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Chloride removal from Eshidiya phosphate mining wastewater

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ABSTRACT

Treatment of industrial wastewater from Eshidiya phosphate mining was studied in this work for reuse possibilities. The wastewater contains sediments and chloride ions. The removal of chloride from the industrial wastewater by adsorption using Amberlite IRA-402 was investigated via batch and continuous adsorptions. In the batch adsorption, the amount of chloride removal reached about 82.5%. The equilibrium data for chloride removal onto Amberlite IRA-402 were fitted to Langmuir and Freundlich isotherms. The data followed the Langmuir isotherm, but not the Freundlich isotherm. The continuous adsorption of chloride ions on Amberlite IRA-402 using packed column was studied using a glass column (22 cm length and 2 cm diameter). The effect of initial concentration, feed flow rate, bed height, and initial pH on the breakthrough curves was evaluated. A decrease in the influent concentration resulted in a delay in the occurrence of the breakthrough curves. Higher flow rates and higher initial pH resulted in a shorter breakthrough time.

Keywords: Industrial wastewater; Phosphate mining; Chloride adsorption; Amberlite IRA-402; Batch; Continuous; Langmuir; Freundlich; Isotherms; Packed column; Bohart and Adams

1. Introduction

Jordan is among a few countries in the world with lowest water resources availability. Water scarcity will become an even greater problem over the next two decades due to population, which is likely to double, and climate change potentially causing precipitation to be more uncertain and variable. Conservation and utilization of water resources is therefore a key issue facing national water authorities. In Eshidiya plant, which is a phosphate mining industry, large amount of water is used in many stages, especially in flotation cells, to wash up clays and the undesired impurities in order to concentrate the phosphate content to above 70%. After the second and third expansion schemes at Eshidiya mine complex, more than 1,000 m^3 of water per hour is discharged after washing, which contains about 20% of solid impurities, mainly phosphates and silicates. This water also contains chloride ions, about 900 ppm.

Several methods such as ion exchange, adsorption, liquid extraction, and membrane technologies are used for the removal of chloride. The ion exchange seems to be the most suitable process because of its simplicity, effectiveness, selectivity, recovery, and relatively low cost [1]. Inaya and Kraishan [2] studied the

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removal of chloride from Eshidiya wastewater by using a copolymer in a batch system; they obtained efficient removal of chlorides, about 85%. Carmona et al. [3] investigated the removal of chloride by ion exchange method from an industrial aqueous solution of polyethylenimine using anion exchange resin (Amberlite IRA-420). Their equilibrium isotherms curves were drawn using the Langmuir model. Kamel and Ismael [4] used solid sheets of kaolinite clay, which they claimed to exhibit a good affinity for the uptake of chloride ions. The uptake mechanism of chloride ions by kaolinite clay is reported to be sorption. The sorption included physical adsorption (following Freundlich isotherm) and absorption due to the pores in adsorbent surface. They obtained about 48% removals of chloride ions.

The aim of this work is to study the chloride removal from wastewater from Eshidiya by batch and continuous adsorptions. Amberlite copolymer was selected as an adsorbent to remove chloride from the wastewater using Amberlite IRA-402 CL.

2. Materials and methods

In all experiments, actual wastewater from Eshidiya phosphate mine was used. The chemical analysis of the wastewater is presented in Table 1.

The chemicals used in this study were Amberlite IRA-402 Cl as an adsorbent, silver nitrate (0.1 N) and potassium chromate (10%) as an indicator. Chloride ion concentration in the raw water (from the floatation unit) and the treated water was estimated by titration with (0.1 N) silver nitrate and using potassium chromate (10%) as an indicator.

In the batch adsorption, different amounts (1, 1.5 … 4 g) of amberlite were added to the raw water in separate flasks. To make the samples homogenous, they were mixed for 2 min using a mixer. After the mixing process, the solutions were allowed to stand for 1.5 h and then were filtered using a filter paper. The filtrate was titrated with silver nitrate (0.1 N) to estimate the chloride ion concentrations in the different samples. As an indicator, 10% potassium chromate solution was added (2–3 drops) before the titration. Finally, the optimum amount of amberlite needed to give the minimum concentration of chloride ions left in the filtrate was determined. In the continuous adsorption, a tubular glass column (25 cm long, 2 cm internal diameter) filled with amberlite was connected to a pump to force the solution through the column. The pump was turned on and a sample was taken from the outlet column and from the middle port every 12 min, and the concentrations of the samples were obtained by titration with silver nitrate to estimate the concentration of the chloride ions present in the samples. The procedure was repeated with different initial concentrations, flow rates and pH values.

