Adsorption Study of Pb (II) Ion Removal From Lead Solution Using a Blend of Activated Carbon and Chitosan From Mussel Shells

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Abstract. A batch adsorption study was carried out to investigate the adsorption of lead (II) ions on the blend of activated carbon and chitosan from the mussel shell of the lead water solution. The optimum chitosan/activated carbon blend dosage was 5 g (2.5 g activated carbon and 2.5 g chitosan). At optimum dosage, the percentage uptake was 83.75%, and 0.134 mg/l of Pb^{2+} was removed, while at an equilibrium contact time of 120 minutes, the percentage uptake was 98.75%. The data generated was used for isotherm studies and kinetic modelling. The Langmuir isotherm fits best with an R^2 value of 0.9776, and the adsorption was favourable at 0.0842 kJ/mol. Also, the adsorption process follows the Pseudo second-order kinetic model with an R^2 value of 0.9981.

Keywords: Isotherm; Kinetics; Activated-Carbon Chitosan; Mussel; Lead; Adsorption.

INTRODUCTION

Heavy metals in wastewater significantly threaten the quality of portable drinking water. An example of such heavy metals is lead, which is highly soluble in water, and some lead salts have a solubility of about 10 g/l [1]. The World Health Organization standard for the maximum amount of safe drinking water is 10 µg/l [2]. Any water with dissolved lead ions more than the above-stated value can be said to be unsafe for human consumption and could have lethal effects if ingested into the human body [3].

Chitosan has been widely used in vastly diverse fields, from waste management to food processing, medicine and biotechnology [4]. In agriculture, chitosan has been established to improve the yield of rice and orchid production [5]. A lot of work has been done on kinetics concerning chitosan and adsorption. The equilibrium and kinetic studies on the adsorption of metallic ions onto chitosan were carried out. Kinetics and equilibrium studies adsorption of Cu(II) and Cr(VI) ions by Chitosan [6]. Studies on the removal of Cr(VI) and Cu(II) ions using Chitosan-grafted-polyacrylonitrile [7]. Recent work was conducted on the Kinetic and Thermodynamic Studies of Chromium Ion Adsorption Using Chitosan from Mussel Shell [8]. Out of the four kinetic models tested, the adsorption process was found to follow the pseudo-second-order kinetic model with an R^2-value of 0.9997; the process was physical with free sorption energy of 0.224 kJ/mol [8].

This work uses batch adsorption studies to further studies using a blend of chitosan from mussels and activated carbon to trap lead (II) ions from a water lead solution.

METHOD

Chitosan Extraction and Characterisation. The chitosan used in this work was extracted by the process described by Abdulkarim et al. (2013),

with a carbon-nitrogen ratio of 5.9 and a degree of deacetylation of 60.69% and 60.66% calculated from the elemental analysis and the FTIR spectra of chitosan respectively. The FTIR spectra for chitosan gave a characteristic –NH_2 band of 3447 cm^{-1} and a carbonyl group band of 1477 cm^{-1}, also the surface area of the chitosan was determined to be 2.7225 ± 0.0741 m^2/g using the BET machine [9].

Preparation of lead solution. 0.256 g of $Pb(NO_3)_2$ was added to 1000 ml of deionised water to synthesise the stock solution from which subsequent solutions were obtained. To obtain the desired concentration in this research, 1 ml of the stock solution was further dissolved in 1 dm^3 of distilled water to obtain a concentration of 0.16 mg/l of lead (II) ions.

Sorbent Preparation and Loading. The 2.5 g of the commercially obtained activated carbon was mixed with 0.5 g of the chitosan sample, turned into 100 ml of Pb salt solution, and stirred continuously for 15 minutes at a rate of 150 rpm. The mixture was then set to settle and form distinct layers. The solution was then passed through a filter to retrieve the clear solution, after which a buffer powder pillow was added to the mixture and shaken thoroughly. The concentration of lead (II) ions in the solution was then determined using the DR 2000 uv-spectrophotometer. This procedure was repeated for chitosan loading at 1.0, 1.5, 2.0, 2.5 and 3.0 g respectively. The optimum dosage of the blend during the work was obtained by considering the mass of chitosan that gave the highest percentage of Pb (II) ion uptake.

