adsoption study: This was carried out with 50ml of sample poured into 100ml conical flask and 0.2g of prepared AC was added, placed on a rotary shaker at 150 revolutions per minute (rpm) at room temperature for 2hrs. The suspension was filtered with Dr. Watts filter paper 12.5cm (100 circles) and the filtrate subjected to AAS analysis.

(iv) Effect of adsorbent dosage: This was studied with varying dosages of 0.2, 0.4, 0.8, and 1.0g into 50ml of samples respectively and agitated at 150 rpm for 60mins at the suspension was filtered with Dr. Watt's filter paper and the filtrate analyzed by AAS.

(v) Contact time study: This was performed as 0.2g of adsorbent was added to different conical flask containing 50 mL of wastewater, the flask was closed and placed in a rotary shaker and agitated at 150rpm for each of the different contact times chosen as 20, 40, 60, 80, 100 and 120 mins. The content of each flask was filtered and analyzed by AAS after each agitation time.

(vi) pH effect on treatment: The 50ml portion in 3 conical flasks had their pH adjusted to 2, 4 and 6 respectively. 0.8g of adsorbent dosage, being the optimum established from the pilot study, was used and subjected to 150rpm rotary incubation for 1hr at 32^0C.

(vii) Rotating speed experiment: 0.8g of the adsorbent was measured into 50ml of the sample and subjected to various agitation rpm starting from 150 to 350 at 50rpm intervals. The filtrate from each batch was then subjected to AAS analysis.

(viii) AAS Analysis: Samples were analyzed using the Flame Atomic Absorption Spectrophotometer (FAAS) Avanta GM model, of the Department of Bio-Technology, NMAM Institute of Technology, Nitte India. The FAAS's main specifications include: sensitivity of up to ppb level; two channels (independent or simultaneous); wavelength range of between 180 nm and 900 nm; and probe of teflon tubing—1.6 mm OD, 0.8 mm ID. The equipment was calibrated using the prescribed procedures. The five Standard samples of pre-determined concentrations on each of the element were used in the correlations of the absorbance with the concentration. It detected the concentrations of Zn, Cu, Mg and Pb. The flame used in the analysis was air-acetylene. The temperature formed in the air-acetylene flame was around 2300˚C. The FAAS technique made use of the fact that neutral or ground state atoms of an element can absorb electromagnetic radiation over a series of very narrow, sharply defined wavelengths. The sample in solution was aspirated as a fine mist into a flame where it was converted into atomic vapor. Most of the

atoms remained in the ground state and were therefore capable of absorbing radiation of a suitable wavelength.
This discrete radiation was supplied by a hollow cathode lamp, which a sharp line source consisting of a cathode was containing the element to be determined along with the tungsten anode. The line characteristic of the element were emitted by the hollow cathode and passed through the flame where they were absorbed by the atomic vapor, since only the test element can absorb this radiation, the method became specific (Ojoawo and Udayakumar, 2014).

(ix) The adsorption studies
The pilot study showed that of all the studied heavy metals, only Pb^{2+} and Cu^{2+} had significant adsorption; they are therefore selected for the adsorption studies.

(a) Sorption Capacity and Removal Efficiency: The sorption capacity qe (mg/g) and removal efficiency Q were obtained according to the Equations (1) and (2), respectively (Song et al, 2014):

$$q_e = \frac{(Co-Ce)V}{W} \qquad (1)$$

$$Q = \frac{(Co-Ce) \times 100}{Co} \qquad (2)$$

where V is the volume of the solution, W is the amount of adsorbent, C_0 and Ce are the initial and equilibrium concentration in the solution.

(b) Adsorption Isotherm
Pb^{2+} and Cu^{2+} adsorption by the AC carbons were analyzed using Langmuir and Freundlich isotherms. The Langmuir isotherm is used to characterize the monolayer adsorption, which is represented by the following linear form (Ding et al, 2012; Ghasemi and Gholami, 2014; Song et al, 2014):

$$\frac{Ce}{qe} = \frac{1}{qmaxb} + \frac{Ce}{qmax} \qquad (3a)$$

or

$$\frac{1}{qe} = \frac{1}{Ce\ qmaxb} + \frac{1}{qmax} \qquad (3b)$$

The essential characteristic of the Langmuir isotherm is expressed in terms of a dimensionless constant separation factor, R_L, which is defined as:

$$R_L = \frac{1}{1+bCa} \qquad (4)$$

where q_e is the equilibrium adsorption uptake of heavy metal ions, q_{max} is the maximum adsorption capacity corresponding to the complete monolayer coverage. b is the Langmuir constant which is related to the energy of adsorption. If $R_L > 1$: unfavourable or non-optimum adsorption; $R_L = 1$: linear adsorption; $R_L = 0$; irreversible adsorption and $0 < R_L < 1$: optimum/favourable adsorption (Chen and Zhao, 2009; Farooq et al, 2010).