Table 1
Chemical analysis of the Eshidiya wastewater sample

Compositions	Concentration (ppm)
pH value	7.3
Calcium ion, Ca^{2+}	234.4
Magnesium ion, Mg^{2+}	58.7
Sodium ion, Na^{+}	411.7
Potassium ion, K^{+}	7.2
Chloride ion, Cl^{-}	886
Sulfate ion, SO_4^{-2}	185

3. Results and discussion

3.1. Batch adsorption experiments

Batch adsorption of chloride ions onto Amberlite IRA-402 was investigated in order to find out the optimum amount of Amberlite IRA-402 needed to reduce the chloride ion concentration to a minimum. A specific amount of the adsorbent was added to 100 ml of wastewater sample. The optimum amount was found to be 4 g as shown in Fig. 1. At this amount of adsorbent, the chloride removal was 82.5%. It is worth mentioning that all experimental runs were repeated to ensure reproducibility of the results. The reported experimental data are the average of two runs.

The adsorption isotherms for chloride ions were obtained using initial concentrations ranging from 200 to 886 ppm. The amount of adsorbent was fixed at 4 g, and the mixture was allowed to equilibrate. Finally, the concentration of chloride remaining in solution was measured, and the adsorption capacity of the adsorbent was calculated. The isotherm is a plot of

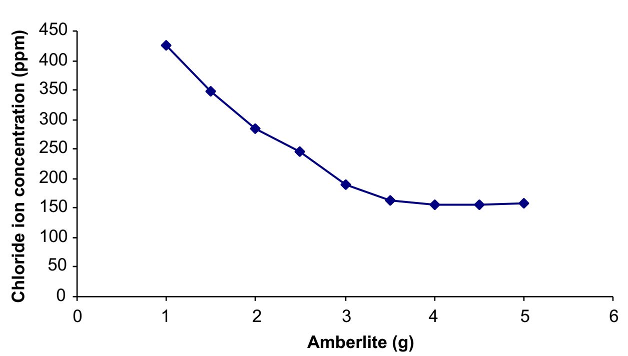

Fig. 1. The chloride ion concentration at equilibrium for different amounts of Amberlite IRA-402 as an adsorbent.

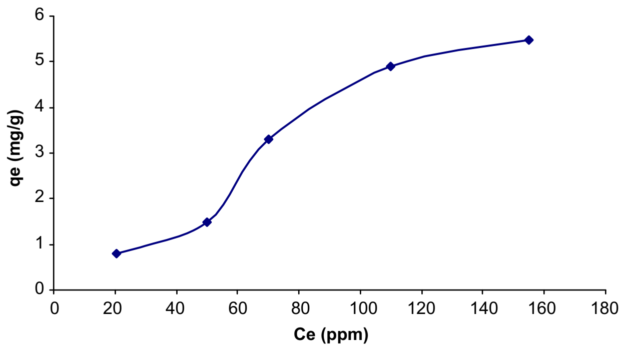

Fig. 2. Adsorption isotherm of chloride ions from the solution onto Amberlite IRA-402 at pH = 7.3 and $T = 25$°C.

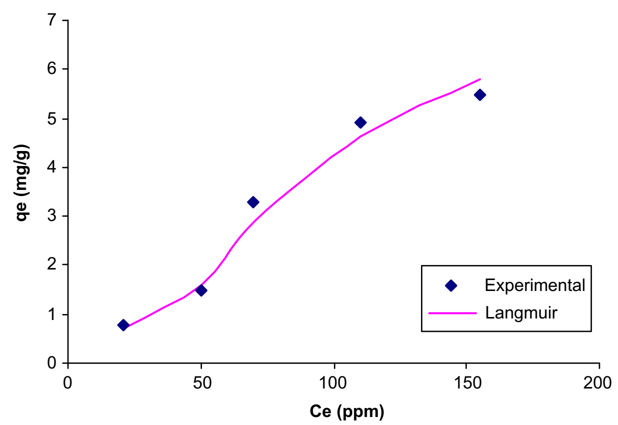

Fig. 3. Langmuir isotherm for chloride adsorption on Amberlite IRA-402 at pH = 7.3 and $T = 25$°C.

milligrams of chloride adsorbed per gram of adsorbent vs. equilibrium concentration of chloride ion. The results are shown in Fig. 2.

