Removal And Regeneration of As(V) In Aqueous Solutions By Adsorption On Calcined Fluorapatite: Kinetics And Thermodynamic Parameters.

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Abstract

In this work, Fluorapatite has been prepared and successfully applied for the removal of As (VI). The materials prepared have been characterized using X-ray diffraction (XRD), infrared transform spectroscopy. Fourier (FTIR), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Thermogravimetric analysis (TGA) and zero load point pH (pH_{PZC}) were also considered as part of these characterizations. In this work, several parameters affecting the adsorption process were studied, such as: the mass effect, time, pH, and the initial concentration effect. The value of the regression coefficient showed that the data The experimental results corresponded best to the pseudo-second order (PSO) model, while the Langmuir adsorption isotherms best described the equilibrium adsorption data with the highest q_m of 43.10 mg / g. Finally, FapC has been successfully reused for more than 5 cycles without significant loss of its sorption capacity.

Introduction

Arsenic is one of the most toxic compounds you can find. Despite their toxicity, inorganic arsenic compounds are naturally present in small amounts on earth. Humans can be exposed to arsenic through food, water and air. Exposure can also occur through skin contact with contaminated soil or water.

Arsenic, classified as a group 1 human carcinogen by the World Health Organization (WHO) (2011), has been reported at significant concentrations in groundwater due to its toxicity and its presence, I World Health Organization (WHO) and the Vietnamese Ministry of Health has set the maximum contaminant for arsenic at 10 μg / L for drinking water (Choong et al. 2007; Sharma and Sohn 2009).

Arsenic can be removed from the water in different ways. Examples of water purification techniques that can be applied are oxidation (van Genuchten et al. 2012), coagulation (Pramanik et al. 2016), chemical precipitation (Harper and Kingham 1992), membrane filtration (Fogarassy et al. 2009), ion exchange (Ning 2002) etc. among these adsorption there are several advantages compared to other methods, due to the low investment cost, ease of use and efficiency of removal of pollutants .

Many absorbents have been reported for the elimination of arsenic (V), such as chitosan (Chen and Chung 2006) Nano-crystalline kaolinie (Amer and Awwad 2018), Treated zeolite (Ahmad and Awwad 2010), activated carbon (Huang and Fu 1984), Natural siderite and hematite (Guo et al. 2007), alumina (Lin and Wu 2001), Fe_7S_8 nanoparticles (Cantu et al. 2016), and Magnetite (Yean et al. 2005). The use of products of natural origin, such as apatite, because they are more abundant and effective as adsorbents

Natural Moroccan phosphates are essentially sedimentary in nature. Phosphate rocks are mainly made up of fluoroapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) which is weakly crystallized and widely used thanks to its adsorption and ion exchange properties (Cao et al. 2009). The presence of minerals such as calcite and dolomite in the sedimentary apatite is very beneficial for the retention of phosphorus thanks to the good dissolution of these carbonate minerals. This results in an increase in the pH of the reaction medium and in the

concentration of Ca^{2+} ions in solution, which promotes the precipitation of calcium phosphate (Mobasherpour et al. 2011). Apatites have been widely used thanks to their great capacity to immobilize different heavy metals such as Cd^{2+} , Pb^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+} , Cr^{6+} (Aklil et al. 2004; Yaacoubi et al. 2014).

The proposed exchange mechanisms are different depending on the element considered and the natural conditions. There are ionic exchanges (exchanges on the cationic sites of Ca^{2+}) associated with a diffusion in the apatitic structure. During this process, the ionic radius and the electronegativity of the metal ion seem to be the main parameters of this mechanism (Cao et al. 2004).

In this work, two objectives were taken into account: The treatment of Moroccan natural phosphate by a heat treatment The second objective is the elimination of As(V) dissolved in synthetic solutions by adsorption on calcined phosphate. In this study, we studied the structure and morphology of FApC using X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Information on the structure was also obtained by spectroscopy measurements. Fourier transform infrared spectroscopy (FTIR) measurements, The adsorption capacity of As (V) has been demonstrated using the ICP technique.

Materials And Methods

2.1. Materials

The chemicals used in this study were: Nitric acid (HNO_3 .Sigma-Aldrich. 65%), Sodium hydroxide (NaOH Sigma-Aldrich 99%), Acidhydrochloric (HCL Sigma-Aldrich, 37%), Sulfuric acid (H_2SO_4 Sigma-Aldrich, 37%), and flourapatite is a sample of khouribga-maroc phosphate.

