Adsorption of Lead and Copper by a Carbon Black and Sodium Bentonite Composite Material: Study on Adsorption Isotherms and Kinetics

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ABSTRACT: *The efficiency of using a composite of carbon black and sodium bentonite in treating drinking water contaminated with lead and copper ions was analysed. The effects of pH, contact time, concentration and adsorbent dosage using an adsorbent composite of 20 % sodium bentonite and 80 % carbon black were studied. The adsorption data was tested with respect to Langmuir, Freundlich and Temkin isotherms. The data fit well with the Langmuir isotherm model with high coefficients of determination for both metal ions adsorption. The adsorption kinetics follows a pseudo second-order model for both metal ions. The maximum metal ion uptake (q_{max}) of the composite adsorbent is 7.69 and 0.80 mg/g for lead and copper respectively.*

KEYWORDS: *Adsorption; Carbon black; Sodium bentonite; Isotherms; Kinetics.*

INTRODUCTION

It is estimated that around the year 2025, up to 3.5 billion people of the world population will live in water stressed countries [1]. Therefore the extent of water recycling and purification is expected to increase to cater for the growing demand for safe drinking water. The concentrations of metal ions in waters from underground and recycling sources may sometimes exceed the required sanitary standards [2]. Industrial wastewater is a major source of environmental water pollution and limits the use of underground water sources unless if proper water management systems are set up [3]. Industries such as paint, lead smelting, battery manufacture, and mining generate wastewater with concentrations of copper, lead and other metals high enough to cause upsets in the ecosystem [4]. Lead, copper and other heavy metals find their way into the drinking water system largely through industrial discharge and surface runoff [5,6]. Also, the piping system for drinking water is made of either copper or lead which corrodes into the water due to age. Drinking water from river and aquifer sources with lead and copper concentrations of above 0.035 ppm and 0.2 ppm respectively has been reported [1, 5-7]. Lead is absorbed into the human blood stream and accumulates in bones, it has been reported to be the cause of cardiovascular

diseases, fetus development, memory and concentration problems, and nervous system disorders [8-9]. Copper has a lesser negative effect on humans as compared to lead, however, copper affects most organisms in the environment and copper excess is toxic [10]. Various methods for removing lead and copper from wastewaters have been studied, namely reverse osmosis, electro-dialysis, ion exchange and chemical precipitation [9].

The use of carbon black in adsorbing dyes from wastewater has been reported and it was shown that polyvinyl alcohol coated carbon black has the ability to remedy water with considerable dye concentrations [11]. The same study also revealed that the kinetics of adsorption best fit the Langmuir and Freundlich isotherms. The use of sodium bentonite in the treatment of oil-water emulsions has been studied [12]. Researchers reported that bentonite was effective as an adsorbent for the removal of oil, the removal percentage increased as the contact time was increased.

In this work, the use of a composite adsorbent of sodium bentonite and carbon black in the lead and copper removal from drinking water is investigated. The factors affecting the adsorption process e.g. solution pH, contact time, solution initial concentration and adsorbent dosage are examined. Adsorption isotherms and kinetic models are tested for the experimental data obtained.

EXPERIMENTAL SECTION
Materials
Carbon black, bentonite and stock solutions of Cu^{2+} and Pb^{2+} were obtained from commercial merchants, A.I. Davis (Pvt) Ltd and William Smith & Gourock. The working solutions were prepared from the stock solutions by dilution to the desired concentration.

Apparatus
The concentrations of copper and lead metals in aqueous solutions were determined by an AA-6300c flame atomic absorption spectrometer (FAAS, Shimadzu Corporation, Japan) with Cu/ Pb hollow cathode lamps and oxy–acetylene flame after appropriating dilutions and acidification to adjust the pH.

Preparation of adsorbent material
1000 g of bentonite was heated at 350 °C in an oven for 2 hours and then socked in 2 M NaOH for 30 minutes so as to increase the adsorption capacity. The prepared clay sample was mixed with 2 M NaOH in the ratio of 1:5 (m/v). The sample was filtered and then rinsed with distilled water several times until the pH became neutral. The sample was then dried in an oven at 100 °C for 2 hours [13]. Carbon black was used in the form of a powder. The composite adsorbent was prepared by mixing 4 g of carbon black per gram of the prepared sodium bentonite sample.