The experimental data were fitted to two adsorption models: Langmuir and Freundlich. Langmuir model fitted the data well as shown in Fig. 3. Table 2 gives the model constant along with values of R^2, which also indicate that the data can be represented by these models.

Freundlich model, as can be seen in Fig. 4, did not fit this adsorption. Although R^2 value for the Freundlich fitting is high, the plot shows that it is not a good representation of the data, mainly at high chloride concentrations.

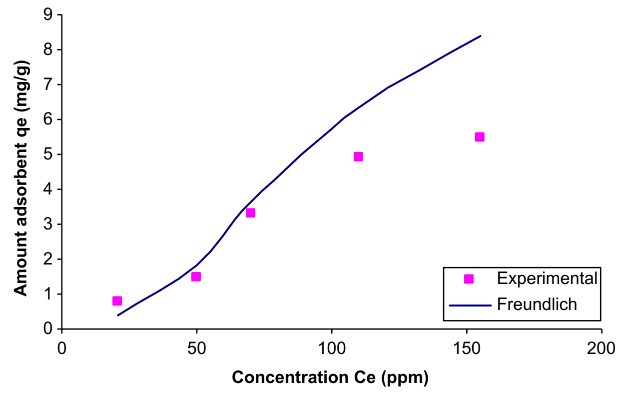

Fig. 4. Freundlich isotherm for chloride adsorption on Amberlite IRA-402 at pH = 7.3 and $T = 25$°C.

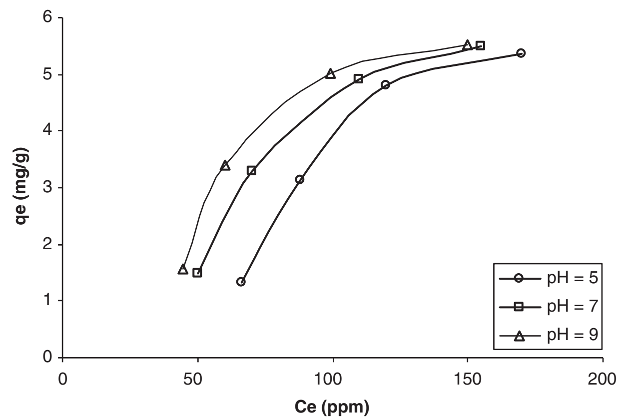

Fig. 5. Effect of initial pH on chloride uptake.

3.1.1. *Effect of initial pH*

Batch and continuous adsorptions of chloride ions by Amberlite IRA-402 were studied at various pH values. Sodium hydroxide and sulfuric acid were used to prepare solutions with different pH values (5, 7 and 9). The increase in concentration of H^+ leads to the following unidirectional reaction and increased uptake: $R–OH + Cl^- + H^+ \Rightarrow R–Cl + H_2O$, where R is the Amberlite IRA-402 ion exchange (adsorbent).

While increasing the pH value, the concentration of OH^- increases and the resin reacts almost reversibly with OH^- of the bulk, and so backward reactions

Table 2
Parameters of the adsorption isotherm models for chloride removal using Amberlite IRA-402

Langmuir			Freundlich		
K_L (l/mg)	b (mg/g)	R^2	K_F (mg/g) (l/mg)	$1/n$	R^2
9.7561	0.0088	0.8838	0.0236	1.1101	0.8788

