Phosphorus removal from aqueous solution using iron coated natural and engineered sorbents

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Abstract

New filtration materials covered with metallic oxides are good adsorbents for both cation and anion forms of pollutants. Sfax is one of the most important industrial towns in Tunisia. Its phosphate manufacture in particular is causing considerable amounts of water pollution. Therefore, there is a need to find out a new way of getting rid of this excessive phosphate from water. This work is aimed to examining the potential of three sorbent materials (synthetic iron oxide coated sand (SCS), naturally iron oxide coated sand (NCS) and iron oxide coated crushed brick (CB)) for removing phosphate ions from aqueous solutions. According to our literature survey CB was not used as adsorbent previously. Phosphate ions are used here as species model for the elimination of other similar pollutants (arsenates, antimonates). Optical microscope and scanning electron microscope (SEM) analyses were used to investigate the surface properties and morphology of the coated sorbents. Infra-red spectroscopy and X-ray diffraction techniques were also used to characterize the sorbent structures. Results showed that iron coated crushed brick possess more micro pores and a higher surface area owing to its clay nature. The comparative sorption of PO_4^{3-} from aqueous solutions by SCS, CB and NCS was investigated by batch experiments. The estimated optimum pH of phosphate ion retention for the considered sorbents was 5. The equilibrium data were analysed using the Langmuir and Freundlich isotherms. The sorption capacities of PO_4^{3-} at pH 5 were 1.5 mg/g for SCS, 1.8 mg/g for CB and 0.88 mg/g for NCS. The effect of temperature on sorption phenomenon was also investigated. The results indicated that adsorption is an endothermic process for phosphate ions removal. This study demonstrates that all the considered sorbents can be used as an alternative emerging technology for water treatment without any side effect or treatment process alteration.
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1. Introduction

Phosphorous is the key nutrient for the growth of algal and other biological organisms, which in excess causes eutrophication of water bodies.

The presence of phosphate industry in Sfax has led to a major problem of water pollution. For this reason, it becomes necessary to evaluate the capacities of some low-cost sorbents to eliminate phosphate ions from water. In this respect, several methods have been developed, among which chemical precipitation (with aluminium, iron and calcium salts), biological processes that rely on biomass growth (bacteria, algae, plants) or intracellular bacterial polyphosphate accumulation [1] and sorption (natural apatite, activated carbon, etc.) [2]. The later method would be comparatively more useful and economical than the others for this aim. Therefore, in recent years considerable attention has been paid, based on economical and environmental concerns, to the investigation of different types of low-cost sorbents, such as alum sludge [3], red mud [4–6], fly ash [7,8], calcite [9], goetite [10], birnesite [11], apatite [12], zeolite (clinoptilolite) [13] and other waste materials [14,15].

Recent studies have shown that some filtration materials such as sand and burned clay coated with oxides (oxyhydroxides) of iron, aluminium or manganese, act as good and inexpensive sorbents [16,17] for both cations (Pb^{2+} [18,19], Mn^{2+} [20]) and anions (PO_4^{3-} [16], AsO_4^{3-} [21]). Sorption on oxide coated sor-

bents can also allow retention of pollutants that are not removed by conventional treatment methods [22]. It is to note that investigations of these coated sorbents were based on the fact that elimination of iron and manganese ions from water is much highly improved by using old sand filters (which become coated during use) than new ones [21–25]. Iron oxides, available only as fine powders, have been also used to eliminate heavy metals from aqueous solutions [23,26,27]. However, the adsorbent properties of these powders were not fully exploited in wastewater treatment operations because of difficulties associated with their separation from the aqueous phase [23].

The sorption efficiency does not only depend on water pH and on the toxic element concentration but also on interfering competitive ions as well as on adsorbent particle size [28–33].

This study investigates the convenience of three sorbents (iron oxide coated sand, iron oxide coated crushed brick and natural iron oxide coated sand) for the removal of phosphate ions from synthetic aqueous solutions by batch experiments. After characterization of sorbents, the effects of some operating parameters (contact time, initial pH, phosphate concentration and temperature) are studied.

2. Materials and methods

2.1. Sorbents

Two materials, sand and crushed brick, were coated before use in this work.

