Adsorption Thermodynamics of Fe$^{2+}$ and Pb$^{2+}$ in Industrial Wastewater Treatment using Melon Husk Activated Carbon

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ABSTRACT

Melon husks obtained from a local market were washed with distilled water to remove impurities, oven-dried at 105°C, and carbonized in a furnace at 550°C. H$_2$SO$_4$ and NaOH were used to modify the carbonized melon husk to catalyze the adsorption rate. The initial and final concentrations of Fe$^{2+}$ and Pb$^{2+}$ in the wastewater were determined with the Flame atomic adsorption spectrometry technique. The industrial wastewater was treated with the adsorbent at various grams, reaction time, and a constant speed of 0.2-1.0 g, 10-100 min, and 150 rpm, respectively. The obtained data were fitted into isotherm models. The adsorption isotherm, Langmuir, and Freundlich $R^2$ values were between 0.888 and 1.000. The adsorption of both metals suit pseudo-second-order kinetics with the coefficient of determination values ranges between 0.203 to 0.923. This study established that melon husk-activated carbon adsorbent is more efficient in the adsorption of Pb$^{2+}$ than Fe$^{2+}$ in industrial wastewater. Melon husk activated carbon modified with H$_2$SO$_4$ is, therefore, recommended for the removal of lead in electroplating industrial wastewater.

Keywords: Kinetics, Isotherms, Melon husk, Freundlich, Langmuir.

Introduction

Heavy metals should be metals. Metals are often characterised and distinguished from non-metals by their physical properties, i.e. the ability to conduct heat and having electric resistance directly proportional to temperature, malleability and ductility and even luster (Housecroft and Sharpe 2008; Muller 2007). Lead is a metal found in industrial wastewater. It can pollute the environment through munitions, lead piping, also from ceramics, batteries, paints, etc. This can affect various parts of the human nervous system. Lead was a natural element and does not have beneficent. It has several advantages, which include being added to pigment. A lithic ion battery can be used in the medical field, Lead can also be used for sterilizing medical equipment. Regardless of these advantages, lead was not without its problems. Industrial plants can lead and other toxic metals into the environment, Lead makes its way through the environment and cannot be destroyed.

Iron was an essential mineral with several advantages on an individual, it can contribute greatly to the human nervous system by giving the human body enough of this vital element. If Iron exceeds the required level in the body it can be toxic. Inline to a write-up from Analytical Research labs detection of iron toxicity often leads to joint pain, amenorrhea, or sudden onset of shortness of breath. This means that there is a need for a thorough treatment of industrial wastewaters to reduce these heavy metals released into the environment.

For proper removal of these heavy metals from industrial water, Adsorption has been an effective method, by definition, Adsorption, “increase in the concentration of a particular component at the surface or interface between two phases”. Adsorption was of two types: chemical and physical adsorption. Chemical adsorption involves chemical-like bonding onto the surface of adsorbents and was typically an irreversible process. Whereas, Physical adsorption process does not involve the sharing or transfer of electrons.

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Materials and Methods

The required material was collected from the melon sellers. The husks were sun-dried for 4 days. The impurities were removed with distilled water and oven-dried at 105°C for a day. The dried material was ground using a mixing grinder. After which, the material was allowed to pass through (75-150 µm).

The wastewater was collected from a Blacksmith workshop, the wastewater was placed in a cemented pit at the Blacksmith workshop in which it was poured into a bottle through a funnel to carry out a research purpose. The Flame Atomic Adsorption Spectrometry (FAAS) technique was used for the concentration of the metals in the water. A quantity of 250 ml of the wastewater was drawn and poured into a 250 ml Erlenmeyer flask. Three (3) grams of the adsorbent were poured into the 250 ml of the wastewater and was shook for thorough mixing. 20 ml of each of this mixture was drawn and poured into 100 ml of 11 different laboratory flasks. The first 20 ml mixture was filtered at five (5) minutes into a container using 42.5 mm filter paper. The other 20 ml sample was placed on a rotary shaker and stirred. The metals concentrations (Fe²⁺ and Pb²⁺) of the treated wastewater were analyzed at 10 minutes intervals, between 0 and 100 minutes. Using 20 ml of the stock solutions at 20 minutes for Fe (II) and 50-70 minutes for Pb (II) depending on the particular modified melon husk use. The dosages of the adsorbents were varied from between 0.2-1.0 g at 0.2 g intervals, while the time and adsorbates concentration were kept constant. Considering the effect of the concentration of the adsorbate, the concentration of the adsorbate was varied using distilled water at constant time and adsorbent dosage. The concentration of adsorbed metal ions, Fe (II) and Pb (II) at any of this experiment was determined by using the standard method of spectrophotometrically (Sun and Shi, 1998).