Effect of pH on metal adsorption
0.8 g of the composite adsorbent was added to each of the four 250 mL volumetric flasks containing 100 mL of a 25 ppm lead solution. Another similar set but containing 2 ppm copper ions was set up. The pH of the solutions was adjusted to 2, 4, 6 and 8 using 0.1 M HCl or NaOH and monitored using a pH meter (Corning pH meter 220, USA). The mixtures were agitated at 160 rpm at room temperature and atmospheric pressure (25 °C) for 2 hours. At the end of the experiment, the solution was filtered to remove the adsorbent and the metal ion concentration analysed using AAS. An average of three AAS measurements was taken as the residual metal ion concentration value.

Effect of dosage on metal adsorption
Varying masses of the adsorbent (0.1 – 1g) were added to 100 mL (in a stoppered conical flask) of a 25 ppm lead solution and the mixture was agitated at 160 rpm for 2 hours. The mixture was filtered and the residual metal ion concentrations of the filtrate were determined using AAS. The process was then repeated using 2 ppm copper ion solutions. An average of three AAS measurements was taken as the residual metal ion concentration value.

Effect of initial concentration on metal adsorption
0.8 g of adsorbent was added to 100 mL of aqueous solutions in the concentration range of 10 to 25 ppm and 0.8 to 2 ppm for lead and copper ions respectively. The mixture was agitated at 160 rpm. Samples were extracted at every 20 minute interval and filtered before analysis. An average of three AAS measurements was taken as the residual metal ion concentration value.

Batch equilibrium study
The adsorption isotherm experiment was carried out in a batch process using a 250 mL stoppered conical flask. A known mass (0.2 - 0.8g) of adsorbent was added

to 100 mL metal containing solution. The mixtures were agitated for 2 hours since initial experiments managed to show that equilibrium was attained within that time frame. The equilibrium concentrations of Pb^{2+} and Cu^{2+} in each sample were determined using AAS after filtration. The amount of metal adsorbed by the adsorbent at equilibrium (q_e) and the percentage removal were calculated according to Eq. (1) and (2) respectively.

$$q_e = \frac{\left(C_i - C_e\right)V}{M} \tag{1}$$

$$\text{removal}(\%) = \left(\frac{C_i - C_e}{C_i}\right) \times 100 \tag{2}$$

where C_i and C_e are the initial and equilibrium concentrations in ppm of the metal ions respectively, V is the volume in litres of the solution and M is the mass in grams of the adsorbent.

Statistical analysis

The measured quantities were reported as an average of three readings. Linear plots with the best R^2 values were chosen as the best representation. A statistical method was used for calculating the margin of errors for the slope and y-intercept of the graphs generated [14]. The process parameters evaluated from the slopes and y-intercepts of graphs were reported with their margin of errors at 95% confidence level.

RESULTS AND DISCUSSION
Effect of pH on metal adsorption

The solution pH is an important parameter which affects an adsorption process as it is closely linked to the surface charge of the adsorbent. Fig. 1 shows the effect of pH on the adsorption of each of the metal ions. For the pH range investigated (pH 2 up to 8), the percentage removal of both metal ions increases with pH in the range pH 2 up to 6 thereafter the percentage removal decreases. The optimum pH value for both metals was found to be 6. These results confirm what other researchers found, where the percentage adsorption increases as the pH increased up to a certain optimum pH value [15]. At low pH values, the solution is characterized by high H^+ ion concentration which results in a high positive charge density on the surface of the adsorbent which repels the positively charged metal ions. On the other hand,
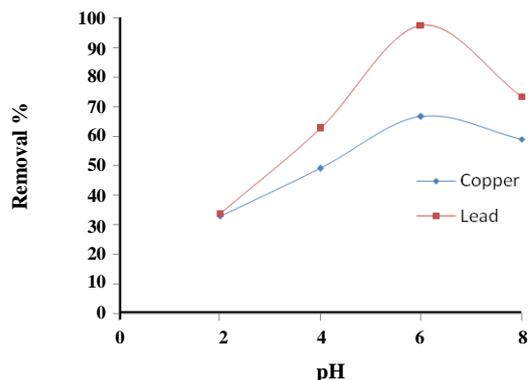
Fig. 1: Effect of pH on the adsorption of lead (II) and copper (II) (Conditions: 0.8g adsorbent dosage, 160 rpm, 2 hours agitation time, temperature 25 ˙C) [one experimental run for each graph, an average of three AAS measurements for each data point].