The effective size of the used sorbents ranged from 0.7 to 1 mm and from 0.8 to 2 mm for sand and crushed brick, respectively. Sorbents were first soaked in an acid solution (HCl 1 M) for 24 h, rinsed with distilled water and then dried at $105 \pm 2\,^{\circ}$C.

The coating process of these sorbents was carried out as described by Lo et al. [34] and adopted by other authors [29,35].

Stock solution of 0.25 M Fe(III) was prepared by dissolving $Fe(NO_3)_3 \cdot 9H_2O$ in distilled water. The coating of 100 g of each sorbent was performed by adding 100 ml of the Fe^{3+} solution. The final pH was adjusted to about 9 with 6 M NaOH. Later, the iron coated sorbent was washed with distilled water until rinsing water became neutral, then the sorbent was dried at $200\,^{\circ}$C for 5 h and finally stored in polystyrene bottles for further use.

According to Benjamin et al. [23], this treatment leads to the formation of an iron oxide layer of about 1–2 mg/g of sorbent.

The third sorbent used in this study consisted of a naturally iron oxide coated sand collected from the Nafza iron ores located at the North West of Tunisia (effective size < 100 μm). It was used without any preliminary treatment.

2.2. Chemicals

Aqueous solutions containing phosphate ions (PO_4^{3-})[1] at various concentrations were prepared from sodium phosphate

salt (NaH_2PO_4). The initial pH of the solutions was adjusted by adding either nitric acid or sodium hydroxide.

All chemicals used for the treatment of the different sorbents ($Fe(NO_3)_3 9H_2O$, NaOH, HNO_3, HCl) and for sorption tests were of analytical quality. All solutions were prepared using deionised water.

Measurements of the initial and final pH of the phosphate ion solutions were carried out using a laboratory pH-meter (model pH 540 GLP) equipped with a combined glass electrode (SENTIX 41). A preliminary calibration is systematically carried out using suitable buffer solutions.

UV-V spectrophotometer (HITACHI U 2000) was used to determine total phosphate concentration using the ascorbic acid method. The selected wavelength was 880 nm.

Metallic species in the different solutions were analysed by atomic absorption spectrophotometry (HITACHI Z-6100).

2.3. Mineral identification of sorbents

The quantity of iron deposited on sorbent was measured after dissolution in nitric acid.

For SCS and CB, the nitric digestion solutions obtained for uncoated sorbents were considered as blanks.

Each sample was mixed at $50\,^{\circ}$C with 10 ml of concentrated nitric acid, then with 20 ml of diluted nitric acid (0.1 N HNO_3). The obtained suspension was filtered and the filtrate was adjusted to 100 ml with distilled water before iron analysis.

All sorbents before and after coating were characterized by IR spectral analysis. An IR transmittance spectrum of the ground sample was obtained in the 4000–500 cm^{-1} range using a SHIMATZU IR 470 spectrometer. The spectra were taken from thin KBr pellets prepared by compacting an intimate mixture of 1.5 mg of sorbent and 300 mg of KBr.

Phases present in the samples were analysed using an X-ray diffractometer (Siemens, Germany) with Cu Kα radiation ($\lambda = 0.154$ nm). Scans were conducted from $0°$ to $60°$ at a rate of 2θ/min.

The specific surface area (m^2/g) of each sorbent before and after coating was determined by the single point BET (N_2) adsorption procedure.

The powder morphology of sorbents before and after coating was obtained using a Philips XL 30 scanning electron microscope (SEM). Elemental spectra were obtained using energy dispersive X-ray spectroscopy during SEM observations.

2.4. Batch experiments

Batch experiments included: the kinetic studies, pH effect and sorption isotherms.

Sorption experiments for the kinetic study were conducted as follow: 1 g of each coated sorbent was suspended in 25 ml solution containing 10 mg/l of phosphate ions. The solution pH was adjusted to 5 with 1 M HNO_3 and 1 M NaOH. The suspensions were stirred for different time intervals.

To determine the influence of pH on phosphate ion sorption, experiments were performed at various initial pH, ranging between 2.3 and 10.8. Initial concentration of 10 mg/l of phos-

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[1] The symbolization of the phosphate ions by PO_4^{3-} does not translate the form under which these ions exist according to the solution pH.

phate ions and 1 g of sorbent per 25 ml of solution were used. The suspensions were stirred for 2 h.