Kinetic studies. The optimum blend obtained from both biosorbents was then used for the time study. The contact time was between 20 and 140 minutes, with a 20-minute interval in each case, thus obtaining six values.

RESULTS AND DISCUSSION

The data used in investigating the kinetics of the adsorption process was obtained by checking the effect of variation of contact time on the final concentration. At a fixed dosage of 2.5 g and a temperature of 28 °C, the equilibrium time for the process was investigated. Figure 2 shows how the reductions in the ion concentration become almost constant from 80 minutes of adsorption time and became constant after 120 minutes of adsorption.

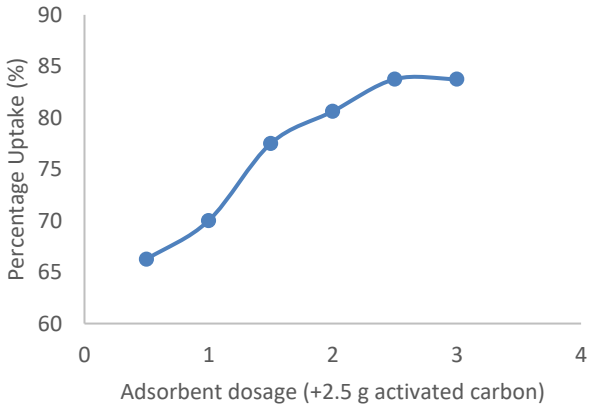

Figure 1 – Graph of concentration of Pb^{2+} ions (mg/l) against dosage (g) of chitosan/activated carbon blend at 25 °C, 5 minutes and 150 rpm

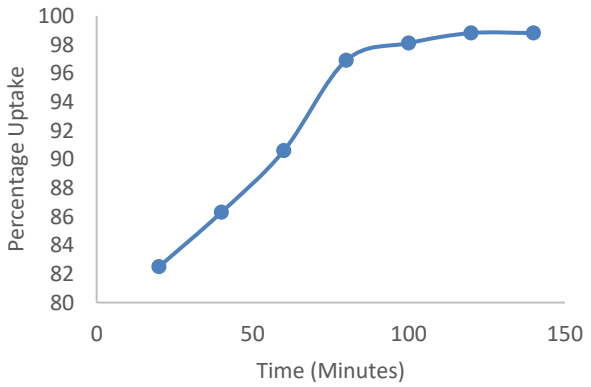

Figure 2 – Relationship between adsorption time and percentage lead ion uptake by the blend

Adsorption Isotherms. The data generated from the work was fit into three different adsorption isotherm models: the Langmuir, the Freundlich and the Dubinin-Radishkevich models, as illustrated in figures 3.0, 4.0 and 5.0, respectively.

The Langmuir isotherm was derived with the assumption that the adsorption is a monolayer adsorption phenomenon on a uniform surface with a finite number of adsorption sites of which, when occupied, no further adsorption is feasible. The Langmuir isotherm equation is shown as Equation 3:

$$q_e = \frac{k_L b C_e}{1+k_L C_e} \quad (1)$$

where b is the Langmuir constant related to the energy of biosorption (L/mg), k_L is the maximum

sorption capacity corresponding to complete monolayer coverage (mg/g), C_e is the equilibrium solute concentration (mg/l), and q_e (equation 2) is sorption capacity (mg of adsorbate/g of adsorbent).

$$q_e = \frac{v(C_o - C_e)}{m} \quad (2)$$

where v is the volume of the solution, C_0 and C_e are the initial and final concentrations of the adsorbate, respectively, and m is the mass of the adsorbent dosage used for the adsorption.