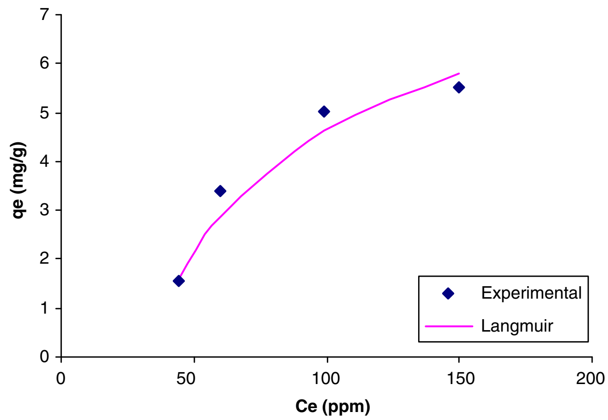

Fig. 6. Adsorption isotherm of chloride ion onto Amberlite IRA-402 fitted by Langmuir isotherm at pH = 9 and $T = 25$°C.

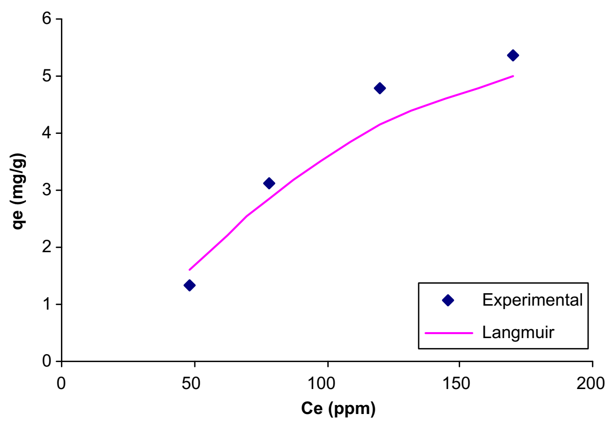

Fig. 7. Adsorption isotherm of chloride ion onto Amberlite IRA-402 fitted by Langmuir isotherm at pH = 5 and $T = 25$°C.

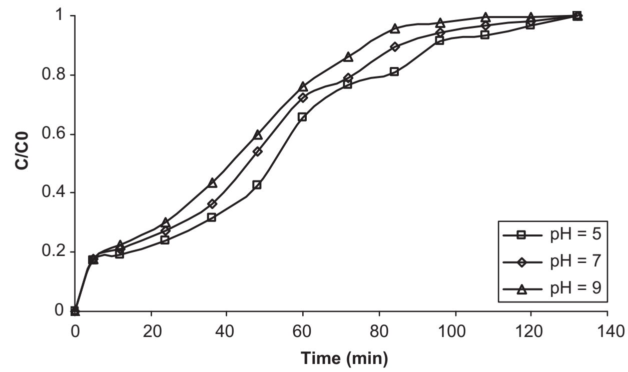

Fig. 8. Effect of feed initial pH on the breakthrough curves at bed height of 22 cm, $C_0 = 886$ ppm, $Q = 50$ ml/min and $T = 25$°C.

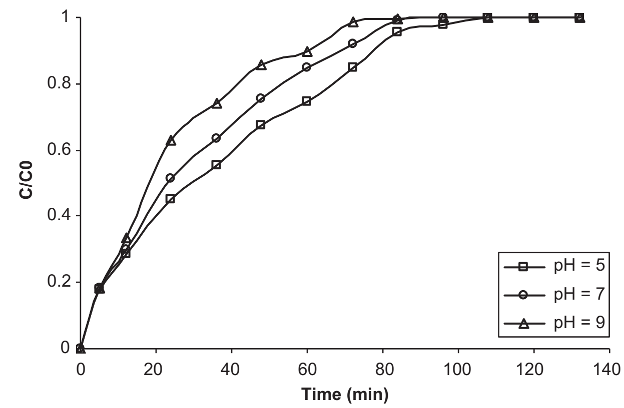

Fig. 9. Effect of feed initial pH on the breakthrough curves at bed height 12 cm, $C_0 = 886$ ppm, $Q = 50$ ml/min and $T = 25$°C.

increase and decrease the uptake: $R–OH + Cl^- \Leftrightarrow R–Cl + OH^-$.

Fig. 5 shows the uptake of chloride ions at different pH values. As shown lower solution pH led to slightly higher chloride uptake.

The two isotherm models, Langmuir and Freundlich, applied here for different pH values. The values of the models' constants are tabulated in Table 3. It is found that Langmuir model is fitting the adsorption of chloride ion onto amberlite at different pH values better than the Freundlich model as presented in Figs. 6 and 7.