Sorption isotherm studies were conducted by adding 5 g of each coated sorbent to a 250 ml solution containing various phosphate ion concentrations (5, 10, 15, 20, 25, 30 mg/l).

The initial pH was maintained at 5 and the suspensions were stirred for 2 h. After filtration through a 0.45 μm membrane filter (MFS), the filtrates were analysed.

In order to determine the effect of temperature on sorption phenomenon, isotherms were established at 10, 20 and 40 °C.

3. Results and discussion

3.1. Physicochemical characterization of sorbents

3.1.1. Determination of iron oxyhydroxide deposit onto each sorbents

As shown in Table 1, the quantity of iron deposit onto natural coated sand is higher than those of the artificially impregnated sorbents. This result leads us to predict good sorption performances for the naturally coated sand compared to synthetic ones.

It is to note that the quantity of iron deposit obtained in this work (Table 1) for the artificially impregnated sorbents was found to be higher than that generally mentioned in the literature, which is about 2 mg/g of sand [34]. This reflects the effectiveness of the coating process used in this study.

3.1.2. Specific surface area

Specific surface areas for uncoated and coated sorbents are listed in Table 1. The data show that the deposited iron oxide contribute to an increase in the surface area. These results confirm those obtained for the quantity of iron deposited and affirm the beneficial part which the deposited oxide play.

3.1.3. X-ray diffraction analysis of coated materials

The two diagrams obtained for uncoated and coated sand (Fig. 1a) are almost identical and characteristic of quartz. However, the XRD pattern of iron coated sand show that a new narrow peak appeared. This peak corresponding to a $d_{hkl} = 3.018$ Å is attributed to the iron oxide deposit [24,30].

Examination of the XRD patterns of uncoated and coated brick (Fig. 1b) reveals also the formation of iron oxide as evidenced by its diffraction peak corresponding to a $d_{hkl} = 3.022$ Å. The increase in the intensity of the peak in this case is associated

Table 1
Quantity of deposited iron oxide on sorbents (SC, coated sand; BC, coated brick; NCS, natural coated sand) and specific surface area (BET) of all sorbents

Sample	Amount of deposited Fe on the sorbent (mg/g)	Specific surface area S_{BET} (m²/g)
US	0.06	1.362
SCS	3.34[a]	2.609
UB	0.91	1.466
CB	4.87[a]	3.325
NCS	5.12	6.972

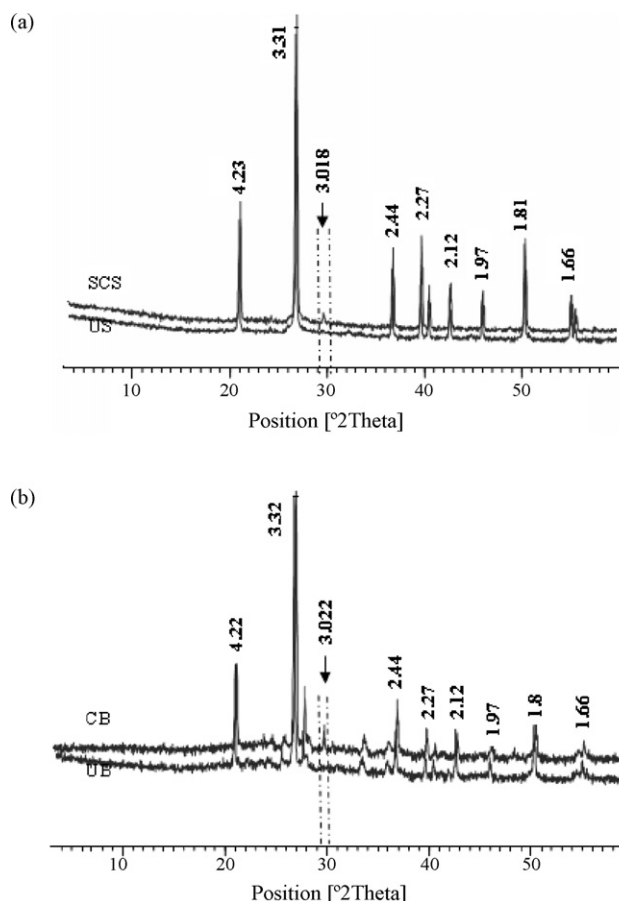[a] Results taking account of iron initially present in sorbents.

