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Characterization of Phosphate and Chromate Adsorption on Commercial Iron Oxide.

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ABSTRACT

In the present study, the adsorption properties of commercial iron oxide were investigated via chromate and phosphate uptake in aqueous solutions. A series of batch experiments were performed to study the influence of adsorbent dose, pH and contact time. The obtained results show that the removal efficiency of chromate is more important than phosphate. The maximum adsorption rate is observed in pH range [3-4] and [4-5] for phosphate and chromate respectively. In the two cases, the adsorption is slow. The application of the various kinetics models to the experimental data reveals that the second order model is more appropriate in the two cases.

Keywords: phosphate; chromate; adsorption; iron oxide

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INTRODUCTION

The development of industrialization and urbanization has induced the discharge of wastewaters with significant quantities of heavy metals like chromium and nutrients substances like phosphorus. Chromium is generally discharged by various industries such as electroplating; it is toxic in its hexavalent form. Contamination of aquatic environment caused by toxic elements such as chromium is receiving increasing attention due to its hazardous risk to the environment [1]. Phosphorus is used in products like detergents and it is often added to soil as a plant nutrient. It is not toxic, but it is one of the main species responsible for eutrophication of freshwater [2, 3].

In water treatment, adsorption is one of the most promising methods due to its low operation costs and high efficiency. As adsorbents, the iron oxyhydroxydes with their chemical nature and high specific surfaces play an important role in the elimination of a large number of pollutants [4, 5, 6]. Iron oxides nanoparticles are efficient adsorbents which couple magnetic separation and ionic exchange capacity [7]. The main objective of the present study is to investigate the removal of chromate and phosphate from aqueous solutions by adsorption on characterized commercial iron oxide.

MATERIAL AND METHODS

Characterization of the iron oxide

Commercial powder iron oxide (Fluka) was used without any chemical treatment. It was characterized in laboratory. The point of zero charge (PZC) was determined by titration method. The infrared spectrum was recorded in the 4000 to 400 cm^{-1} range using a spectrophotometer Shimadzu Hyper IR E. X-ray powder diffraction pattern was recorded using PERTE PANAYTICAL diffractometer employing $\text{Cu-K}\alpha$ radiation.

Adsorption experiments

All chemicals reagents used in this study were of analytical grade; all solutions were prepared with distilled water. The stock solutions of phosphate and chromate were prepared by dissolving KH_2PO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ respectively. The pH was adjusted by adding NaOH or HCl solution prior to each experiment.

The adsorption experiments were performed in batch system. The effects of adsorbent dose, time and pH were evaluated. In all experiments, the anions analyses were performed in solutions obtained after centrifugation and filtration through $0.45\text{ }\mu\text{m}$ membrane. The adsorption progress of phosphate and chromate was measured by molybdenum and diphenyl carbazide methods respectively using UV-Visible SCHIMADZU 1650 PC spectrophotometer. The removal efficiencies were calculated from the differences between the initial and the final concentrations in each case.