at higher pH values the dominant OH^- ions on the surface of the adsorbent induce a high negative charge density which attracts more metal ions.

Effect of dosage on metal adsorption

The amount of adsorbent in the mixture translates into the number of active sites available for the adsorption process; therefore the metal uptake is expected to increase with an increase in the amount of adsorbent. This phenomenon is shown in Fig. 2, for a pH of 6, as the amount of adsorbent increases from 0 to 0.8 g, the percentage adsorption of lead and copper ions also increases from 0 to 70 % and 0 to 83 % respectively. This phenomenon has been attributed to the overcrowding of the adsorbent particles as the dosage is increased thereby creating an overlap of adsorption sites [16]. 0.8 g of adsorbent was selected as adsorbent dosage for all experiments that required a fixed amount of adsorbent because of the high percentage removal that is shown in Fig. 2.

Also to be noted in Fig. 2 is that copper removed more than lead and this is due to the size of Cu^{2+} (0.069 nm) and Pb^{2+} (0.120 nm), thus more Cu^{2+} will be adsorbed.

Effect of contact time on metal adsorption

Contact time is an important variable for adsorption experiments and actual process design. A short contact time means fewer chances of attaining equilibrium and
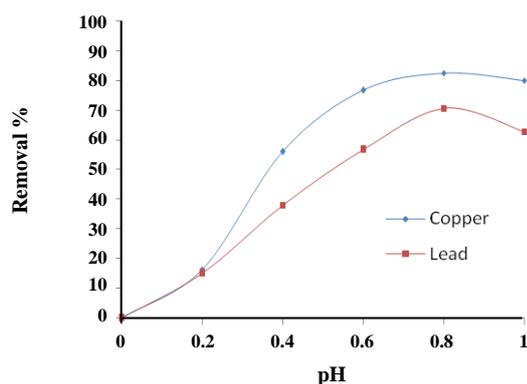
Fig. 2: Effect of adsorbent dosage on the adsorption of lead (II) and copper (II) (Conditions: 25ppm lead & 2 ppm copper, 160 rpm, 2 hours agitation time, temperature 25 ˙C) [one experimental run for each graph, average of three AAS measurements for each data point].

a longer contact time means the higher the chances of the metal-adsorbent complexes formed breaking down into individual species. Figs. 3 and 4 show the adsorption of lead and copper ions respectively, as a function of contact time for varying concentrations. It is shown that for both metal ions adsorption, the percentage removal increases rapidly up to 1 hour then stays constant for the remaining time up to 2 hours. According to Figs. 3 and 4, the equilibrium is attained after 60 minutes and the concentration of the metal ions in solution stays constant up to 2 hours. Therefore for all the experiments where equilibrium was supposed to be attained, a contact time of 2 hours was used.

Effect of initial concentration on metal adsorption

The relationship between initial concentration and the percentage of metal removal for a dosage of 0.8 g adsorbent in 100 mL solution is shown in Figs. 3 and 4. Generally, according to Eqs. (1) and (2), the initial concentration is a parameter affecting the amount of metal uptake and percentage removal. The magnitude of the difference between the initial and equilibrium concentration called the concentration gradient directly affects the amount of metal adsorbed. The results presented in Figs. 3 and 4 indicate that as the concentration of the solution is increased the amount of metal ion adsorbed per unit adsorbent mass increases. The equilibrium adsorption of lead increased from 0.98 to 2.31 mg/g with an increase of 10 to 25 ppm lead ion concentration, also the equilibrium

adsorption of copper increased from 0.07 to 0.24 mg/g with an increase of 0.8 to 2 ppm copper ion concentration.