Fig. 1. XRD patterns of (a) uncoated (US) and coated sand (SCS) and (b) uncoated (UB) and coated brick (CB).

with the increase in the quantity of deposited iron oxide for the coated brick.

3.1.4. Infra-red spectroscopy analysis of coated sorbents

The infra-red absorption spectra of the sorbents before and after coating were recorded (not shown). The spectrum of uncoated sand showed three bands located at 1082, 786 and 485 cm⁻¹ and corresponding to those characteristic of silica (SiO_2). For uncoated brick, the bands located at 1079, 783.7 and 471.9 cm⁻¹ corresponds to aluminosilicate. For the coated materials, the band located at 1382 and 1382.94 cm⁻¹ for sand and brick, respectively, is attributed to the goethite FeOOH. Therefore, the iron product deposited in our conditions is an oxyhydroxide.

The infra-red absorption spectrum of natural coated sand showed that in addition to bands characteristic of silica and iron oxide, others bands appeared (3600 and 3800 cm⁻¹). They were attributed to clay.

3.1.5. Particle morphology

Optical micrographs of sand and brick surface particles before and after deposition of iron oxyhydroxide (not shown) revealed on the one hand the heterogeneity of the iron deposit on sand and the change of brick particle colour which became little more sunk as a consequence of the
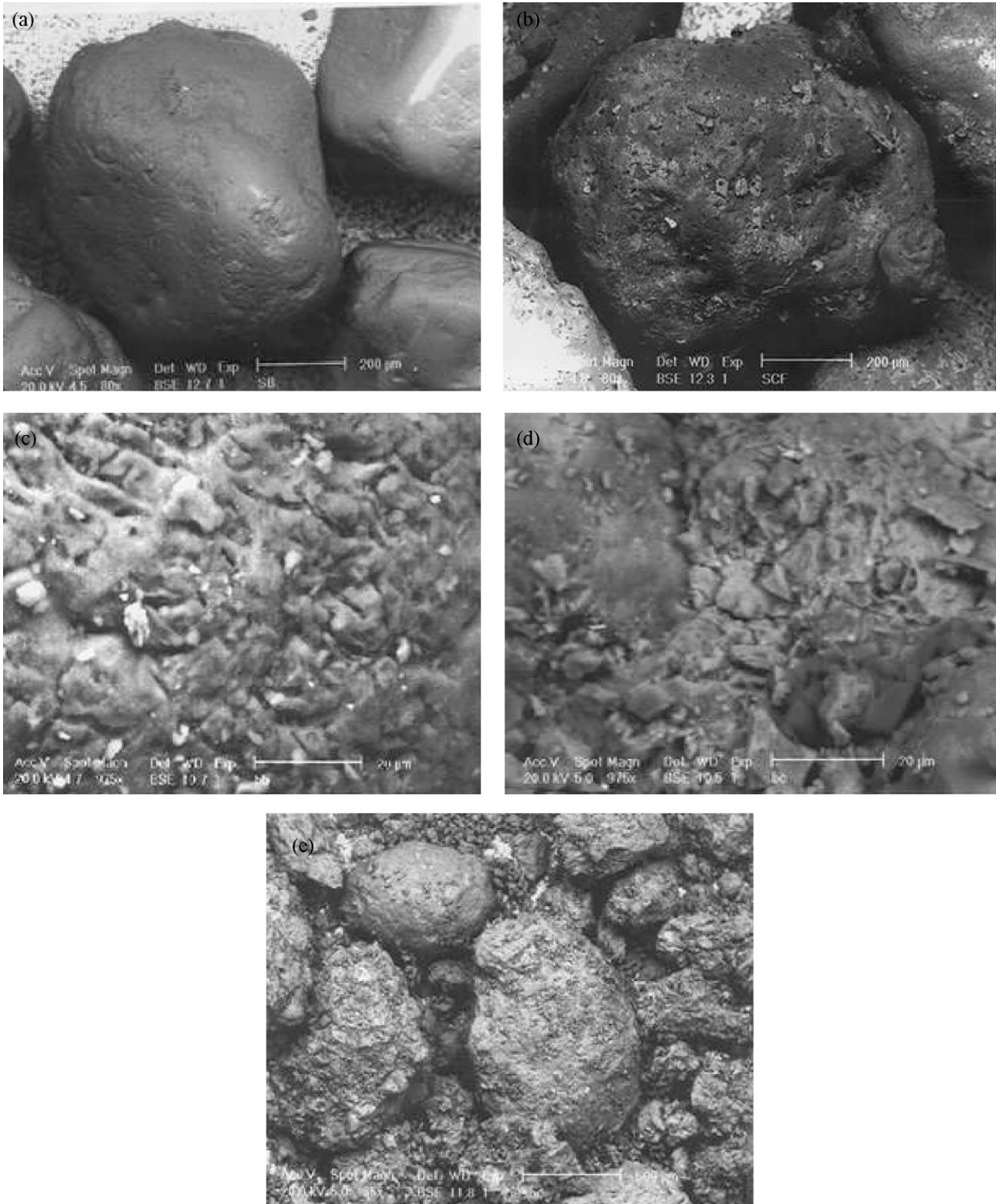
Fig. 2. SEM micrograph of sample: (a) US, (b) SCS, (c) UB, (d) CB and (e) NCS.