2.2. Adsorbents preparation

2.2.2. Preparation of Fluorapatite (FAP) Calcined

The natural phosphate used in this work comes from an ore located in Khouribga (Morocco). A determined mass of natural phosphate (25 g) was transferred to a 500 ml conical flask, adding a volume of 250 mL of distilled water at 75 ° C for 2 hours. The precipitate is filtered under vacuum, washed with distilled water and then dried in an oven at 100°C. The dried phosphate was subjected to two treatments, first by nitric acid (1 M) for 2 hours. Filtered, washed and dried, the solid was calcined at 900°C. and ground to obtain nanopatites having a grain size of less than 80 mesh.

2.3. Characterizations

X-Rays Diffraction analysis was carried out using an Bruker D8 diffractometer operating at 45 kV/100 mA, using CuK α radiation with Ni filter. The surface morphology of the samples was obtained from scanning electron microscopy (SEM) Philips XL 30 ESEM (Acc spot Magn 20.00 kv). FT-IR spectrometer was obtained using a Thermo-scientific Spectrometer in the mid-infrared region between 400 and 4000

cm⁻¹ with a resolution of 4 cm⁻¹. Thermogravimetric analysis was performed using a Discovery TGA from TA instruments at a heating rate of 10°C/min under nitrogen atmosphere.

2.4. Adsorption studies

The adsorption experiments of As(V) onto composite were carried out in a batch system. The adsorption tests were conducted in glass beakers (150 mL) containing 50 mL of As(V) solutions at a consistent stirring rate. The effects of experimental parameters such as pH, adsorbent mass, contact time, initial chromium concentration on the adsorption process were examined. The initial pH of the solution was adjusted by the addition of 0.1 M HCl or 0.1 M NaOH. The concentration of As(V) in the solution was determined ICP. The adsorption capacity q_t (mg/g) and adsorption percentage (%Removal), at a specified contact time, were calculated using the following equations:

$$q_t = \frac{(C_o - C_t)V}{m} \quad (1)$$

$$\%Removal = \frac{(C_o - C_t)}{C_o} \times 100 \quad (2)$$

Where C_o and C_t are the amounts of initial and retained Cr (VI) in the solution at time t (mg/L), respectively. V is the solution volume (L) and m is the mass of adsorbent (g).

2.5. Data Analysis

In order to describe the mechanism involved in the adsorption process, the experimental kinetic data were analyzed by application of the pseudo-first-order (PFO), the pseudo-second-order (PSO), while Langmuir and Freundlich models were applied to describe the obtained isotherms to propose the sorption mechanism involved (Table 1). Thermodynamic parameters including the Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were also analyzed to predict the feasibility and determine the nature of the adsorption process in the temperature range of 20–60°C.

Table 1. Kinetic and isotherm models

Model	Equation	Description
Kinetic models (Liu et al. 2015; Zhang et al. 2016)		
PFO	$Q_t = Q_e(1 - e^{-k_1 t})$	k_1 (min ⁻¹): the PFO rate constant; t (min): the contact time of adsorbent and adsorbate; Q_t (mg g ⁻¹): the amount of paraquat adsorbed at time t ;
PSO	$\frac{t}{\left[\frac{1}{k_2 Q_e^2}\right] + \left[\frac{1}{Q_e}\right]}$	Q_e (mg g ⁻¹): the calculated amount of paraquat adsorbed at equilibrium K_2 : rate constant(g mg ⁻¹ min ⁻¹)
Isotherm models (Freundlich 1907; Langmuir 1916)		
Langmuir	$Q_e = \frac{K_L q_m C_e}{1 + K_L C_e}$	q_e (mg g ⁻¹): the adsorbed amount of Cr(VI) at equilibrium C_e (mg L ⁻¹): Concentration of Cr(VI) at equilibrium. K_L (L mg ⁻¹): Langmuir constant; q_m : maximum adsorption capacity.
Freundlich	$Q = K_f C_e^n$	K_f (mg g ⁻¹): Equilibrium Freundlich constant. n : Adsorption intensity.
Thermodynamic data (Tsai and Chang 1995; Hameed et al. 2007)		
Gibbs free energy	$\Delta G = -RT \ln k_d$	ΔG (kJ mol ⁻¹): Gibbs free energy change; K_d : equilibrium constant; R : gas constant; T (°K): temperature.
Van't Hoff	$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$	ΔS° (kJ mol ⁻¹): Entropy change; ΔH° (kJ mol ⁻¹): Enthalpy change R : Gas constant (8.314 J.mol ⁻¹ .K ⁻¹)

2.6. Regeneration study

Regeneration tests were studied using 100 mg FapC and As(V) and 50 ml of NaOH solution (0.5 N) under stirring for 2 hours; afterward, the recycled FapC was filtered and washed. The sorption regeneration was repeated five times.