Adsorption Isotherms

The adsorption isotherms of the process were evaluated. The experimental data were fitted into three models, Langmuir, Freundlich and Temkin models which have been widely used to describe metal ion adsorption processes [17-18].

Langmuir Isotherm

The Langmuir isotherm was developed based on the assumption that each site can accommodate only one molecule of the adsorbate with no molecule migration and the energy of adsorption is constant all over the surface [19]. The maximum adsorption occurs when the monolayer of adsorbate molecules becomes saturated on the adsorbent surface and having a constant energy of adsorption. The linear form of the model is:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max}bC_e} \tag{3}$$

Where q_e is the equilibrium metal ion concentration on the adsorbent (mg/g), q_{max} is the maximum adsorption capacity on monolayer adsorbent saturation (mg/g), C_e is the equilibrium metal ion concentration in solution (ppm), b is the Langmuir affinity constant (L/mg). A plot of $1/q_e$ against $1/C_e$ for each metal ion gave a straight line with a slope of $1/q_{max}b$ = 11.8 and 9.54 and y-intercept of $1/q_{max}$= 0.13 and 1.25 for lead and copper respectively (figures not shown).

The dimensionless quantity, the separation factor, R_L (Eq. 4) was used to confirm the favourableness of the adsorption process for the conditions used in the experiment.

$$R_L = \frac{1}{1 + bC_0} \tag{4}$$

Where C_0 is the highest initial metal ion concentration in solution. Assuming the adsorption follows the Langmuir isotherm, the parameters are listed in Table 1. R_L values are less than 1 indicating that lead and copper adsorption using the composite adsorbate at room temperature and pressure is favourable. The adsorption capacity of the adsorbent is large for lead, 7.69 compared

Table 1: Langmuir parameters for the adsorption of lead and copper at 25 ˙C.

Parameter	Lead adsorption	Copper adsorption
q_{max} (mg/g)	7.69	0.80
b (L/mg)	0.011	0.130
R_L	0.78	0.79
R^2	0.920	0.916
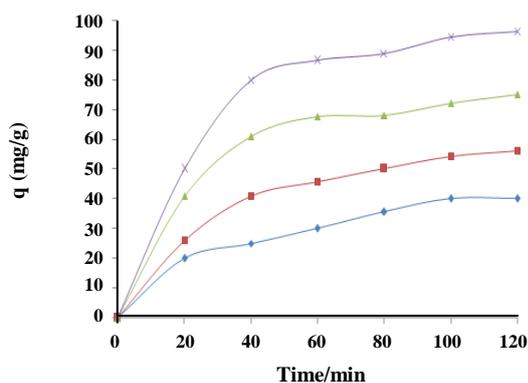
Fig. 3: Effect of contact time at the differential initial concentration on the adsorption of lead (II) (Conditions: 0.8g adsorbent dosage, 160 rpm, 2 hours agitation time, temperature 25 ˙C) [one experimental run for each graph, average of three AAS measurements for each data point].
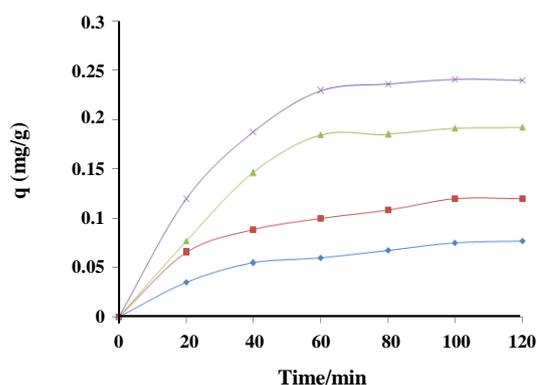
Fig. 4: Effect of contact time at the differential initial concentration on the adsorption of copper (II) (Conditions: 0.8g adsorbent dosage, 160 rpm, 2 hours agitation time, temperature 25 ˙C) [one experimental run for each graph, average of three AAS measurements for each data point].

to 0.80 mg/g for copper. This implies that there is a higher adsorbate-adsorbent affinity between the composite material and lead. The results compare well with previous studies where low values of q_{max} and b for adsorption of copper onto natural bentonite were reported [17].