deposition of the iron product on their surface on the other hand.

SEM photographs of synthetic sorbents (Fig. 2) showed that the uncoated sorbents have smooth surfaces. On the contrary, the surfaces of the coated ones appeared to be rough because of the deposited iron oxyhydroxide [24]. This roughness contributed to the increase of the specific surface area already mentioned for the coated materials.

Elemental composition of the sorbents was determined from their EDAX spectra (not shown). The EDAX spectrum of sand before coating showed only the signals of quartz (SiO_2). After coating, the peak of iron appeared providing evidence for the presence of iron oxyhydroxide deposit.

The EDAX spectra of brick before and after coating, showed the presence in both cases of various peaks characterizing magnesium, potassium, calcium and iron. After coating, the peak of iron increased in intensity.

3.2. Batch experiments

3.2.1. Kinetic study

The effect of contact time on the sorption of phosphate ions (PO_4^{3-}) was studied for an initial concentration of 10 mg/l and a fixed pH solution of 5.0. The data showed that the sorption of phosphate ions on CB and SCS was very fast and the equilibrium was reached after only 15 and 25 min, respectively (Fig. 3). For longer periods, sorption trend seems to remain constant. In the case of NCS, the equilibrium was reached after a contact time of 60 min. It is interesting to notice that the fixation capacities of phosphate ions on these sorbents are different despite the same experimental conditions. The differences in sorption capacities for the different sorbents can be related to the differences of their surface areas.

In order to ensure that the equilibrium time was largely attained, subsequent experiments were carried out at a contact time of 2 h for all sorbents.

3.2.2. Effect of initial pH

When the initial pH of the solutions increases from 2.3 to 10.8, the removal of phosphate ions increases first and then decreases (Fig. 4). The maximum sorption capacity is observed at around pH 5. According to other works dealing with sorption of phosphate ions on hematite and Al_2O_3 [36], ion exchange fiber [37], alunite [38] and bauxite [39], the removal decreases continuously for pH values ranging between around 4 and 10.

The decrease in the phosphate ion uptake, occurring beyond pH 5 (Fig. 4), implies probably a competition between phosphate
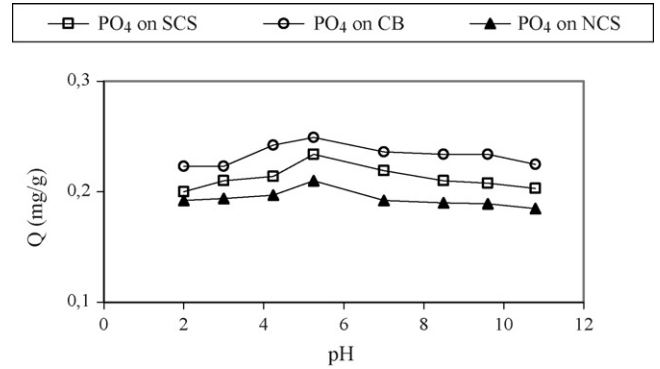
Fig. 4. Effect of pH on sorption of PO_4^{3-} on all used sorbent, $[PO_4^{3-}] = 10$ mg/l.

and hydroxyl ions for the sorption on the surface Lewis acid sites of the sorbent.