The Langmuir adsorption isotherm can be transformed to a linear form to estimate the parameters graphically or with linear regression. A popular linear form is the reciprocal linear equation (Equation 3):

$$\frac{C_e}{q_e} = \frac{1}{k_L b} + \frac{1}{b} C_e \quad (3)$$

The Langmuir adsorption isotherm is mainly employed to describe the nature of the adsorption process by determining an important parameter R_L (Equation 4):

$$R_L = \frac{1}{1 + bC_o} \quad (4)$$

The value of R_L indicates the type of the isotherm to be either unfavourable (R_L>1), linear (R_L =1), favourable (0<R_L<1) or irreversible (R_L = 0). R_L is a positive number whose magnitude determines the feasibility of the adsorption process [10]; from the Langmuir plot, it can be seen that the R^2 value is 0.9776, which is the highest compared to the other isotherm models fitted with the adsorption data. From Table 1, the calculated R_L= 0.0131; thus, the adsorption is favourable.

Table 1 – Freundlich, Langmuir and D-R constants determined from the isotherms plotted

Isotherm	R^2	Slope	Intercept	b_F or q_D	a_F	n	k_L	b or B_D	R_L
Langmuir	0.9776	0.2131	0.0042	-	-	-	50.7381	4.6926	0.0131
Freundlich	0.9392	0.3387	1.7997	0.3387	9.3027	2.9525	-	-	-
D-R	0.9393	-0.3518	2.2866	9.8414	-	-	-	7.05E-05	-

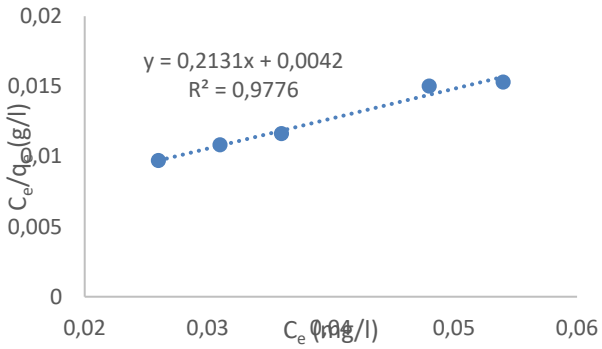

Figure 3 – Langmuir isotherm plot using the reciprocal linear equation

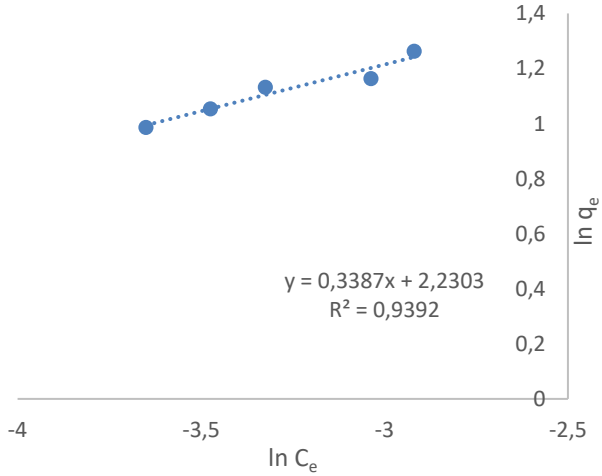

Figure 4 – Freundlich isotherm plot

Figure 4 below shows the plot using the Freundlich isotherm model. It is an empirical equation and can be employed to describe heterogeneous systems expressed as follows:

$$q_e = a_f C_e^{b_F} \quad (5)$$

The Freundlich isotherm was derived with the assumption of an exponentially decaying sorption site energy distribution [9]. The linearised Freundlich equation is shown as Equation 6:

$$\ln q_e = \ln a_F + b_F \ln C_e \quad (6)$$

Some critical parameters can be deduced from the Freundlich isotherm, which can help characterise the nature of the adsorption. The n or $1/b_F$ value indicates the degree of non-linearity between solution concentration and adsorption as follows: if $1/b_F = 1$, then adsorption is linear; if $1/b_F < 1$, then adsorption is a chemical process; if $1/b_F > 1$, then adsorption is a physical process [11].

From the plot (Figure 4), the R^2 value is high (0.9392) but less than that of the Langmuir isotherm, and from Table 1, the value of n or $1/b_F$ calculated is 2.9525, which is greater than unity; thus, the adsorption process in this case is dominantly physical.

