

Optimized Activation of Bentonite for Adsorption of Magnesium and Cadmium from Phosphoric Acid

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Abstract: The adsorption of magnesium (II) and cadmium (II) from industrial phosphoric acid onto 4 samples of clays: crude (a), purified (b), activated (c) and purified-activated (d) bentonite have been studied using a batch adsorber. The parameters that affect the magnesium (II) and cadmium (II) adsorption, such as bentonite amount, temperature, contact time and solution pH have been investigated and optimized conditions determined (bentonite amount 12g/ 100mL of industrial phosphoric acid; temperature 293.15 K; contact time 15 min; pH 1.78±0.1). The loading capacity values were found respectively to be 51.21% and 56.25% for magnesium and cadmium using the purified-activated bentonite.

Keywords: Phosphoric Acid, Bentonite, Adsorption, Magnesium, Cadmium

1. Introduction

The heavy metals are always present as impurities in the manufacturing process of industrial phosphoric acid (IPA) and phosphated fertilizers. The industrial wet process phosphoric acid uses sulphuric acid to leach the phosphate rock, whereas in the alternative process, nitric acid is used. In both cases, the leach liquor obtained is a complex solution with organic and inorganic impurities (heavy metals). The removal of heavy metals from these effluents is environmentally important referring mainly to their toxicity [1]. It is for this reason that historically, the wet process produced phosphoric acid has not been used in the food, detergent and in other industries where high-purity acid is necessary, only phosphoric acid produced by the thermal route with higher purity was used. Because of the large quantities of energy required to manufacture thermal phosphoric acid, its cost has raised considerably, the separation techniques have therefore been developed to purify wet-phosphoric acid so that it can replace the thermal phosphoric acid [2]. Separation processes of heavy metals based on precipitation [2–4] and solvent extraction by

organophosphorus and organophosphorus derivatives [5–9] have been proposed to deal with the problem. This led us to search for methods of treating the least expensive and most feasible. The choice focused on the process of adsorption by Tunisian bentonite of Oued Tfal [10]. The clays used are purified, activated and purified-activated.

Many authors [11, 12, 13] reported the physicochemical properties and the methods of preparation of purified and activated bentonite. Few researchers have used bentonite for the adsorbability of heavy metals and other impurities such as organic matter [14, 15, 16] from phosphoric acid.

In this paper, the effect of the adsorbent bentonite amount, temperature, contact time and solution pH have been investigated and optimized conditions determined.

2. Material and Methods

2.1. Industrial Phosphoric Acid

The phosphoric acid used in this investigation contains numerous impurities; the chemical analysis of IPA is measured and the results are shown in table 1

Table 1. Chemical analysis of Tunisian industrial phosphoric acid 28% of P₂O₅ (GCT).

Cd ²⁺ (ppm)	SiO ₂ %	Solid matter%	Al ₂ O ₃ %	Fe ₂ O ₃ %	Cl ⁻ %	P ₂ O ₅ g/L	SO ₃ %	Fluor%	Density	MgO%	CaO%	P ₂ O ₅ %
16	0.12	0.57	0.31	0.20	0.62	333.8	0.79	0.46	1.272	0.82	0.23	26.17

2.2. Bentonite

Crude bentonite

The Bentonite, which was used, collected from the deposit of "Wad Tafal" of "Gafsa", located in south Tunisia. The cation exchange capacity (CEC) determined by the methylene blue method before purification was about 54,23 meq/100g air-dried bentonite.

Purified bentonite

The content of impurities was decreased or removed completely by applying a purification protocol proposed by H. van Olphen [17]. This was achieved by dispersing the crude lumps in hydrochloric acid solution (0,1M) to facilitate elimination of carbonates by controlled acid attack but not to destroy the structure of the used clay.

This argillaceous suspension is agitated mechanically during 4 hours then centrifuged at 3500 rpm during 15 min. Supernatant is removed, the remaining argillaceous fraction is mixed by 400 ml of NaCl solution (1M). The clay suspension is shaken for 12 hours. Then centrifuged at a speed of 3000 rpm for 5 minutes. The clay phase is recovered and the NaCl solution is rejected. This cycle of agitation-centrifugation is carried out under the same conditions in order to exchange the interfoliaceous cations against those of sodium and to eliminate impurities by sedimentation is repeated 7 times.

After these exchanges, clay is washed 3 times with distilled water. The suspension obtained is put in dialysis membranes making it possible by osmosis to eliminate the

chloride ions adsorbed on the surface from the layers. The dialysis water is renewed until what the test with silver nitrate indicates the absence of ions chloride. The purified clay suspension is then dried in an oven at a temperature not exceeding 60°C in order to activation later. The cation exchange capacity (CEC) determined by the methylene blue method after purification was about 93,28meq/100g air-dried bentonite.