The results of continuous adsorption are shown in Figs. 8 and 9; it is shown that the higher pH resulted in a shorter breakthrough time.

The chloride ion uptake of the column at different pH values is shown in Table 4; it is shown that lower pH led to slightly higher chloride uptake.

Table 3
Parameters of the adsorption isotherm models for chloride removal using Amberlite IRA-402 at different initial pH values

	Langmuir			Freundlich		
pH	K_L (l/mg)	b (mg/g)	R^2	K_F (mg/g)(l/mg)	$1/n$	R^2
5	7.9448	0.00716	0.8561	0.0041	1.4406	0.8556
7	9.8561	0.00586	0.8838	0.0236	1.1101	0.8788
9	15.898	0.00324	0.8441	0.0486	0.9762	0.8321

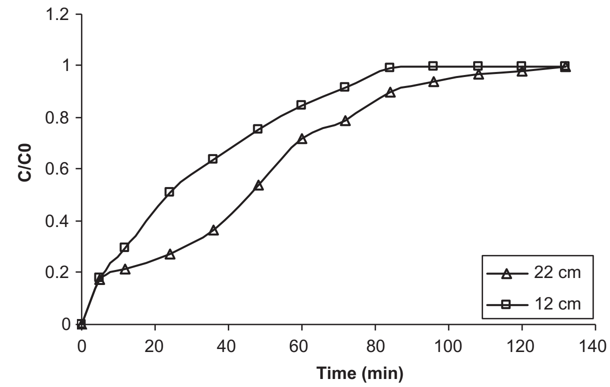

Fig. 10. Adsorption of chloride ion through packed column at $Q = 50$ ml/min, pH = 7.3, $C_0 = 886$ ppm and $T = 25$°C.

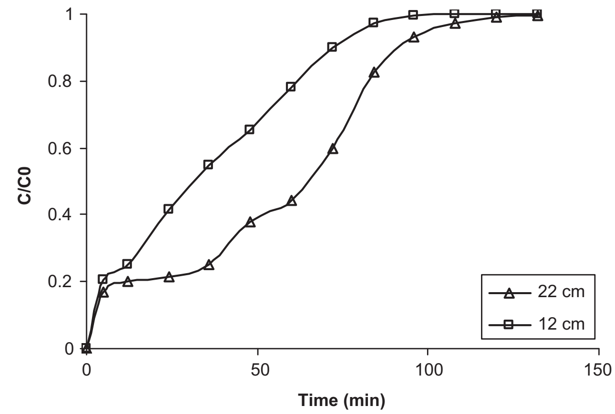

Fig. 12. Adsorption of chloride ion through packed column at $Q = 50$ ml/min, pH = 7.3, $C_0 = 200$ ppm and $T = 25$°C.

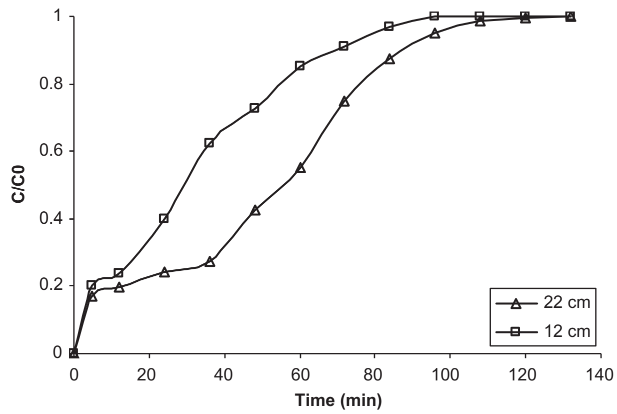

Fig. 11. Adsorption of chloride ion through packed column at $Q = 50$ ml/min, pH = 7.3, $C_0 = 400$ ppm and $T = 25$°C.