The stock solution concentrations were determined to serve as a control measure. After adsorption, the amount of the iron (II) and lead (II) adsorbed, qt (mg/I) at the time (t) was calculated. \(C_0\) and \(C_e\) were the metal ions concentrated in mg/l initially at a particular time, and V is the volume of the adsorbates and M is the mass of the adsorbent in gram.

The percentage removal (R² metal %) was calculated using equation,

\[
R_{Fe \text{ (ii)}}(\%) = \frac{C_0 - C_e \times 100}{C_0} \tag{1}
\]

\[
R_{Pb \text{ (ii)}}(\%) = \frac{C_0 - C_e \times 100}{C_0} \tag{2}
\]

\[
q_e = C_0 - C_e \tag{3}
\]

Results and Discussion

Adsorption isotherm models are used to present the quantity of solute adsorbed per unit of adsorbent, as a function of equilibrium concentration in bulk solution at a constant temperature. The equilibrium data obtained from Iron and Lead sorption capacities of the adsorbent were fitted to Langmuir and Freundlich isotherm. The graph of 1/q against 1/ C showed the adsorption followed the Langmuir model (Figs.5-8). The correlation coefficient R² for all the sorptions was 1. The graph of Log qe against Log Ce shows that the adsorption also followed the Freundlich model. (Figs.9-12). The concentration coefficient R² is 1 for both NaOH and H₂SO₄.
According to Igwe and Abia (2007), in the equilibrium sorption isotherm studies of iron. The data fitted to the graph. The linearised plot of both Langmuir and Freundlich produced \( R^2 \) values from the range of 0.888 to 1. This shows that Urea, NaOH, and \( \text{H}_2\text{SO}_4 \) modified melon husks are all efficient adsorbents in the removal of iron and lead. Isotherm studies on heavy metal adsorption on rice husk by Mohan et al., (2008) showed that the adsorption data fitted better with Freundlich to Langmuir model. Adsorption characteristics of heavy metals ions onto a low-cost biopolymeric sorbent from aqueous solution by Unlu and Ersoz (2005) fitted to Freundlich type isotherm model. Langmuir model fitted better in the biosorption of lead from industrial wastewater using Chrysophyllum albidum seed shell. Amuda et al., (2007), Boucher et al., (2008), and Saikaew et al., (2009), in their separate work of heavy metals adsorption using agricultural waste, reported that the data fitted better to Langmuir isotherm model. The experimental data of the present work fitted to both Langmuir and Freundlich isotherm mode.

Fig.1. Adsorption isotherms model for sorption of iron (Fe\(^{2+}\))

Fig.2. Adsorption isotherms model for sorption of lead (Pb\(^{2+}\))

Fig.3. Adsorption isotherm model for sorption of iron (Fe\(^{2+}\))
Fig. 4. Adsorption isotherms model for sorption of Lead (Pb$^{2+}$)

Fig. 5. Langmuir equilibrium isotherm model for sorption of Iron (Fe$^{2+}$)

Fig. 6. Langmuir equilibrium isotherm model for sorption of Lead (Pb$^{2+}$)

Fig. 7. Langmuir equilibrium isotherm model for sorption of Iron (Fe$^{2+}$)
**Fig. 8.** Langmuir equilibrium isotherm model for sorption of Lead (Pb$^{2+}$)

**Fig. 9.** Freundlich equilibrium isotherm model for sorption of Iron (Fe$^{2+}$)

**Fig. 10.** Freundlich equilibrium isotherm model for sorption of Lead (Pb$^{2+}$)

**Fig. 11.** Freundlich equilibrium isotherm model for sorption of Iron (Fe$^{2+}$)
Fig. 12. Freundlich equilibrium isotherm model for sorption of Lead \((\text{Pb}^{2+})\)