Activated bentonite

Acid-activation [13] was carried out with sulfuric acid (1.5M) in a jacketed glass reactor equipped with a reflux condenser, a thermometer and a stirrer. At the end of each experiment, the solid content was immediately filtered, washed free of sulfate with hot water until the washing water was neutral, and dried at 110°C for a few hours, in order to obtain dehydrated samples and a constant mass. The cation exchange capacity (CEC) determined by the methylene blue method after activation was about 73,33meq/100g air-dried bentonite.

Purified-activated bentonite

The purified bentonite must be activated later by the same method described for the purification and activation, The cation exchange capacity (CEC) determined by the methylene blue method after purification activation was about 120,82 meq/100g air-dried bentonite.

Table 2 presents the chemical composite of the crude bentonite "WTcr", simple activated bentonite "WTa", purifying bentonite "WTp" and purified-activated bentonite "WTpa" at 20°C.

Table 2. Chemical composition (in wt%) of the bentonite.

M _x O _y (%)	SiO ₂	Al ₂ O ₃	MgO	Na ₂ O	K ₂ O	Fe ₂ O ₃	CaO	P ₂ O ₅	MnO	Ignition loss
WTcr	50.09	22.52	1.25	0.66	0.95	6.18	17.04	0.20	0.03	25.24
WTp	61.05	27.98	1.68	0.28	1.05	5.79	1.46	0.05	0.02	12.66
WTa	58.54	19.81	1.02	0.46	0.88	5.87	12.43	0.12	0.02	22.96
WTpa	75.42	20.62	1.20	0.06	0.02	1.24	1.1	0.05	0.00	08.12