Freundlich Isotherm

The Freundlich isotherm was developed so as to model the multilayer adsorption on heterogeneous surfaces [20]. The linear form of the model is:

$$Lnq_e = Lnk_f + \left(\frac{1}{n}\right)LnC_e \qquad (5)$$

Where q_e is the amount of metal ion adsorbed at equilibrium (mg/g), C_e is the concentration of the adsorbate at equilibrium (ppm), k_f is the Freundlich constant related to adsorption capacity and n is a dimensionless heterogeneity coefficient. A plot of lnq_e against LnC_e for each metal ion gave a straight line with a slope of $1/n = 0.98$ and 0.96 and y-intercept of $Lnk_f = -2.52$ and -2.35 for lead and copper adsorption respectively

(figure not shown). The Freundlich parameters are shown in Table 2. The values of the coefficient, n, are greater than one, indicating that according to the Freundlich model, the process of adsorption of both metal ions is favourable. The k_f values for both metals indicate that the capacity of the adsorbent is low.

Temkin Isotherm

The effects of adsorbate interactions on adsorption were investigated and it was noted that in these interactions the energy of adsorption of all the molecules in a layer is a function of temperature and it will decrease linearly as the adsorbent surface is loaded with an adsorbate. The Temkin isotherm has been used in gas and protein adsorption studies [17]. The linear form of the model is [20]:

$$q_e = \frac{RT}{b}LnA + \frac{RT}{b}LnC_e \qquad (6)$$

Where q_e is the amount of metal ion adsorbed at equilibrium (mg/g), C_e is the concentration

Table 2: Freundlich parameters for the adsorption of lead and copper at 25 °C.

Parameter	Lead adsorption	Copper adsorption
n	1.02	1.04
k_f (mg/g)	0.08	0.10
R^2	0.923	0.853

Table 3: Temkin parameters for the adsorption of lead and copper at room temperature and pressure.

Parameter	Lead adsorption	Copper adsorption
T (K)	298	298
A (L/g)	0.29	4.02
b (J/mol)	3260	35907
R^2	0.886	0.742

of the adsorbate at equilibrium (ppm), *b* is the Temkin constant related to the heat of adsorption (J/mol), *A* is the Temkin isotherm constant (L/g), R is the gas constant (8.314 J/mol.K) and *T* is the absolute temperature (K). A plot of q_e against $\ln C_e$ for each metal ion gave a straight line (figure not shown). The constants A and b are reported, in Table 3, as 0.29 L/g and 3260 J/mol respectively, for lead and 4.02 L/g and 35907 J/mol respectively, for copper. Assuming the adsorption process follows the Temkin model, the interactions between the metal ions and the adsorbent are more pronounced for copper than for lead. This phenomenon is evidenced by a comparison of the values of the Temkin constant, b, (=3260 and 35907 J/mol for lead and copper respectively) which is a direct measure of the maximum binding energy for each of the metals' adsorption processes.

Adsorption Kinetics

The reaction kinetics of the adsorption process was evaluated using the model based approach. The experimental data were fitted to two models, pseudo first-order kinetics and the pseudo second-order kinetic models which have been used to describe the kinetics of metal ion adsorption processes [22-24].

Pseudo first-order kinetics

The adsorption process was tested for pseudo first-order kinetics by using the model which can be written as follows [22]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{7}$$

Where q_t is the amount of metal ion adsorbed (mg/g) at time t, k_1 is the pseudo first-order rate constant (min⁻¹). If the process follows pseudo first-order kinetics, a plot of $\log(q_e - q_t)$ against t (Fig. 5 & 6) should give a straight line enabling the calculation of k_1 and q_e from the gradient and y-intercept respectively. The model parameters are shown in Table 4. It can be deduced that the adsorption of either of the two metal ions at all the initial conditions used does not follow pseudo first-order kinetics because the calculated q_e values do not match with the experimental values. Furthermore, the coefficients of determination are not satisfactory and the relative errors are high in the order of above 2 times.