The Freundlich isotherm is generally applicable to the adsorption as they occur on heterogeneous surface. The linear form is shown:

$$\log qe = \log KF + \frac{1}{n}\log Ce \qquad (5)$$

where KF and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. If $\frac{1}{n} = 0: \text{Irreversible adsorption process}; \frac{1}{n} > 1: \text{non} - \text{optimum adsorption};$ and $0 < \frac{1}{n} < 1: \text{optimum adsorption process}$ (Ghasemi and Gholami, 2014)

(c) Adsorption Kinetics
In order to investigate the mechanism of adsorption, kinetic models such as the pseudo-first order and the pseudo-second order kinetic models were applied to study the adsorption dynamics.

The Lagergren's-first-order kinetic model can be expressed in linear form:

$$\log(qe - qt) = \log qe - \frac{k1}{2.303}t \qquad (6)$$

The pseudo-second-order kinetic model is used in the following linear form:

$$\frac{t}{qt} = \frac{1}{k2(qe)(qe)} + \frac{1}{qe}t \qquad (7)$$

where k1 and k2 are the adsorption rate constants of pseudo-first-order and pseudo-second-order kinetic models, respectively, qt is adsorption uptake at time t.

(x) SEM/EDX Analysis: Specimens for SEM/EDX were prepared by carbon taping. They were stuck on the carbon tape plate and subjected to detail-obscuring conducive coating, gold coating using Auto-fine coater equipment JEOL, JEC-1600 to improve the conductivity of specimen since it is a non-conductive sample. The carbon-taped sample was transferred into JEOL fine-coater at pressure of 30Pa and allowed to be pressurized to a value <5Pa, creating a vacuum inside. After which certain rays were displayed, coating the specimen and the timing count-down was from 60 to 0 sec. Coated specimens were immediately transferred into the Specimen Stage of the SEM (Model: JEOL JSM-6380LA, Analytical Scanning Electron Microscope) after its cooling system has been topped with liquid nitrogen coolant. The surface morphology of the specimens were then examined by SEM and monitored on the attached PC. At the same time EDX of the specimens were performed and the elements present in the specimens identified with their concentration levels.

3. RESULTS AND DISCUSSIONS

The results from all laboratory analyses carried out are as presented in Tables 1 to 5 and Figures 1 to 4.

(i) Heavy metal concentration of the samples before treatment: AAS detected the initial concentrations of Zn^{2+}, Cu^{2+}, Mg^{2+} and Pb^{2+} present in the wastewater samples and the results are shown in Table 1.

Table 1: Concentrations of the heavy metals in the wastewater samples prior to treatment

Metal/Sample	Zn^{2+} (µg/l)	Cu^{2+} (µg/l)	Mg^{2+} (µg/l)	Pb^{2+} (µg/l)
Domestic sewage (as control)	0.43	0.95	5.18	0.01
Foundry wastewater	0.55	1.28	2.65	0.07

It is noted that Zn^{2+}, Cu^{2+} and Pb^{2+} all have higher concentrations in foundry wastewater; only Mg is more pronounced in domestic wastewater sample. This trend could be attributed to the constituents of each type of wastewater resulting from the source activities.

Adsorption and the dosage concentration study: From Table 2 it is observed that only Zn has nearly same percent removal values with the increasing dosage concentration from 0.2 to 1.0g. The rest metals display varying removal efficiencies with dosage.

Table 2: Dosage concentration effect of AC on the heavy metal removal

Metal/ Dosage concentration of AC-250 (g)	Zn^{2+} (µg/l)	% removal of Zn^{2+}	Cu^{2+} (µg/l)	% removal of Cu^{2+}	Mg^{2+} (µg/l)	% removal of Mg^{2+}	Pb^{2+} (µg/l)	% removal of Pb^{2+}
	0.55		1.28		2.65		0.07	
0.2	0.03	94.5	0.02	98.4	1.34	49.4	0.07	0
0.4	0.06	89.1	0	100	1.46	44.9	0	100
0.6	0.02	96.4	0	100	1.57	40.8	0.05	28.6
0.8	0.03	94.5	0	100	1.41	46.8	0	100
1.0	0.06	89.1	0	100	1.10	58.5	0	100

AC-250 dosage of 0.2, 0.4, 0.6, 0.8 and 1.0g gave % removal efficiencies of 96.4, 100, 58.5 and 100 respectively for Zn^{2+}, Cu^{2+}, Mg^{2+} and Pb^{2+}. The optimum AC dosage was 1.0g. Figure 1 gives the graphical representation of the adsorption and dosage concentration treatment result. Removal efficiency of the metals here was of the order $Cu^{2+} > Zn^{2+} > Pb^{2+} > Mg^{2+}$.