The sorption of phosphate onto hydroxylated mineral surface can be described by a ligand exchange mechanism [40,41], which causes an increase in pH due to the hydroxyl ions released from the oxidic sorbent. In the present study, the final pH was found to be >8.0 for all the initial pH values studied. This confirms that such a mechanism operates in the adsorption of phosphate on the Fe(III) oxyhydroxide surface.

3.2.3. Retention of PO_4^{3-} by coated sorbents at 20 °C

Phosphate ion sorption isotherms obtained for coating sorbents are shown in Fig. 5. These isotherms represent the sorption behaviour of phosphate ions on the different sorbents as a function of increasing aqueous phosphate concentration, for a contact time of 2 h.

The Freundlich isotherm model used for phosphate sorption (Fig. 6) is the earliest known relationship describing the sorption equilibrium. This fairly satisfactory empirical model can be used for non-ideal sorption and is expressed by the following equation:

$$Q = K_F C_e^{1/n} \qquad (1)$$

where K_F and n are constants related to the sorption capacity and affinity, respectively. The equation is conveniently used in the linear form by taking the logarithm of both sides as:
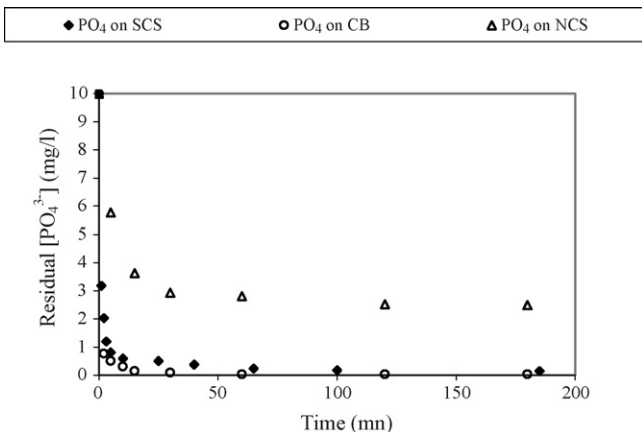
$$\log(Q) = \log K_F + 1/n \log C_e \qquad (2)$$

Fig. 3. Kinetic study for phosphate ion sorption on all sorbent, 5 g solid/250 ml, $[PO_4^{3-}] = 10$ mg/l.
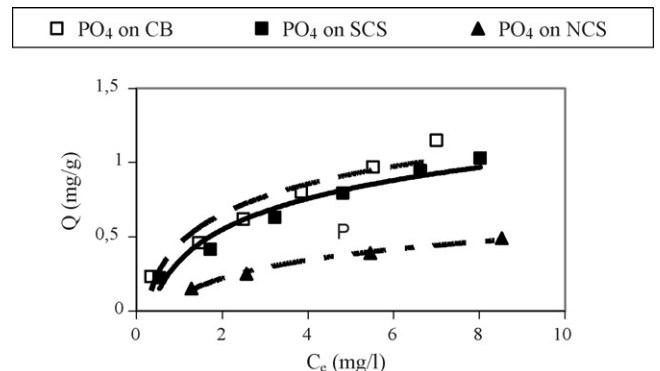
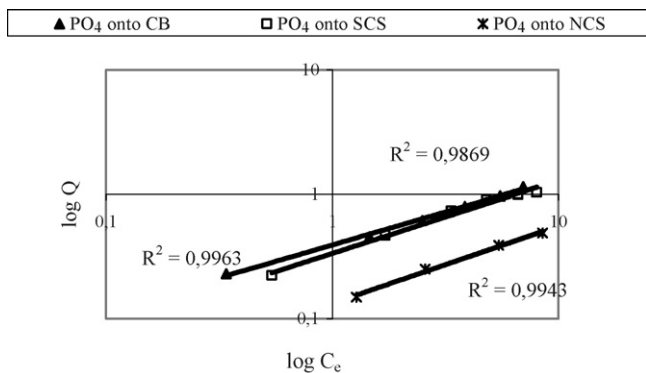Fig. 5. Sorption isotherms of PO_4^{3-} on all used sorbent.

Fig. 6. Freundlich isotherms for the sorption of PO_4^{3-} at 20 °C on SCS, CB and NCS.