Results And Discussion

3.1 Characterization of FapA

Figure 1a, shows a good resolution of the XRD peaks, which proves a good crystallinity of the sample, They consist of an apatitic structure, as main constituent, accompanied by quartz SiO_2 and fluorite CaF_2 , CaO . As can be seen in Fig. 1b, all the FapC diffraction peaks are in agreement with the standard fluorapatite model (JCPDS file no. 15-0876) with a hexagonal structure (Sebti et al. 2003; Billah et al. 2020).

The characterization of fluorapatite by infrared spectroscopy is illustrated in Fig. 2b, all the bands that we have found in this fluorapatite spectrum are in good agreement with the studies reported in other natural or synthetic apatitic phosphates (Mouflih et al. 2005; Elouear et al. 2008).

The IR spectrum of Fapc is characterized by peaks for OH- at 3570.57 cm^{-1} and 630.02 cm^{-1} , a group of photos for PO_4^{3-} at 566.97 cm^{-1} , 602.64 cm^{-1} , $961, 34 \text{ cm}^{-1}$, $1042, 80 \text{ cm}^{-1}$ and at 1091.61 cm^{-1} and a group of photos for CO_3^{2-} at 1413.57 cm^{-1} and at 1455.03 cm^{-1} . The ion absorption bands PO_4^{3-} are characterized by two absorption areas located between $1100 - 900 \text{ cm}^{-1}$ and $600 - 500 \text{ cm}^{-1}$ depending on the type of apatite (Raynaud et al. 2002). The bands of the first domain correspond to the symmetrical and antisymmetric vibrations of the P-O bond (Mouflih et al. 2005) and those of the second domain are attributable to the deformation vibrations of the O-P-O bond (Elouear et al. 2008).

The surface morphology of the FapC has been investigated using SEM. The SEM image of obtained Fap was presented in Fig. 1d. shows that the morphology of the phosphate rock consists mainly of irregularly shaped particles. Other particles are linked to the presence of organic residues and grains of quartz (Aouad et al. 2004a). Coupled with energy dispersive X-ray analysis (EDX) is shown the presence of Ca, P, O, C, F and traces of other elements. This observation confirmed the results found by XRD, IR.

The thermal behavior of Crude and Processed Phosphate was studied by thermogravimetric analysis ATG and its derivative DTG (Fig. 1C). Analysis of the thermogram shows three main mass losses.

The TGA curve of the phosphate studied indicates a first weight loss of 0.52% between 25°C and 250°C corresponding to the desorption of water (Aouad et al. 2004b). The second mass loss (4.27%) Processed Phosphate begins around 200°C and which spreads up to 550°C corresponds to the elimination of organic matter (El Asri et al. 2009). The last weight loss of 5.38% between 450°C and 1100°C is attributed to the decomposition of mineral carbonates (El Asri et al. 2009).

The DTA curve showed the presence of an endothermic effect at 60°C attributed to the evaporation of water adsorbed on the surface of the phosphate and exothermic peak at 360°C and picendothermiqu 697°C attributed respectively to combustion of organic matter and decomposition of carbonates (Aouad et al. 2004a).

3.2. Adsorption studies

3.2.1. The effect of pH

The influence of pH on the adsorption of As (V) on FapC was studied in a pH range of 1.0 to 12, using 0.1 g of FapC in a solution of 50 ml of As (V) (10 mg L^{-1}) for 1 hour at room temperature. The pH was adjusted using 0.1 M NaOH and 0.1 M HCl. The results are shown in Fig. 2a. shows that the percentage of As (V) elimination increases sharply with the increase in the pH of As (V) from 1.0 to 8.0 and then remains stable between 8 and 12. The Pourbaix diagram for As species (Garcia et al. 2014) indicates that the stable oxidation state, As (V) in the aqueous system is a monovalent anion (H_2AsO_4^-) in the pH range of 3.0-6.8 or equivalent (HAsO_4^{2-}) anion in the pH range of 7.0–11.0. The removal efficiency of As (V) increases on the negatively charged surface ($> \text{pH}_{\text{PZC}}$) of the adsorbents. The results therefore indicate the exchange of arsenate for phosphate in the FapC structure (Çiftçi et al. 2011).