RESULTS AND DISCUSSION

Characterization of the iron oxide

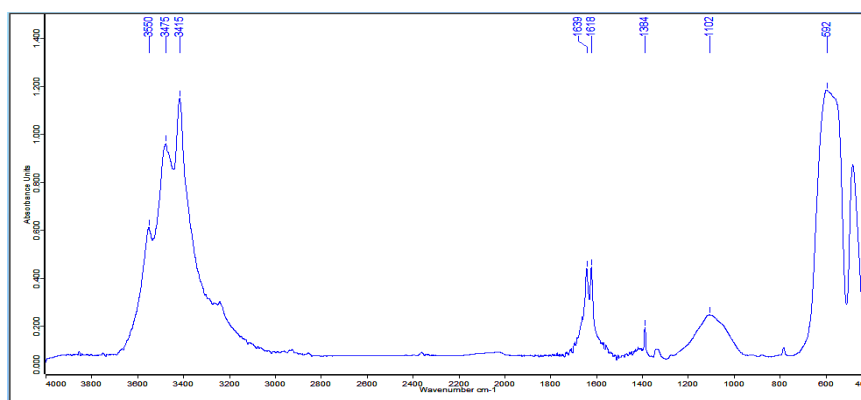


Figure 1: FTIR spectrum of the iron oxide

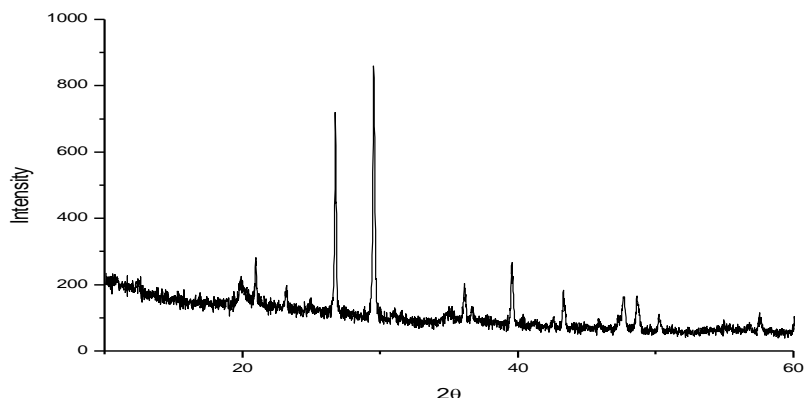


Figure 2: X-ray powder diffractogram of the iron oxide

In the FTIR spectrum shown in Figure 1, the absorption band in the $3400\text{-}3600\text{ cm}^{-1}$ interval corresponds to the OH vibration elongation, the band at 1639 cm^{-1} is related to the HOH bending of adsorbed water [8]; the broad bands at 499 and 692 are characteristic of the Fe-O bond [9]. The intense band at 1384 cm^{-1} may be attributed to the presence of carbonate due to contamination by the atmospheric CO_2 [10]. In the XRD pattern (Figure 2), the main peaks are attributed to maghemite ($\gamma\text{Fe}_2\text{O}_3$); the bands related to akaganeite, lepidocrocite and ferroxide are also observed [11]. The iron oxide used is characterized by neutral PZC equal to 7.15.

Effect of adsorbent dose

The evolution of the ions removal versus adsorbent dose (Figure 3) shows that the iron oxide is more effective in removing chromate than phosphate. The removal efficiency of chromate increases gradually with the increase of iron oxide dose, due to greater availability of surface area for adsorption. A removal of about 65 % is reached for a dose of 5 g/L. However, the phosphate adsorption increases rapidly to attain stability for 1 g L^{-1} adsorbent dose; beyond that the adsorption efficiency remains quasi constant and further dose increase does not affect the phosphate removal.

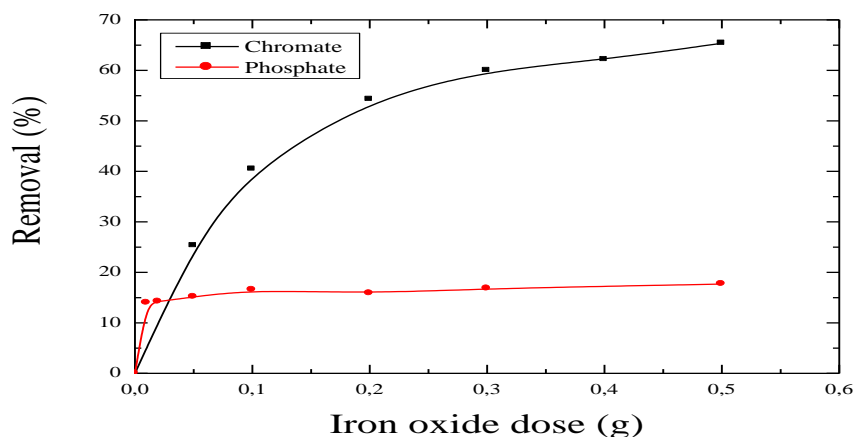


Figure 3: Evolution of phosphate and chromate adsorption-Effect of adsorbent dose ($C_0=10\text{mg/l}$)