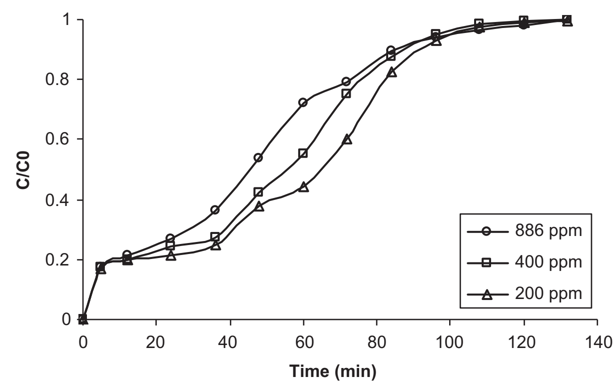

Fig. 13. Effect of influent chloride concentration on the breakthrough curves at bed height = 22 cm, $Q = 50$ ml/min, pH = 7.3 and $T = 25$°C.

3.2. Continuous adsorption of chloride ions

As discussed above, Amberlite IRA-402 was used for chloride removal using batch process. However, it is known that using continuous packed column is more practical and economical to operate than the batch column. In this study, a column with 25 cm length and 2 cm diameter was used. Different parameters that influence the performance of packed bed column adsorption capacity, namely flow rate, initial concentration of chloride ion and solution pH, were investigated.

3.2.1. Effect of influent concentration

The wastewater obtained from Eshidiya had chloride concentration of 886 ppm. To obtain different initial concentration, distilled water was added to obtain solutions with 200 and 400 ppm. A flow

Table 4
Effect of feed initial pH on the chloride ion uptake at $C_0 = 886$ ml/min, $Q = 50$ ml/min, amount of packed adsorbent 18 g

Feed initial pH	Collected volume (L)	Concentration of chloride ion in the collected water (ppm)	Chloride ion uptake (mg/g)	Amount of chloride ion removed (%)
5	12	376	340.0	57.6
7	11.5	436	287.5	50.8
9	10.5	480	236.8	45.8

Table 5
Effect of influent concentration on the chloride ion uptake at $Q = 50$ ml/min, amount of packed adsorbent 18 g, and $T = 25$°C

Influent concentration (ppm)	Collected volume (L)	Concentration of chloride ion in the collected water (ppm)	Chloride ion uptake (mg/g)	Amount of chloride ion removed (%)
886	10.5	451.8	241.61	49.1
400	11	197.6	123.69	50.6
200	12	101.5	65.67	49.2

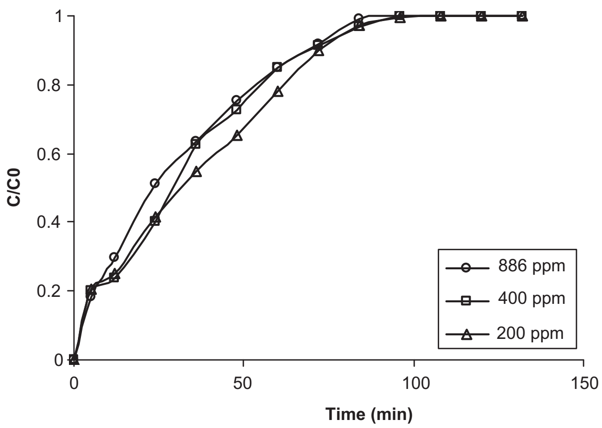

Fig. 14. Effect of influent chloride concentration on the breakthrough curves at bed height = 12 cm, $Q = 50$ ml/min, pH = 7.3 and $T = 25$°C.

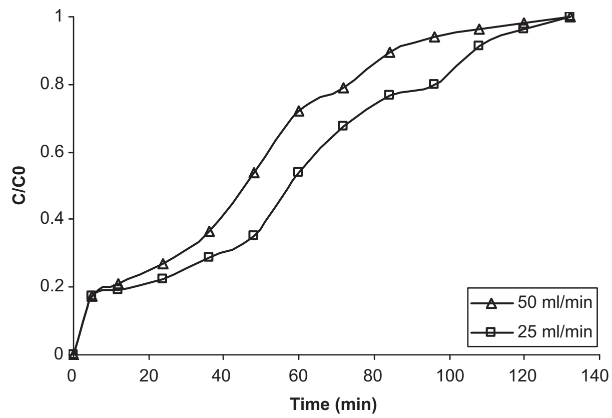

Fig. 16. Effect of influent flow rate on the breakthrough curves at bed height = 22 cm, $C_0 = 886$ ppm, pH = 7.3 at $T = 25$°C.