3.2.2. The effect of adsorbent mass

The effect of the dose of FapC on removal of As (V) displayed in Fig. 2b The influence of the mass of the adsorbent has been studied in the range 0.025–0.400 g shows that the percentage of elimination of As (V) increases with the increase in the quantity of adsorbent then it remains stable. As in Fig. 3 shows that 100 mg of FapC is capable of fixing a maximum of As (V) on the order of 90 % of As (V) ($C_i : 100 \text{ mgL}^{-1}$). The amounts of As (V) fixed must be in accordance with the doses of adsorbent in solution to ensure an equivalent number of adsorption sites (Sebti et al. 2003).

3.2.2. The effect of contact time

Figure 2c illustrates the adsorption of metal ions of As (V) on FapC with different contact times (0 to 120 min) with the at pH 8 and the mass equal to 100 mg. The retention of As (V) on FapC increases with increasing contact time and reaches a saturation phase at around 60 minutes, from which time the retention becomes almost constant. It's a two-phase process. In the first phase, contact time less than 60 minutes, the adsorption is due to the availability of a large number of active sites as well as to the rapid diffusion of metal ions, from the solution to the surface of the solid. In the second phase, the adsorption reached a saturation equilibrium of the adsorbent sites on the FapC.

3.2.3. Adsorption kinetics

To examine the adsorption kinetics of As (V) metal ion onto FapC and the mechanism and rate-controlling step in the whole adsorption process, the nonlinear forms of pseudo-first-order (PFO), Table 2 summarizes the analogous parameters for the adsorption of As (V) metal ions on FapC. The results showed that the R^2 of PSO exhibits a honeyed connection of the metal ion As (V) on FapC as opposed to the PFO parameters. In addition, the PSO model shows well-coordinated correlations between the calculated values of Q_{cal} (Fa: 23.49 mg g^{-1}) and the experimental values of Q_e (Fa: 22.68 mg / g) pseudo-second -order (PSO) are used (Table 2).

Table 2
Kinetics adsorption parameters of As(V) on FapC.

	$Q_{e,exp}$ (mg g ⁻¹)	Pseudo-First-Order model			Pseudo-Second-Order model		
		$Q_{e,cal}$	K_1	R^2	$Q_{e,cal}$	K_2	R^2
		(mg g ⁻¹)	(min ⁻¹)		(mg g ⁻¹)	(g mg ⁻¹ .min ⁻¹)	
CS	22.68	25.73	0.1	0.981	23.49	0.003	0.999

3.2.4. Adsorption isotherms

The Langmuir and Freundlich isotherms (Table 2) have been useful in defining the adsorption capacity of FapC for the metal ion As (V) (van Genuchten et al. 2012). The adjustment diagrams of the Langmuir and Freundlich isotherm models for the adsorption of As (V) on Fapc are presented in Fig. 4. The calculated isotherm parameters, as well as the correlation coefficients (R^2), are defined in Table 3. Rendered at R^2 values, the Langmuir model was better suited than the Freundlich model to experimental data for the adsorption of metal ions As (V). Due to the Langmuir model established on the assumption of homogeneous adsorption, it can be said that the adsorption of the metal ion As (V) on the surface FapC is homogeneous.

Table 3
Equilibrium adsorption parameters of As(V) on FapC.

	Langmuir			Freundlich		
	Q_{max}	K_L	R^2	K_F	n	R^2
	(mg/g)	(L.min ⁻¹)		(mg/g)		
FapC	43.10	0.25	0.979	10.65	0.39	0.968

3.2.4. Thermodynamics study

Thermodynamic parameters are one of the essential tools for predicting the adsorption mechanism, whether it is a physisorption or chemisorption process. Thermodynamic parameters could be determined from the thermodynamic laws as they are. presented in Table 4 (Fig. 5). The positive amounts of ΔH° (-32.549 and - 20.095 J / mol) confirm that the adsorption of the metal by the marl clay is endothermic. This means that the system absorbs heat from the outside environment. We also found a positive value of ΔS which suggests that the As (V) are adsorbed in a random way on the surface of the Fap. The negative values of ΔG° indicate that the adsorption of the As (V) on Fapc is spontaneous (Cao et al. 2004).