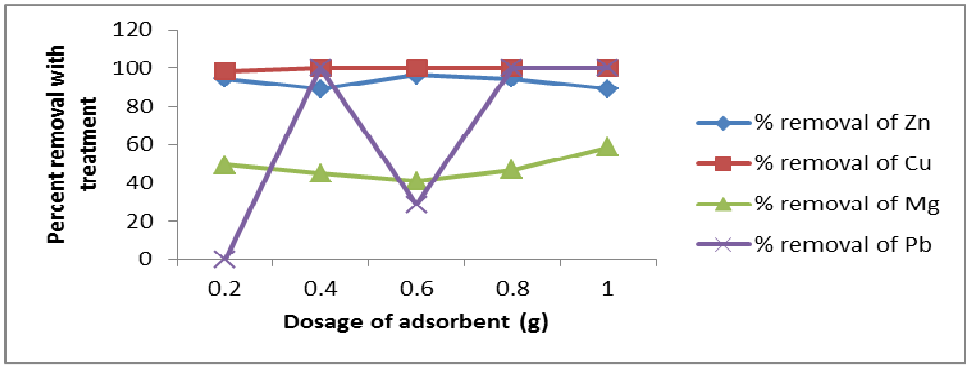

Fig.1: Percent removal trend with adsorbent concentration

(ii) Contact time effect on the adsorption treatment: For Zn^{2+}, the percent removal increases with increase in contact time, the trend was in contrast for Mg with decreasing percent removal. Both Cu^{2+} and Pb^{2+} have 100% removal all through the process (Table 3). The peak of removal percentages in Zn^{2+} and Mg^{2+} stand at 98.2 and 52.1 respectively. The optimum contact time was 40mins. From the results it was noted that contact time variation has no effect on Cu^{2+} and Pb^{2+}. From Figure 2 the trend observed indicates that Mg was least removed in the treatment.

Table 3: Effect of contact time of adsorbent on the heavy metal removal

Metal/ Contact time of adsorbent (mins)	Zn^{2+} (µg/l)	% removal of Zn^{2+}	Cu^{2+} (µg/l)	% removal of Cu^{2+}	Mg^{2+} (µg/l)	% removal of Mg^{2+}	Pb^{2+} (µg/l)	% removal of Pb^{2+}
	0.55		1.28		2.65		0.07	
20	0.08	85.5	0	100	1.28	51.7	0	100
40	0.01	98.2	0	100	1.40	47.2	0	100
60	0.04	92.7	0	100	1.27	52.1	0	100
80	0.03	94.5	0	100	1.68	36.6	0	100
100	0.05	90.9	0	100	1.43	46.0	0	100
120	0.04	92.7	0	100	1.34	49.4	0	100

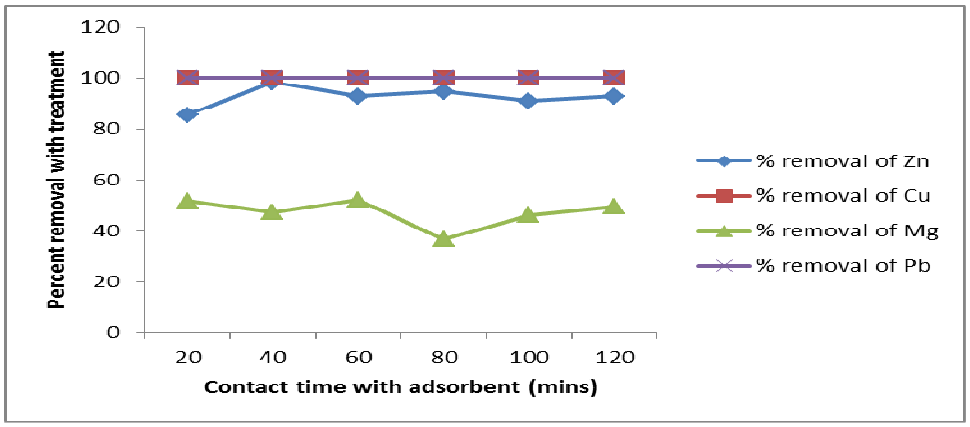

Fig.2: Percent removal trend with contact time of adsorbent

(iii) Effect of pH on the adsorption treatment: At pH of 2 Mg^{2+} and Pb^{2+} were not removed while about 2% of Zn^{2+} was removed. As the pH changes from acidic to being neutral, the removal efficiencies of Zn, Cu and Mg increased. At pH of 4 and 6 the removal efficiency of Pb^{2+} was 100% (Table 4). The pH values of 2, 4 and 6 resulted into respective % removal efficiencies of 90.9, 96.9, 77.4 and 100. The optimum pH value for the treatment was 6. Figure 3 presents the graphical trend in the removal efficiencies. The increase in percentage removal of metal ions as noted may be explained by the fact that at higher pH the adsorbent surface is de-protonated and becomes negatively charged, hence attraction between the positively metal cations occurred (Lohani et al., 2008).