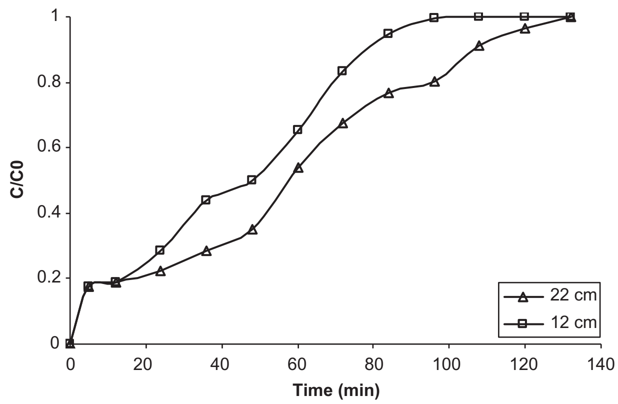

Fig. 15. Adsorption of chloride ion through packed column at $Q = 25$ ml/min pH = 7.3, $C_0 = 886$ ppm at $T = 25$°C.

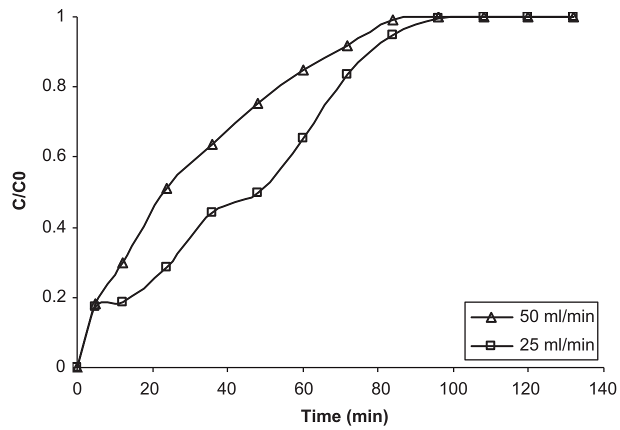

Fig. 17. Effect of influent flow rate on the breakthrough curves at bed height = 12 cm, $C_0 = 886$ ppm, pH = 7.3 at $T = 25$°C.

rate of 50 ml/min moving downward was used. Two ports located in the column at 12 and 22 cm were used to withdraw the samples. The process continued until the chloride concentration from the port of the column became the same as the influent concentration. As expected, the 22 cm port required more time to achieve saturation. The results are presented in Figs. 10–14. The results show that a decrease in the influent concentration resulted in a lag in the occurrence of the breakthrough as the bed needed more time to become saturated with chloride ion.

The adsorption uptakes in the bed for different influent concentrations are shown in Table 5.

Table 6
Effect of influent flow rate on the chloride ion uptake at $C_0 = 886$ ml/min, amount of packed adsorbent 18 g, and $T = 25$°C

Flow rate (ml/min)	Collected volume (L)	Concentration of chloride ion in the collected water (ppm)	Chloride ion uptake (mg/g)	Amount of chloride ion removed (%)
25.00	5.500	395.8	149.8	55.3
50.00	11.00	436.0	275.0	50.8

3.2.2. Effect of influent flow rate

Two influent flow rates (25 and 50 ml/min) at initial chloride concentration of 886 ppm were used through the column. The process continued until the chloride concentration from the bottom of the column became the same as the influent concentration. The results are shown in Figs. 10 and 15–17.

The column uptake is shown in Table 6. The effect of flow rate was small on the chloride removal.

4. Conclusions

In this paper, the removal of chloride ions from Eshidiya wastewater based on batch and continuous adsorptions was investigated. The following are concluded from this investigation:

- Amberlite IRA-402 is found to be a suitable adsorbent to remove chloride ions from Eshidiya phosphate mine wastewater. It is able to remove up to 82.5% in a batch process at equilibrium and up to 50% in a continuous adsorption.
- Langmuir model is the best model to fit the batch adsorption of chloride ions onto Amberlite IRA-402.
- A decrease in the influent concentration resulted in a longer breakthrough times, while higher flow rates and initial pH resulted in shorter breakthrough times.

Acknowledgment

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