Table 4
Thermodynamics parameters of Cr(VI) using CS and CS-Fa

	ΔH° (KJ/mol)	ΔS° (J/mol. K)	ΔG° (KJ/mol)		
			298 K	318 K	333 K
FapC	5.133	15.921	-2.876	-4.368	-9.142

3.3. Regeneration

The capacities of fapC composites to regenerate after adsorption of metals using various desorbing agents (NaOH, NaCl and HCl) with a concentration of 0.5 M, is described in Fig. 6. The best results were obtained using 0.5 M NaOH for a contact time of 16 h, and allowed 90% of adsorbed As (V) to be recovered. After the desorption experiment with 0.5 M NaOH, the adsorbent was filtered from solution, washed with distilled water, dried at 100°C and reused for the adsorption of As (V). The figure shows Fapc desorption. We can see that the absorption capacity of As (V) using FapC composite decreased slightly after two cycles from 90.8–82.5% in the fifth cycle. The performance decreased by 8.3%, Les results concluded that Fap is reusable and effective for four cycles of desorption.

3.8. Adsorption mechanism of As(V) on FapC.

The FTIR spectra of FapC before and after the adsorption of As (V) are presented in Fig. The FTIR spectra were obtained in order to analyze the mechanism of the Adsorption of As (V) and identification of the functional groups on the surface Fluorapatite. As revealed in Fig. 7 the peaks correpond to PO43- have been moved from 1021.2, 560.7 and 600.3 cm⁻¹ to 1019,8, 558.04 and 599.3 cm⁻¹, respectively. This can be attributed to the complexation between As (V) ions with a PO43- group.

Conclusion

The results obtained in this research work demonstrated the effectiveness of calcined Fluorapatite (FapC) as an effective and environmentally friendly adsorbent for the removal of As (V) from aqueous solutions. The results of XRD, SEM/EDS and FTIR and TGA/TDA have shown that the conditioning methods allowed to generate a material with adsorbent properties ideal for the removal of arsenic from contaminated water. The adsorption kinetic data of As (V) onto FapC fitted well the pseudo-second-order kinetic. The coefficientof regression (R2) that was obtained using the Langmuir model was higher compared to that obtainedusing the Freundlich model. Values of thermodynamic functions show that the reaction is endothermic, random and beneficial .Moreover, FapC showed high sorption efficiency of As (V) (90.8%) after 2 Cycles of adsorption-regeneration. it can be concluded that FapC had an effective adsorbent which can be used in many environmental applications. After emphasizing above mentioned adsorptive features, the adsorption capacity of FacC for arsenic ions were compared with those extracted from literature. As can be seen in Table 5, FapC is potential adsorbent with comparable capacity.

Table 5
Comparison of As (V) adsorption capacity by different adsorbents.

Adsorbent	$Q_{\max}$ (mg.g ⁻¹)	Reference
Chitosan	1.94	(Sethy and Sahoo 2019)
Nano-crystalline kaolinie	43.67	(Salgado-gómez et al. 2014)
Treated Zoelite	18.35	(Yu et al. 2017)
Microporous Activated Carbone	132	(Chen et al. 2013)
Natural siderite and hematite	0.16	(Li et al. 2013)
Alumina	25	(Xiao et al. 2013)
Fe ₇ S ₈ nanoparticles	31.30	(Zhang et al. 2016)
Magnetite	46.70	(Liu et al. 2015)
FapC	43.10	This study

Declarations

Author contributions:

Rachid EL Kaim Billah, wrote the paper, conducted review and editing, designed research ; Savaş Kaya , wrote the paper, conducted review and editing, designed research ; Selçuk Şimşek, wrote the paper, conducted review and editing, designed research ; El Mahdi Halim, wrote the paper, designed research ; Mahfoud Agunaou, wrote the paper, designed research ; Abdessadik Soufiane, wrote the paper, designed research

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Figures

Figure 1

X-Rays patterns (a), FTIR spectra (b), TGA and DTA (c) curves, and SEM image (d) of Fluorapatite (FapC)

Figure 2

Effect of pH solution (a), adsorbent mass (b), and contact time (c) on adsorption of As (V).

Figure 3

Kinetic studies by PFO, PSO.

Figure 4

Nonlinear representations of the Langmuir and Freundlich models for the adsorption of As(V) ion onto FapC

Figure 5

Plot of $\ln(K_d)$ versus $1000/T$ for As(V) adsorption onto FapC.

Figure 6

Recycling study of FapC adsorbents

Figure 7

FTIR analysis of FapC after and before sorption of As (V).