Table 4: Effect of pH of the sample on the adsorption process

Metal/ pH of the sample	Zn^{2+} (µg/l)	% removal of Zn^{2+}	Cu^{2+} (µg/l)	% removal of Cu^{2+}	Mg^{2+} (µg/l)	% removal of Mg^{2+}	Pb^{2+} (µg/l)	% removal of Pb^{2+}
	0.55		1.28		2.65		0.07	
2	0.54	1.8	0.17	86.7	2.65	0	0.07	0
4	0.19	65.5	0.06	95.3	1.27	52.1	0	100
6	0.05	90.9	0.04	96.9	0.60	77.4	0	100

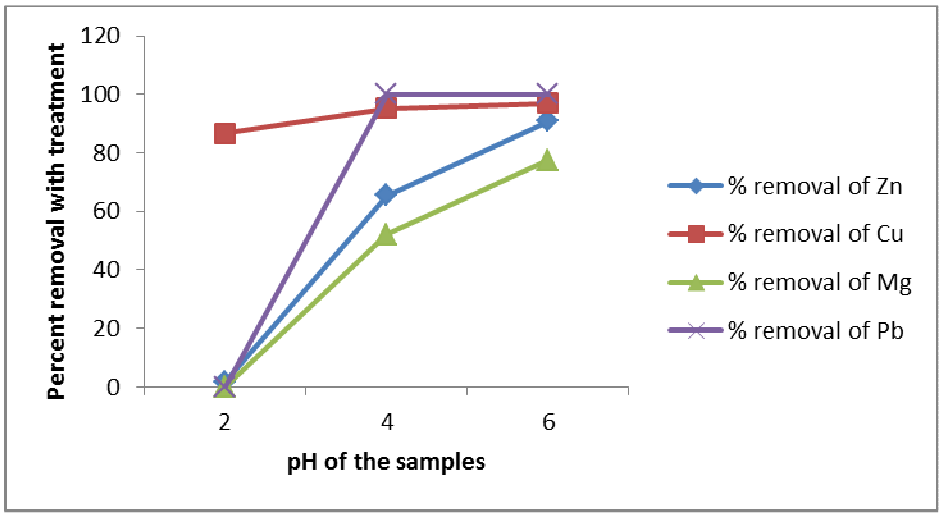

Fig.3: Percent removal trend with pH of the samples

(iv) Effect of rotating speed on the treatment: As the rotating speed increases from 150 to 350 rpm, the percent removals in Zn^{2+} and Pb^{2+} also largely increased. There was however an irregular pattern noticed in the removal of Cu^{2+} and Mg^{2+}. Rotating speeds of 150 to 250 rpm facilitated optimum % removal efficiencies which were 94.5, 100, 57.4 and 100 respectively for Zn^{2+}, Cu^{2+}, Mg^{2+} and Pb^{2+}. Variation in the rotary speed has no noticeable effect on the removal of Pb^{2+} as the percentage removed remain constant all through. The trend in each of the studied metal is further illustrated in Figure 4.

Table 5: Effect of rotating/shaking speed of rotary incubator on the heavy metal removal process

Metal/ Rotating speed (rpm)	Zn^{2+} (µg/l)	% removal of Zn^{2+}	Cu^{2+} (µg/l)	% removal of Cu^{2+}	Mg^{2+} (µg/l)	% removal of Mg^{2+}	Pb^{2+} (µg/l)	% removal of Pb^{2+}
	0.55		1.28		2.65		0.07	
150	0.03	94.5	0	100	1.41	46.8	0	100
200	0.08	85.5	0.05	93.8	1.13	57.4	0	100
250	0.04	92.7	0.04	96.9	1.36	48.7	0.07	0
300	0.07	87.3	0	100	1.29	51.3	0	100
350	0.04	92.7	0.02	98.4	1.24	53.2	0	100