Pseudo second-order kinetics

The pseudo second-order kinetic model is given as [23]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{8}$$

Where k_2 is the pseudo second-order rate constant (g/mg min). A plot of t/q_t against t (Fig. 7 & 8) gives a straight line that enables the determination of q_e and k_2 from the slope and y-intercept respectively. The experimental data for the adsorption of both metal ions at all the initial concentrations fit the pseudo-second order kinetic model with a high coefficient of determination ranging from 0.952 to 0.997. For example considering copper adsorption at an initial concentration of 0.8 ppm the R^2 value for pseudo second-order model is 0.989 as compared to that of pseudo first-order model which is 0.974.

Table 4: Pseudo first-order kinetic model parameters (Conditions: 0.8g adsorbent dosage, 160 rpm and temperature 25 ˙C).

Lead adsorption					Copper adsorption				
C_i (ppm)	$q_{e, exp}$ (mg/g)	k_1 (min^{-1})	$q_{e, cal}$ (mg/g)	R^2	C_i (ppm)	$q_{e, exp}$ (mg/g)	k_1 (min^{-1})	$q_{e, cal}$ (mg/g)	R^2
25	2.312	0.111	41.21	0.678	2.0	0.238	0.064	0.549	0.981
20	1.816	0.032	1.514	0.954	1.6	0.190	0.058	0.360	0.978
15	1.376	0.032	1.667	0.945	1.2	0.119	0.044	0.204	0.822
10	0.972	0.037	1.469	0.856	0.8	0.077	0.021	0.057	0.974
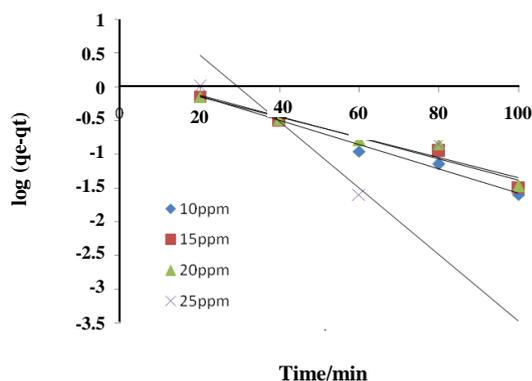
Fig. 5: Pseudo first-order plot for the adsorption of lead (II) on sodium bentonite/carbon black composite adsorbent (Conditions: 0.8g adsorbent dosage, 160 rpm, and temperature 25 ˙C.
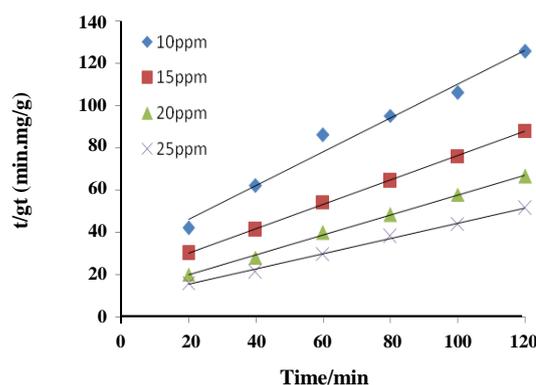
Fig. 7: Pseudo second-order plot for the adsorption of lead (II) on sodium bentonite/carbon black composite adsorbent (Conditions: 0.8g adsorbent dosage, 160 rpm and temperature 25 ˙C).
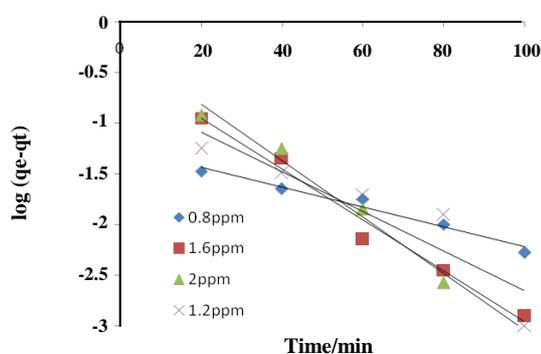
Fig. 6: Pseudo first-order plot for the adsorption of copper (II) on sodium bentonite/carbon black composite adsorbent (Conditions: 0.8g adsorbent dosage, 160 rpm and temperature 25 ˙C).
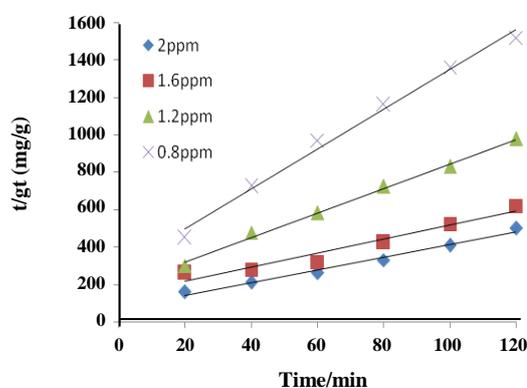
Fig. 8: Pseudo second-order plot for the adsorption of copper (II) on sodium bentonite/carbon black composite adsorbent (Conditions: 0.8g adsorbent dosage, 160 rpm, and temperature 25 ˙C.