The Freundlich isotherm constants obtained for the sorption of phosphate ions at 20 °C on the different sorbents are mentioned in Table 2. The data showed that the K_F constant remained higher for coated crushed brick than for the two other sorbents. Values obtained of $1 < n < 10$ imply favourable sorption of phosphate ions for all sorbents [17]. This is an agreement with the observations of previous reports on the sorption of anions onto oxide surfaces [17,23].

The results of phosphate ion sorption onto all sorbents (Fig. 5) were also analysed by using the Langmuir model to evaluate parameters associated to the sorption behaviour. The linear form of Langmuir equation at a given temperature is represented by:

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q} \tag{3}$$

where C_e is the aqueous phase equilibrium concentration (mg/l), q_e the amount of phosphate ions sorbed onto 1 g of the considered sorbent, b the sorption constant (l/mg) related to the energy of sorption and Q is the maximum sorption capacity (mg/g).

For the three sorbents the sorption data fit to the linear form of the Langmuir equation (Fig. 7). This linear plot was employed to obtain the values of Q_0 and b from the slope and intercept of the plot (Table 2). The correlation coefficients (R^2) given in
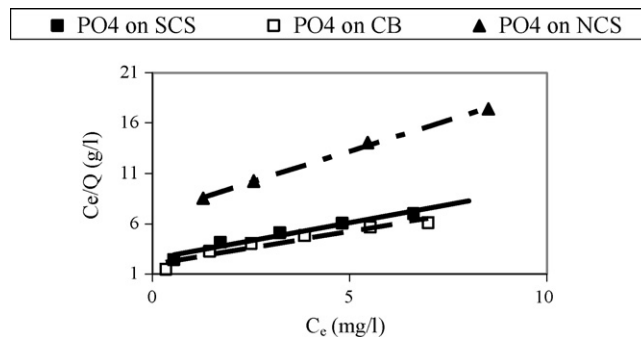

Fig. 7. Langmuir isotherms for the sorption of PO_4^{3-} at 20 °C on SCS, CB and NCS.

Table 2 show that the Langmuir equation gives also a fairly good fit to the sorption isotherms.

Results in Table 2 show that Q_0 remains the highest for phosphate ion sorption onto coated crushed brick followed by coated sand and then by naturally coated sand.

3.2.4. Effect of temperature

The free energy change is obtained using the following relationship:

$$\Delta G° = -RT \ln b \tag{4}$$

where R is the gas constant, b the equilibrium constant (obtained from Langmuir equation) and T is the temperature (K). The negative values obtained for $\Delta G°$ indicate the spontaneous nature of sorption (Table 3). Other thermodynamic parameters such as enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) are evaluated using Van't Hoff equation:

$$\log b = \frac{\Delta S°}{2.303R} - \frac{\Delta H°}{2.303RT} \tag{5}$$

Values of $\Delta H°$ and $\Delta S°$ were calculated from the slope and intercept of the Van't Hoff linear plot of $\log b$ versus $1/T$ (Fig. 8). The positive values of $\Delta H°$ (Table 3) confirm the endothermic nature of sorption. The positive values of $\Delta S°$ show the increased

Table 2
Freundlich and Langmuir constants for PO_4^{3-} sorption at 20 °C on all sorbent

	Freundlich constants			Langmuir constants		
	K_F	$1/n$	R^2	Q (mg/g)	b (l/mg)	R^2
PO_4^{3-} on SCS	0.314	0.578	0.990	1.5	0.20	0.9985
PO_4^{3-} on CB	0.392	0.529	0.98	1.75	0.23	0.9963
PO_4^{3-} on NC S	0.0723	0.867	0.99	0.88	0.17	0.9939

Table 3
Thermodynamic parameters for the adsorption of PO_4^{3-} at various temperatures on SCS, CB and NCS