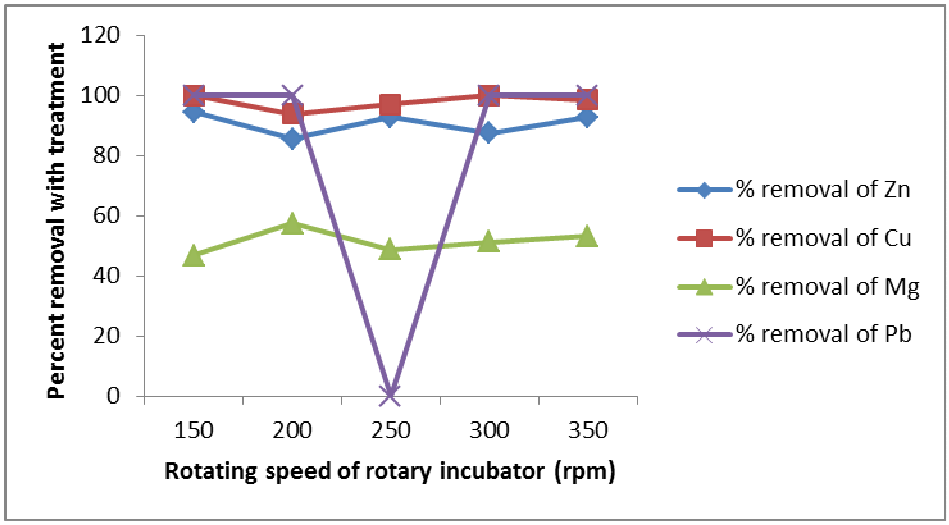

Fig.4: Percent removal trend with rotating speed of rotary incubator

(v) Results of adsorption isotherms and kinetics by AC-250

(a) Isotherm biosorption of Pb^{2+} and Cu^{2+}

(i) Langmuir Isotherm model: The results obtained from Langmuir isotherm model of Pb^{2+} and Cu^{2+} with the plot of 1/qe against 1/Ce are summarized in Figures 5 and 6. For Pb^{2+} the equation of a straight line obtained is:

$y = 9.8723x + 177.43$ and

$R^2 = 0.173$.

Comparing this with Eqn 3b above,

$q_{max} = 0.00564$ and $b = 17.97$

Using the values of b and Co in eqn 4, the separation factor R_L that is a basic and characteristic index of the Langmuir isotherm model is obtained. $R_L = 0.443$, as this lies between 0 and 1, thus giving an optimum adsorption (Chen and Zhao, 2009; Farooq et al, 2010).

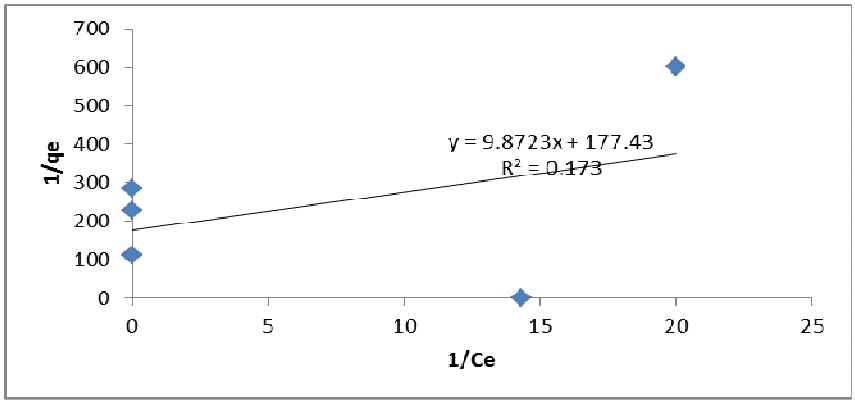

Figure 5: Langmuir isotherm model for Pb^{2+} adsorption

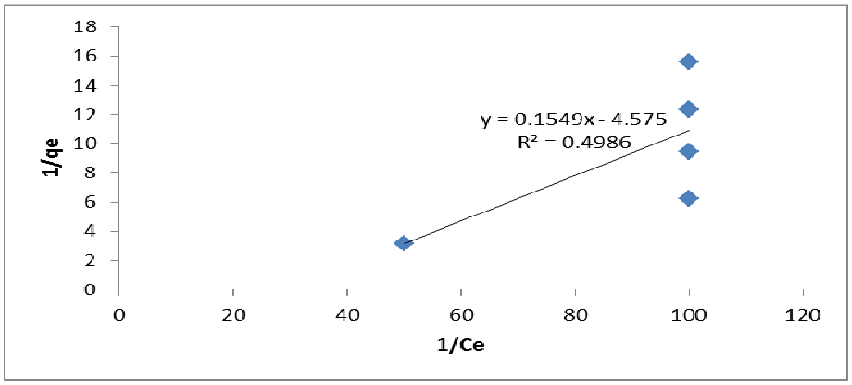

Figure 6: Langmuir isotherm model for Cu^{2+} adsorption

On the other hand, the straight line equation from the adsorption of Cu^{2+} (Figure 6) is:

$y = 0.1549x – 4.575$

$y = 0.1549x – 4.57$ and $R^2 = 0.4986$.

Comparing this with Eqn 3b,

$q_{max} = - 0.22$ and $b = -29.53$

Substituting the values of b and Co in eqn 4, the separation factor $R_L = 0$, which is described as an irreversible adsorption (Chen and Zhao, 2009; Farooq et al, 2010). It is therefore observed that only Pb^{2+} experienced monolayer sorption in its remediation phases, in contrary to the Cu^{2+} adsorption.