Fig. 13. Pseudo-first order sorption kinetics of Iron \((\text{Fe}^{2+})\)

Fig. 14. Pseudo-first order sorption kinetics of Lead \((\text{Pb}^{2+})\)

Fig. 15. Pseudo-first order sorption kinetics of Iron \((\text{Fe}^{2+})\)
**Fig. 16.** Pseudo-first order sorption kinetics of Lead (Pb\(^{2+}\))

**Fig. 17.** Pseudo-second order sorption kinetics of Iron (Fe\(^{2+}\))

**Fig. 18.** Pseudo-second order sorption kinetics of Lead (Pb\(^{2+}\))

**Fig. 19.** Pseudo-second order sorption kinetics of Iron (Fe\(^{2+}\))
The data were fitted into Pseudo-second-order adsorption kinetics. The result shows that the adsorbent enhanced the equilibrium sorption capacity of the melon husk towards both metal ions. Figs.13-20 indicates the Pseudo-first order sorption kinetics of both Iron and Lead by NaOH and H$_2$SO$_4$ modified melon husk. The R$^2$ values (coefficient of concentration) ranges between 0.004 and 0.272.

Ho et al., (1995) in the sorption kinetics of Iron and Lead ions reported that the data were fitted into Pseudo-second order kinetics. The coefficient of concentration (R$^2$), from the Pseudo-second-order rate model showed that R$^2$ values are greater than 0.990 for both metals with or without modification. The R$^2$ values of the Pseudo-second-order rate for the present work ranges from 0.203-0.923 which is similar to that obtained by Ho et al., (1995). The R$^2$ values for Iron are 0.203, 0.652, and 0.547, while those for Lead are 0.493, 0.793, and 0.923 with NaOH and H$_2$SO$_4$ modified melon husks respectively. Unlu and Ersoz (2006) reported that the environmental data of the adsorption characteristics of heavy metal ions onto a low-cost biopolymeric sorbent from an aqueous solution followed the Pseudo-second-order adsorption kinetics. Saikaew et al., (2009) also reported a similar result of Pseudo-second sorption kinetics on the biosorption of Iron ions from aqueous solution using Pomelo peel, an agricultural waste. The R$^2$ values for the Pseudosecond order kinetics showed that Pb (II) was better adsorbed than Fe (II) by all the three modified melon husks.

Using the pairwise t-test, the result also showed a significant difference in the adsorption of Fe (II) and Pb (II) ions since the significant values (2-tailed) are less than $\alpha = 0.05$. Lead was better adsorbed, this is an agreement with the studies of Samaghandi et al., (2006) and some researchers. There is a significant difference (P < 0.05) in the adsorption of Iron and Lead, with Lead being better adsorbed from the paired sample test (Appendix F). H$_2$SO$_4$ was also found to be a more effective adsorbent of the three followed by NaOH modified melon husk and Urea modified melon husk is the least effective.

**Conclusion**

The present study was carried out on the Adsorption Thermodynamics of Fe$^{2+}$ and Pb$^{2+}$ in industrial wastewater treatment using melon husk activated carbon and from the study, the following conclusions are drawn:

(1) The removal of Iron and Lead was found to be dependent on adsorption concentration. The lower the concentration, the more adsorption of the Iron and Lead.
(2) The equilibrium data obtained from the Iron and Lead sorption capacities of the adsorbent were fitted to both isotherm models. The R² values range from 0.888 to 1, which shows that NaOH, H₂SO₄ modified melon husks have high adsorption capacities for the removal of Iron and lead ions.

(3) The rate of adsorption of Iron and Lead onto urea, NaOH and H₂SO₄ modified melon husks followed Pseudo-second-order sorption kinetics.

Recommendations

(1) It is recommended that modified melon husk with H₂SO₄ is very suitable in the removal of electroplating industrial wastewater at low-cost adsorbent because of its highest adsorption compared to Urea and NaOH modified melon husk.

(2) The melon husk is a very good adsorbent because it follows both isotherm models which almost all the Reynolds values (R² = 1).

Declarations

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Consent for publication

Authors declare that they consented for the publication of this research work.

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