Effect of pH

The effect of pH on the adsorption of phosphate and chromate ions is shown in Figure 4. It is obvious that the removal percentage of the two ions depends strongly on the pH. In the pH range studied, the removal of chromate ions is more important. In the two cases, the removal rate increases with the pH increase in acidic

range. The maximum adsorption occurs at acidic pH values where $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- and H_2PO_4^- are the prevalent species. According to the PZC value, the surface of the iron oxide is positively charged at pH less than 7 favoring the adsorption of anions. Consequently, the low adsorption observed at $\text{pH} < 3$ is in a relation to the competition with protons. The maximum adsorption for phosphate is observed in the pH range [3-4], this result is not in agreement with that found for phosphate adsorption on hematite ($\alpha\text{Fe}_2\text{O}_3$) where the maximum removal has been observed at $\text{pH} \leq 5$ [12]. In the case of chromate, the maximum adsorption is observed in the range [4-5] implying that HCrO_4^- has more affinity to the iron oxide than $\text{Cr}_2\text{O}_7^{2-}$. In the two pH ranges, an increase in solution pH has been observed during adsorption for the two ions implying their exchange with the adsorbent surface hydroxyl. Beyond these pH ranges, a decrease in the two ions uptake is observed for greater pH values. This can be attributed to the repulsion of negatively charged ions induced by the increase in negative surface sites.

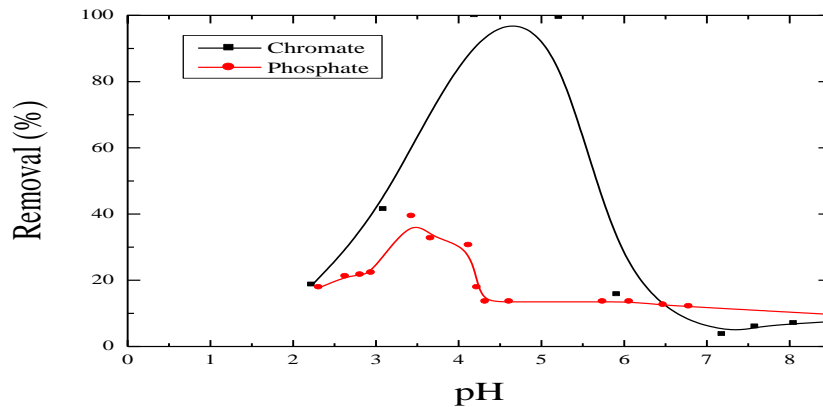


Figure 4: Evolution of phosphate and chromate adsorption-Effect of solution pH ($C_0 = 5 \text{ mg/l}$, $t: 60 \text{ min}$; adsorbent dose: 3 g/L)

Effect of time

The Figure 5 shows the evolution of adsorbed chromate and phosphate versus contact time at pH 4 and 3 respectively. The obtained curves have the same shape. The percentage of adsorption increases with increasing contact time. The adsorption process can be divided into two steps: a fast adsorption at first then a slower adsorption at longer time. For the initial concentration used (5 mg/L), the first step takes about 6 hours where 64 % of chromate and 44 % of phosphate are adsorbed. After this time, the ions removal becomes more slow. This may be due to less surface sites available for the adsorption. In the two cases no equilibrium is observed before 24hours.

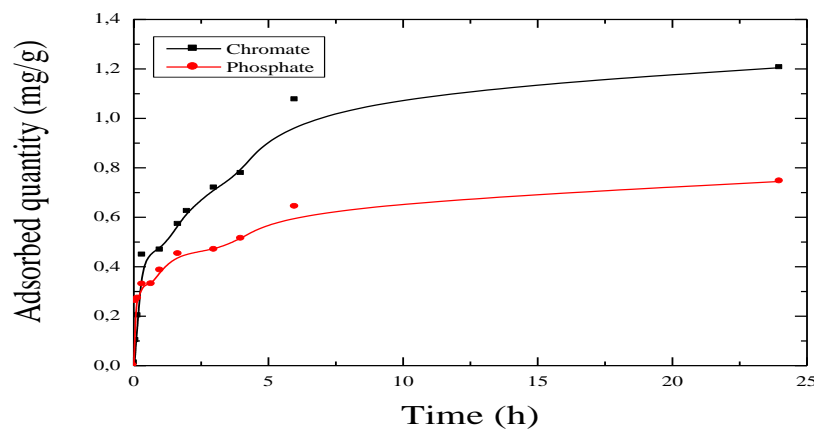


Figure 5: Evolution of phosphate and chromate adsorption-Effect of time ($C_0=5\text{mg/l}$, adsorbent dose 3g/L)