(ii) Freundlich isotherm model: The Freundlich isotherm models behavior for Pb^{2+} and Cu^{2+} are represented in Figures 7 and 8 respectively. The plot of log qe vs log Ce gives straight line graphs with correlation coefficients being nearer to unity in the case of Pb^{2+} than Cu^{2+}. In the case of Pb^{2+} the equation obtained is:

$y = -0.7925x – 3.867$ and $R^2 = 0.8245$

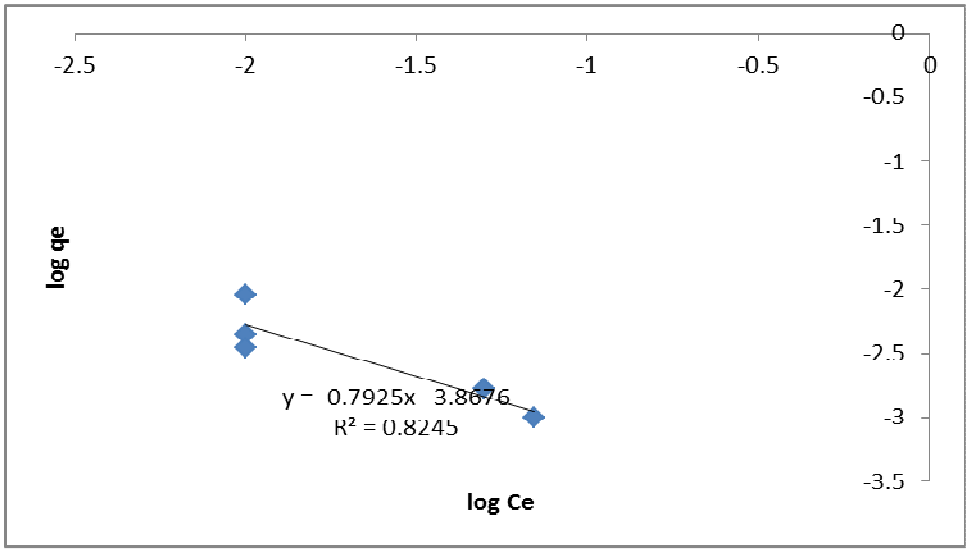

Figure 7: Freundlich isotherm model for Pb^{2+} adsorption

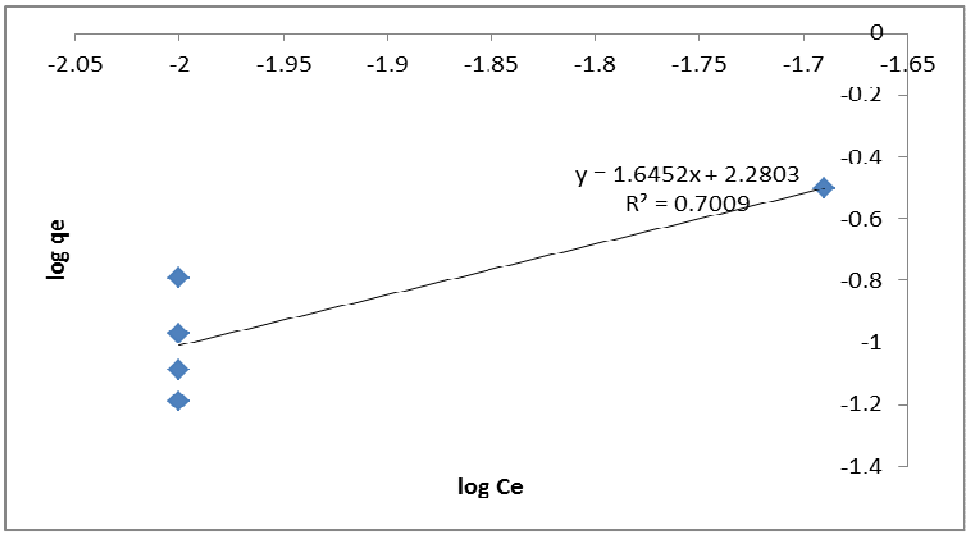

Figure 8: Freundlich isotherm model for Cu^{2+} adsorption

Comparing this with eqn 5, m = 1/n which tends toward zero. Hence it depicts an irreversible adsorption process (Ghasemi and Gholami, 2014).

For Cu, the equation obtained is:

$y = 1.6452x + 2.2803$ and $R^2 = 0.7009$

Comparison of this with eqn 5 shows that, m = 1/n = 1.6452 which exceeds unity. This is a non-optimum adsorption (Ghasemi and Gholami, 2014).

(b) Biosorption kinetics models of Pb^{2+} and Cu^{2+}

(i) Lagergren's-first-order kinetic equation: This reflects the relationship between rate of sorption and time. The results of both Pb^{2+} and Cu^{2+} as subjected to the 1st order kinetic model, using equation 6 above, are as shown in Table 6.