The free sorption energy (E_s). This parameter further confirms whether the adsorption process is either physisorption or chemisorption [9]. The sorption energy (E_s) can easily be calculated using the Dubinin-Radishkevich (D-R) isotherm given as:

$$q_e = q_D \exp(-B_D[RT \ln(1+\frac{1}{C_e})]^2) \quad (7)$$

Some authors have reported that the characteristic sorption curve is related to the porous structure of the sorbent [12].

The D-R isotherm can be written in a linear form as:

$$\ln q_e = \ln q_D - 2B_D RT \ln(1+ {}^{1}\!/_{C_e}) \quad (8)$$

where q_D is the D-R isotherm constant, B_D is related to the free energy of sorption per mole of the sorbate as it migrates to the surface of the adsorbent from an infinite distance in the solution [12].

The relationship between the free energy of sorption (E_s) and B_D is given by Equation 9:

$$E_s = \frac{1}{\sqrt{(2B_D)}} \quad (9)$$

The mean free energy of sorption gives information about the biosorption mechanism, physical or chemical. Suppose E_s value is between 8 and 16 (kJ/mol); the sorption process follows chemisorption, and if E_s<8 (kJ/mol), the sorption process is of a physisorption [13]. The sorption energy was calculated to be E_s= 0.0842 kJ/mol, which further confirms the deduction made from the Freundlich isotherm that the adsorption process was physical.

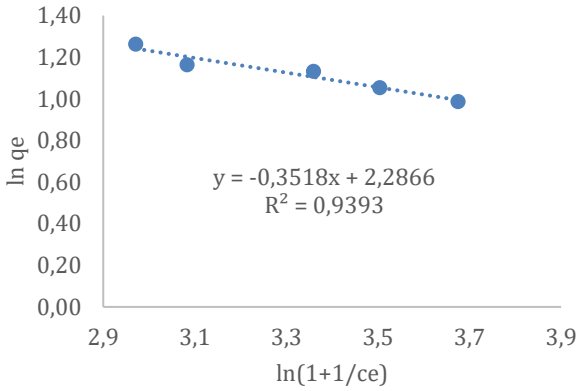

Figure 5 – Dubinin-Radishkevich (D-R) isotherm

Determination of kinetic models for chromium (VI) removal using chitosan. Three kinetic models were tested to determine the model describing the kinetics of lead (II) ion removal from lead water solution using an activated carbon/chitosan blend. The essence of kinetic investigation is determining the decisive stage in the adsorption reaction rate. Therefore, using kinetic models to fit the time-dependent experimental data is vital to the adsorption study [14].

Figure 6 shows the plot obtained using the integrated linear form of the pseudo-first-order kinetic model proposed by Lagergren (Equation 10).

$$\ln(q_e - q_t) = \ln q_e - kt \quad (10)$$

where q_e is the amount of chromium (VI) ion adsorbed at equilibrium (mg/g), q_t is the amount of chromium (VI) ion adsorbed at time t (mg/g), k is the first order rate constant (min^{-1}) and t is the time (min).

Hence, a linear trace is expected between the two parameters log (q_e–q_t) and t, provided the biosorption follows the pseudo-first-order kinetics [8]. The plot shows an R^2 value of 0.835.

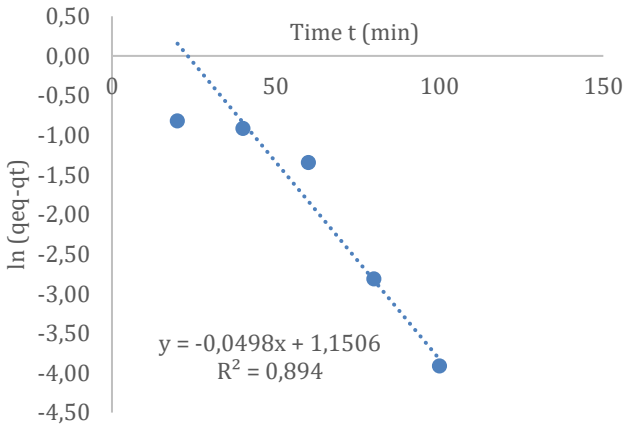

Figure 6 – Testing the Pseudo First-Order Kinetic model

The second-order kinetic model was also tested using the generated data from the adsorption process. The integrated form of the model (Equation 11) is given as:

$$\frac{1}{C_e} = k_2 t + \frac{1}{C_o} \quad (11)$$

The plot obtained using Equation 11 is presented in Figure 8. It is visible from the R^2 values that the pseudo-first-order kinetic model fits better with the generated experimental data than the second-order kinetic model.

Figure 9 shows the behaviour of the data when using the pseudo-second-order kinetic model. The equation used for the plot is presented as Equation 12.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (12)$$

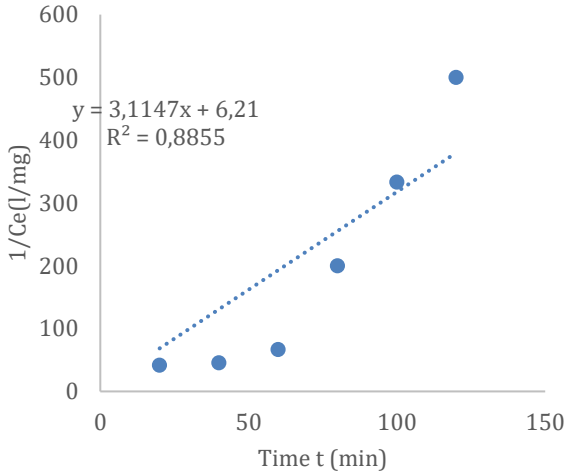

Figure 8 – Testing the Second-Order Kinetic Model

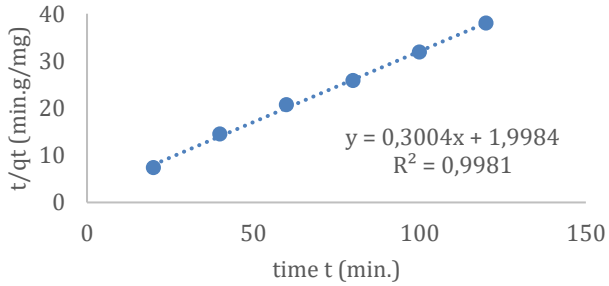

Figure 9 – Testing the Pseudo Second Order Kinetic Model

The pseudo-second-order kinetic model gave the highest R^2 value of 0.9981 (almost close to unity). Thus, the adsorption can be said to follow the pseudo-second-order kinetic model.

Table 2 – Summary of evaluated constants obtained from the tested kinetic models

Kinetic model	R^2	Slope	Intercept	Rate constant	Other constants
Pseudo-first order	0.8350	-0.0498	1.1506	0.0498	q_e=-3.1600
Second order	0.7610	3.1147	6.2100	3.1147	C_0=0.16
Pseudo-second order	0.9981	0.3004	1.9984	0.0452	q_e=3.3290

CONCLUSIONS

The optimum dosage of the chitosan/activated carbon blend was determined to be 5 g (2.5 g activated carbon and 2.5 g chitosan). The initial Pb^{2+} concentration was 0.16 mg/l. At optimum dosage, the percentage uptake was 83.75%, and 0.134 mg/l of Pb^{2+} was removed, while at an equilibrium contact time of 120 minutes, the percentage uptake was 98.75%. The Langmuir plot gave the best fit with an R^2 value of 0.9776, and since the R_L value is 0.0131, which is between 0

and 1 the adsorption is favourable. Also, according to [11], the adsorption is physical with $1/b_F$ value greater than unity. This was later confirmed by the sorption energy (0.0842 kJ/mol) calculated using the Dubinin-Radishkevich isotherm, which is within the range for physisorption processes. Out of the three kinetic models tested, the data generated fits best with a pseudo-second-order plot.

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