It can, therefore, be concluded that the adsorption of the two metal ions follows pseudo second-order kinetics. The model parameters together with their margin of errors are shown in Table 5. It is clear that the experimental and calculated values of q_e are in good agreement.

CONCLUSIONS

This study has shown that a composite mixture of carbon black and sodium bentonite can be used as an adsorbent for aqueous solutions containing copper and lead ions. The adsorption data were tested for Langmuir,

Table 5: Pseudo second-order kinetic model parameters (Conditions: 0.8g adsorbent dosage, 160 rpm and temperature 25 °C).

C_i (ppm)	$\frac{1}{q_e}$ (g/mg)	$\delta\left(\frac{1}{q_e}\right)$	$q_{e,\,exp}$ (mg/g)	$\delta\, q_e$	$q_{e,\,cal}$ (mg/g)	$\frac{1}{k_2 q_e^2}$ (mg/g.min)	$\delta\left(\frac{1}{k_2 q_e^2}\right)$	k_2 (g/mg.min)	$\delta\, k_2$	R^2
Lead adsorption kinetics										
25	0.3601	± 0.0164	2.312	± 0.1265	2.778	7.736	± 1.275	0.017	± 0.0032	0.991
20	0.4703	± 0.0133	1.861	± 0.0601	2.128	9.432	± 1.035	0.023	± 0.0029	0.996
15	0.5608	± 0.0137	1.376	± 0.0436	1.786	19.62	± 1.070	0.016	± 0.0012	0.997
10	0.7884	± 0.0601	0.972	± 0.0966	1.269	29.56	± 4.684	0.021	± 0.0046	0.977
Copper adsorption kinetics										
2.0	3.373	± 0.2027	0.296	± 0.0178	0.297	81.99	± 15.79	0.139	± 0.0316	0.985
1.6	3.885	± 0.4362	0.257	± 0.0288	0.257	137.5	± 33.97	0.110	± 0.0367	0.952
1.2	6.826	± 0.2171	0.147	± 0.0046	0.146	185.5	± 16.91	0.249	± 0.0276	0.996
0.8	10.91	± 0.5536	0.092	± 0.0047	0.092	286.6	± 43.12	0.412	± 0.0750	0.989

Freundlich and Temkin isotherms. The data fitted well with the Langmuir isotherm with R^2 value of 0.92 for both lead and copper adsorption. The maximum adsorption capacities for lead and copper are 7.69 and 0.80 mg/g respectively, indicating that the adsorbate is more suitable for lead adsorption. The separation factor R_L was found to be 0.78 and 0.79 for lead and copper respectively indicating favourable adsorption for both metals. Furthermore, pH has been shown to affect the adsorption process such that the optimum pH is 6. A kinetic study shows that the adsorption process follows a pseudo second-order model for each of the metals.

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