The phosphate and chromate adsorption kinetics data are fitted with several kinetics models. Namely: the pseudo-first-order, pseudo-second order, Elovich and diffusion model. Their linear forms are given respectively below:

$$\ln(Q_e - Q_t) = \ln Q_e - Kt \dots\dots (1)$$

$$\frac{t}{Q_t} = \frac{1}{KQ_e^2} + \frac{1}{Q_e} t \dots\dots\dots (2)$$

$$Q = a + b \ln t \dots\dots\dots (3)$$

$$Q_t = K\sqrt{t} + C \dots\dots\dots (4)$$

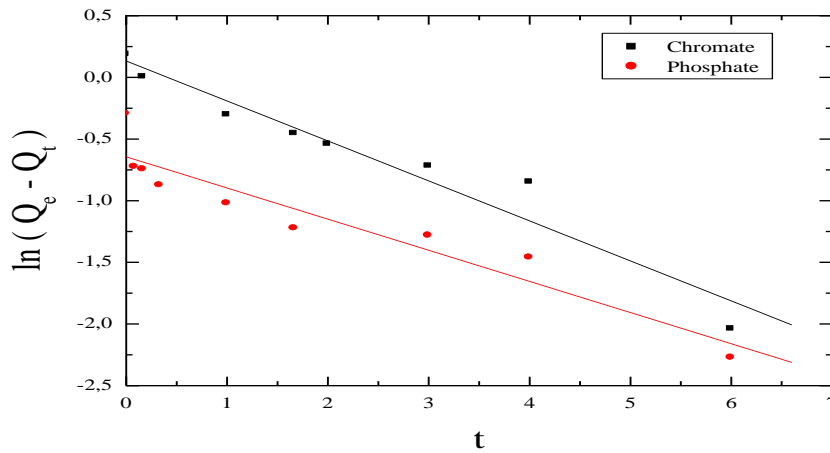


Figure 6: Pseudo-first-order plots for phosphate and chromate adsorption

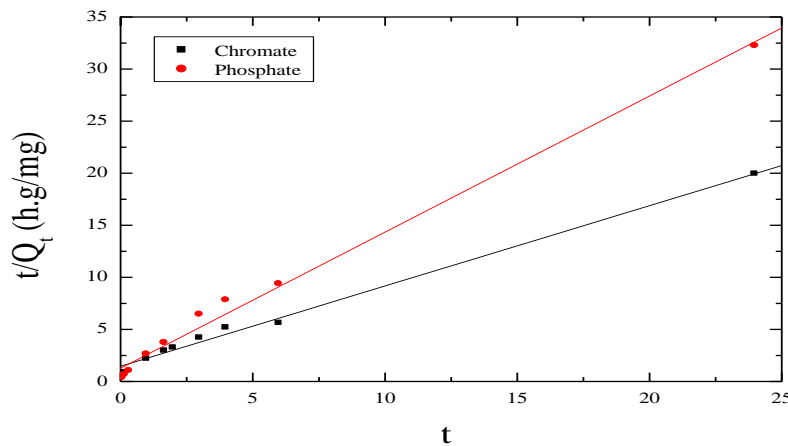


Figure 7: Pseudo-second order plots for phosphate and chromate adsorption

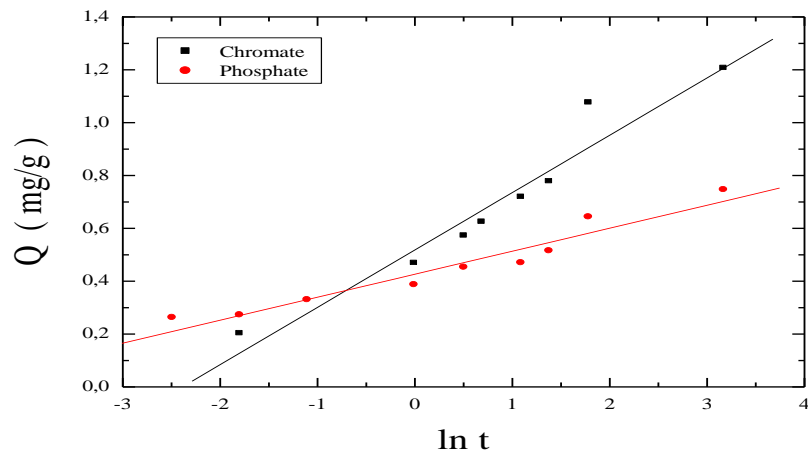


Figure 8: Elovich plots for phosphate and chromate adsorption

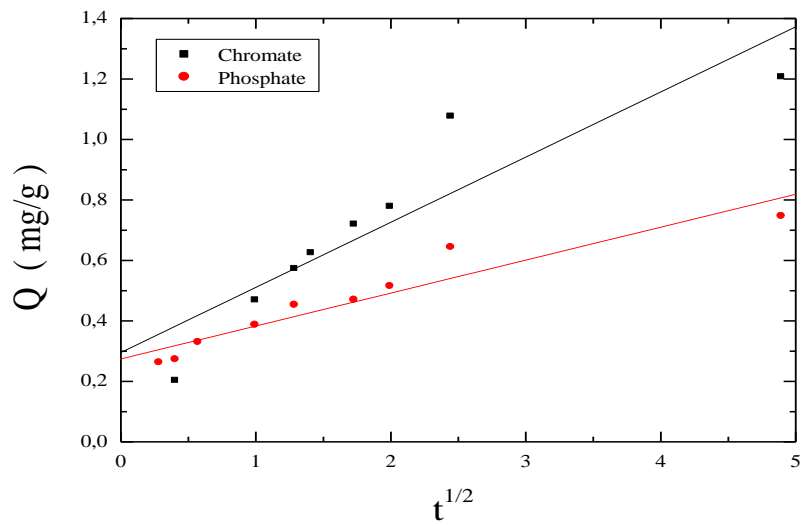


Figure 9: Diffusion plots for phosphate and chromate adsorption

Table 1: Kinetics models parameters

Kenitics model	Phosphate	Chromate
First order	K=0.2526 Qe=0.525 R=0.948	K=0.3243 Qe=1.142 R=0.970
Second order	K=1.3503 Qe=0.765 R=0.996	K=0.4075 Qe=1.297 R=0.997
Elovich	a=0.426 b=0.087 R=0.967	a=0.518 b=0.217 R=0.969
Diffusion	K=0.109 C=0.274 R=0.952	K=0.215 C=0.295 R=0.909

The obtained results are presented in Figures (6, 7, 8, 9) and the calculated parameters are given in Table 1. According to the calculated correlation coefficients, the phosphate and chromate adsorption kinetics follow the models in the order:

Phosphate: first order ~diffusion < Elovich < second order.

Chromate: diffusion < first order ~ Elovich < second order.

The calculated rate constants of the second order model show that the adsorption of phosphate on the iron oxide is more rapid.

The calculated kinetics curves are presented in Figure 10. The first order kinetics model is ruled out; a large difference is found between experimental and calculated adsorption capacities at equilibrium. The kinetics of chromate adsorption on the iron oxide can be described by either the second order or Elovich equations. The predicted adsorbed amount calculated by the two models at equilibrium agrees with the experimental data. In the case of phosphate, the second order model is more satisfactory. The diffusion model is more suitable to explain the experimental data of chromate and phosphate adsorption in the first step.

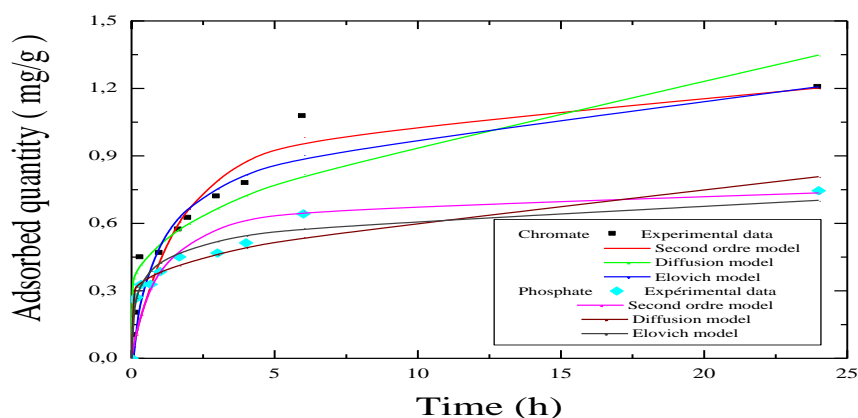


Figure 10: Adsorption kinetics of phosphate and chromate adsorption - Kinetics models

CONCLUSION

On the basis of the results of the present study, the following conclusions may be drawn:

- The commercial iron oxide used is more efficient to the removal of chromate ions than phosphate.
- The optimum pH range to achieve a maximum removal is [3-4] for phosphate and [4-5] for chromate.
- The adsorption kinetics can be described by the second order model.

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