Table 6: Simulation of Lagergren's first-order kinetic equations and corresponding parameters

	qe (experiment) in mg/g	qe (modeled) in mg/g	k1/min^{-1}	R^2
Pb^{2+}	0.0175	0.004	0	0.002
Cu^{2+}	0.321	0.001	0	0.004

From the Table it is observed that the experimental and the modeled sorption capacity (qe) values are wide apart. The correlation coefficients in both metals are apparently zero. It therefore shows that the adsorption of neither of the metals by AC-250 followed the first-order-kinetic model.

(ii) Pseudo-second-order kinetic equation: This as well predicts the sorption rate's relationship and the contact time. Figures 9 and 10 show the behavioural patterns of both metals under the 2nd-order-kinetic modeling, while Table 7 presents their results of simulation using second-order kinetic equations and corresponding parameters.

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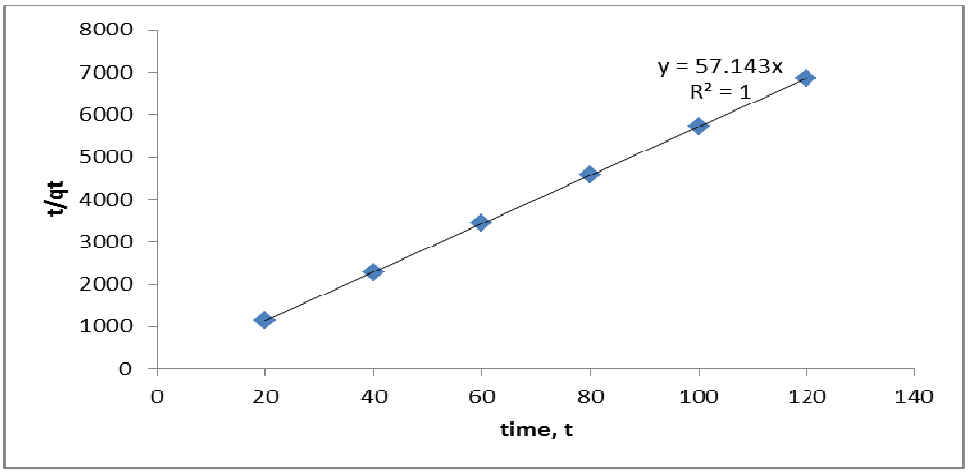

Figure 9: Pseudo-second order model simulation of Pb^{2+} by the AC-250 adsorbent

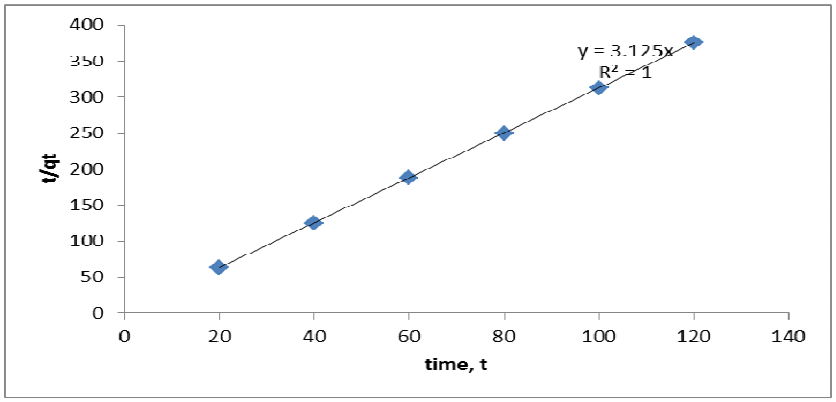

Figure 10: Pseudo-second order model simulation of Cu^{2+} by the AC-250 adsorbent

For Pb^{2+} adsorption kinetics, the straight line equation obtained (Figure 9) is:

$y = 57.143x$ and $R^2=1$. Thus in comparison with equation 7 above,

$1/qe = m = 57.143$

From where $qe = 0.0175$ and $k2 = 0$. In the same vein, the respective equation for Cu^{2+} (Figure 10) is:

$y = 3.125x$ and $R^2=1$. Again in comparison with equation 7,

$1/qe = m = 3.125$

From where $qe = 0.32$ and $k2 = 0$

Table 7: Simulation of second-order kinetic equations and corresponding parameters

	qe (experiment) in mg/g	qe (modeled) in mg/g	k1/min^{-1}	R^2
Pb^{2+}	0.0175	0.0175	0	1.00
Cu^{2+}	0.32	0.32	0	1.00

The results all point to the fact that the adsorption process of both metals perfectly follows the pseudo-second order kinetic model, with correlation coefficient in both cases being unity ($R^2=1$). Also the sorption capacities obtained from both the experimental and simulated results are same in the cases of the metals (Table 7). The pseudo-second order kinetic mode was based on the fact that chemical sorption controls the sorption rate (Ding et al, 2011). At the beginning of the process the sorption sites at the surface of the AC-250 were free and could easily bind the metal ions. With time the sites gradually became saturated and the ion concentration at the interface gradually decreased as well as the sorption rate (Kim et al, 2005; Ding et al, 2012).