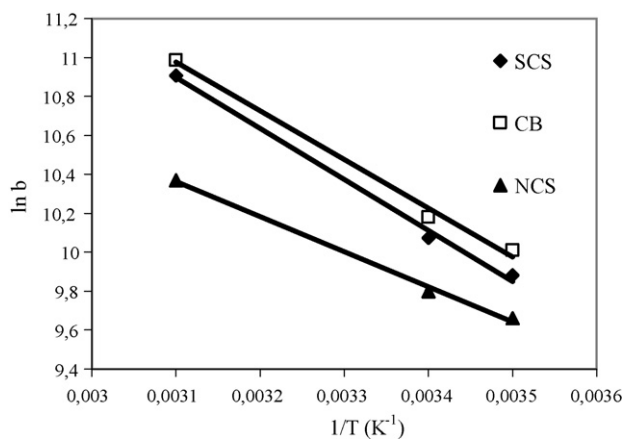| Temperature (°C)	SCS			CB			NCS		
	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (kJ/(kmol))	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (kJ/(kmol))	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (kJ/(kmol))
10	−23.68	20.76	0.155	−23.94	21.73	0.157	−23.04	14.98	0.132
20	−24.51	20.76	0.155	−24.78	21.73	0.157	−23.86	14.98	0.132
40	−26.19	20.76	0.155	−26.47	21.73	0.157	−25.49	14.98	0.132

Fig. 8. Vant't Hoff plot for the sorption of PO_4^{3-} on all considered sorbent, $[PO_4^{3-}] = 10\,mg/l$.

randomness at the solid/solution interface during the sorption of PO_4^{3-}.

3.2.5. Solid phase examination after sorption of phosphate ions

Examination of the solid phases after sorption of phosphate ions by SEM was carried out on the three sorbents. EDAX analysis (Fig. 9) provides the direct evidence for the sorption of phosphate ions on the surface of all sorbents whether they were naturally or artificially coated.
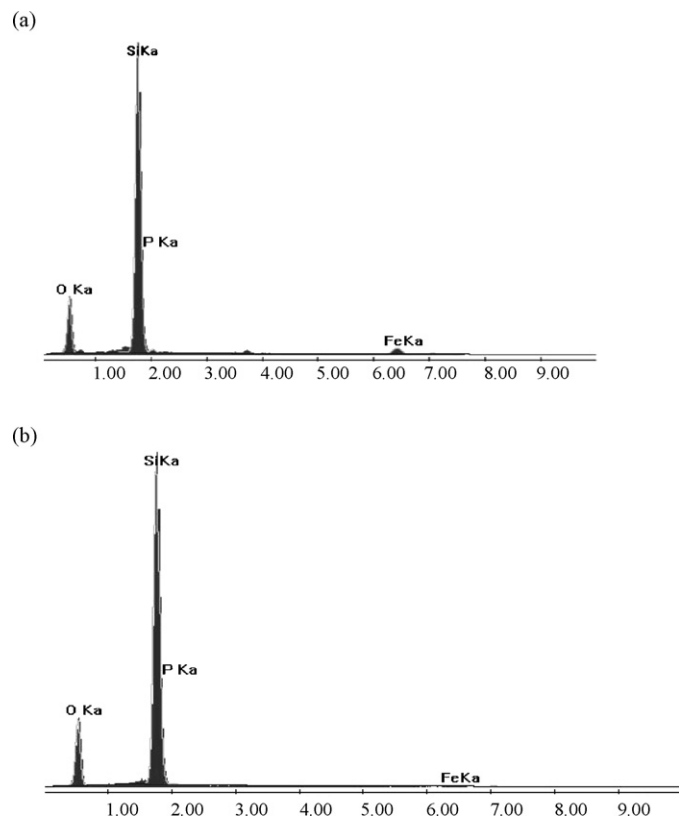
(a)

(b)

Fig. 9. EDAX spectrum of (a) SCS under adsorbed phosphate ions (100 mg/l of PO_4) and (b) NCS under adsorbed phosphate ions (100 mg/l of PO_4).

4. Conclusion

The results reported here can provide a process for developing a low-cost technology based on sorption by artificially iron oxide coated sand and crushed brick for phosphate ions removal from water. The performances of these two sorbents were compared to those of a naturally iron oxide coated sand.

The wide range of experiments performed showed essentially that:

- the three coated sorbents had a higher specific surface area due to their iron oxide deposits, and they can efficiently remove phosphate ions from contaminated water;
- infra-red spectral analysis showed that the iron compound deposited in our experimental conditions on sand and brick is the oxyhydroxide FeOOH;
- the sorption of phosphate ions depended on the solution pH. Maximum retention of phosphate occurred at around pH 5;
- for the sorption isotherms of phosphate ions, both Langmuir and Freundlich equations were fitted to experimental data satisfactory.

These results lead to classify the iron oxide coated materials as new low-cost sorbents of some well-known sorbents for wastewater clean up.

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