(vi) Morphology of the adsorbed particles: SEM and EDX analysis confirmed the presence of the adsorbed metals in the pellets, with traces of Al, Si and Fe. The images from SEM analyses are as shown in Figures 11 and 12 while EDX result is shown in Fig 13.

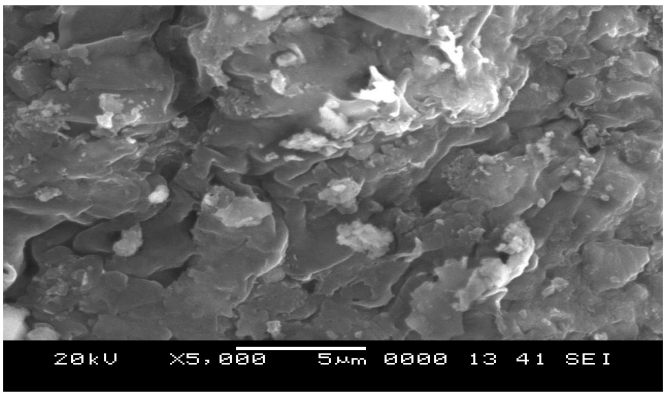

Figure 11: SEM image of the AC prior to the treatment, at 5,000 x

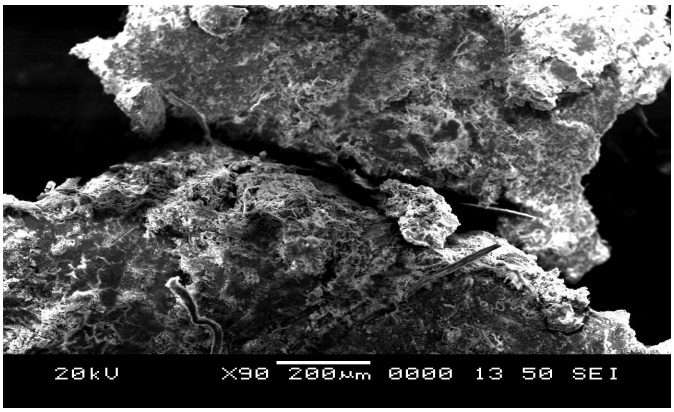

Figure 12: SEM image of the adsorbate after the treatment, at 90 x

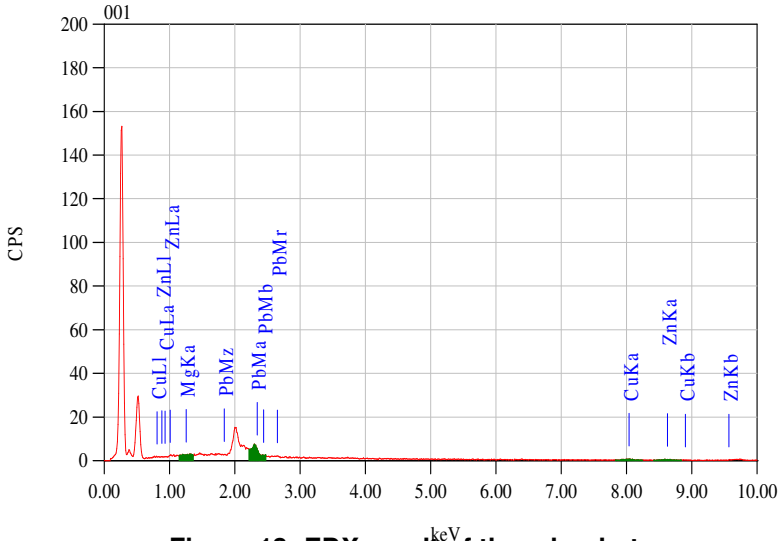

Figure 13: EDX result of the adsorbate

4. CONCLUSION

The results from this research established the effectiveness of Activated Carcoal-250 (AC-250) as an adsorbent for heavy metal remediation in fresh foundry wastewater. The optimum values of AC-250 dosage for treating the wastewater was 1.0g, contact time, 40mins and pH, 6. Only the Pb^{2+} adsorption is optimum and fits well with Langmuir isotherm. The adsorption behavior of both the Pb^{2+} and Cu^{2+} can be perfectly described by the pseudo-second-order kinetic model. The study concludes that the commercially-sourced AC-250 is very efficient in remediation of Pb^{2+} and Cu^{2+} from the fresh foundry effluent, efficient in Zn^{2+} removal but fairly efficient in Mg^{2+} remediation. It is therefore recommended as an adsorbent for treatment before discharging the foundry effluent into the larger water body.

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