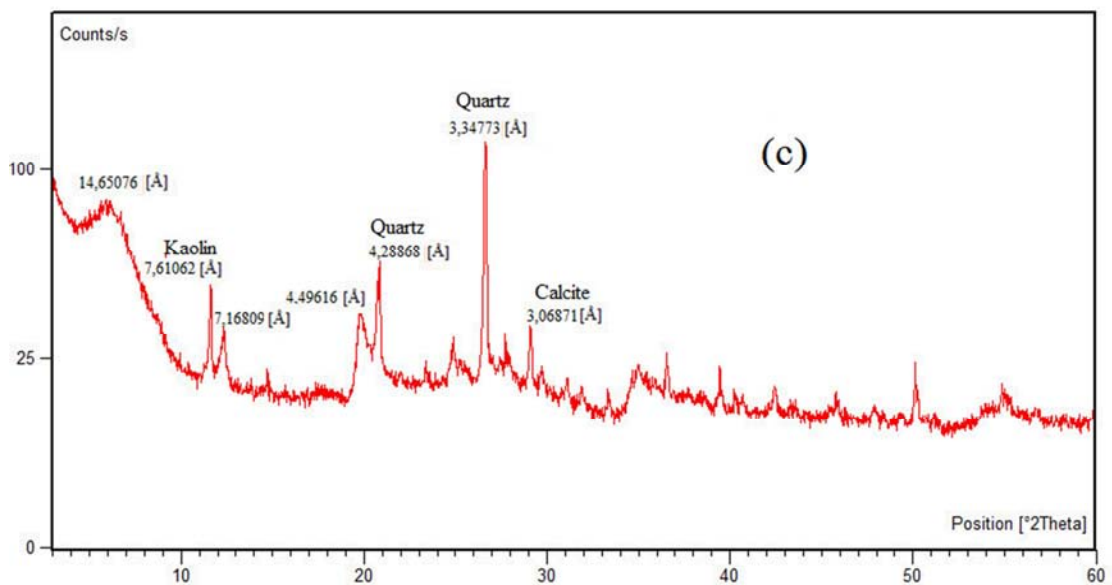
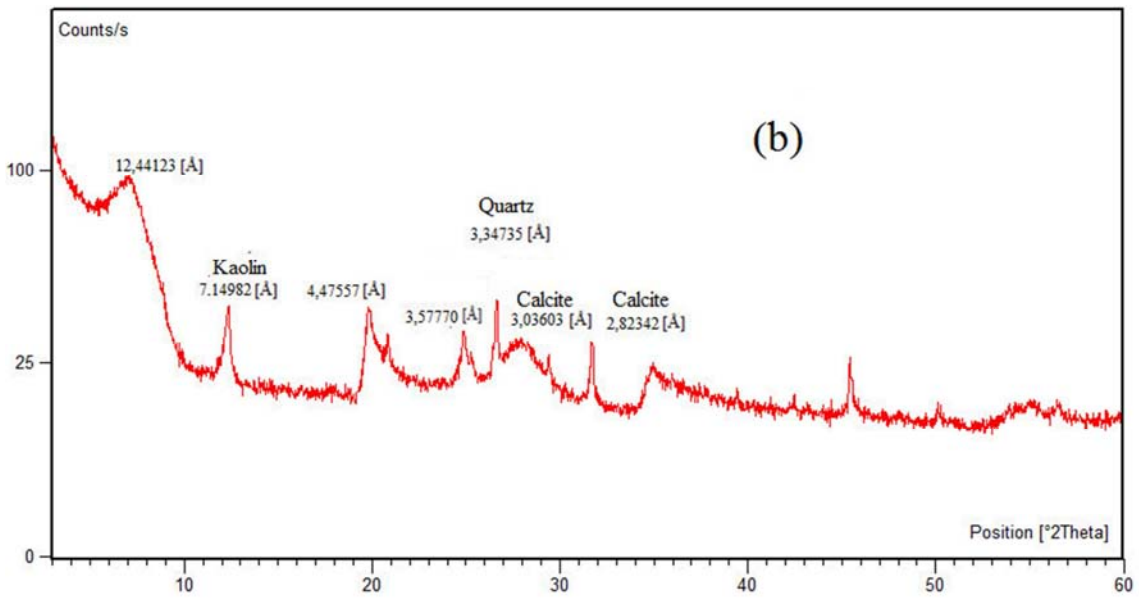
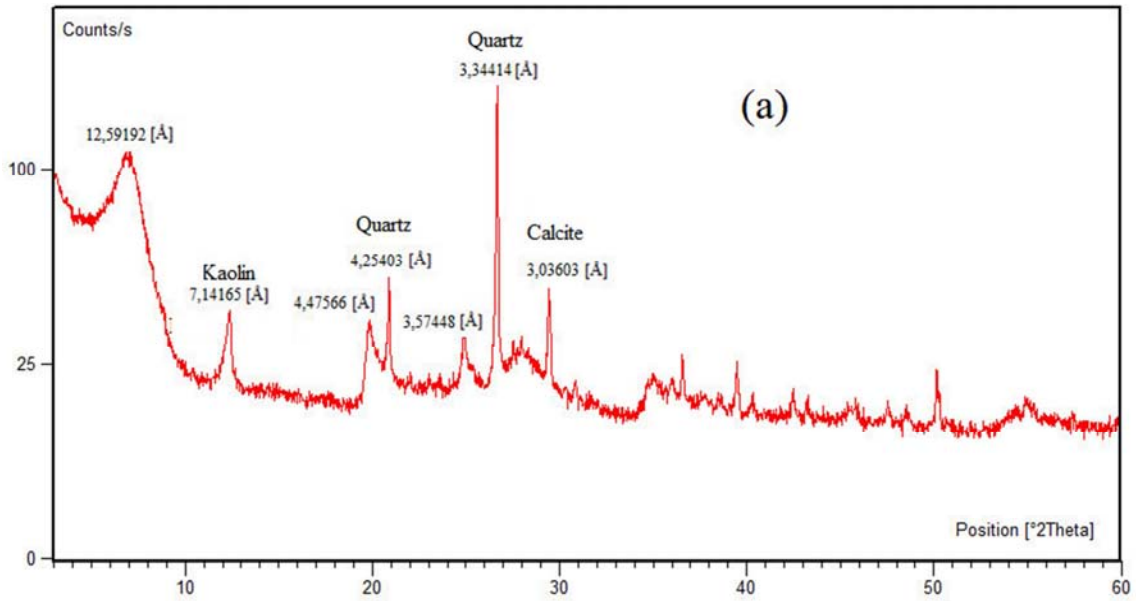
And table 3 presents the CEC of the crude bentonite "WTcr", simple activated bentonite "WTa", purified bentonite "WTp" and purified-activated bentonite

Table 3. CEC of the bentonite.

Bentonite	CEC (meq/100g)
WTcr	54,23
WTp	93,28
WTa	73,33
WTpa	120,82

Finally, an X-ray diffraction analysis (PANalytical X-Ray Diffractometer "X'Pert PRO "WITH CERAMIC TUBE X-

ray diffraction, CU, 2.2KW SYSTEM X'Pert) and an Infrared Spectroscopy (SHIMADZU 8400S) were performed and the results presented successively in Figure 1 and Figure 2 confirms that the sample belongs to the family of montmorillonite bentonites and the distinct increase of infrared absorbency at 3610-916 cm⁻¹, confirms the dominant presence of dioctahedral smectite with Al-Al-OH stretching and bending bands. An X-ray diffraction analysis and Infrared Spectroscopy confirms that the used bentonite is purified and activated and the presence of calcite and quartz was decreased.



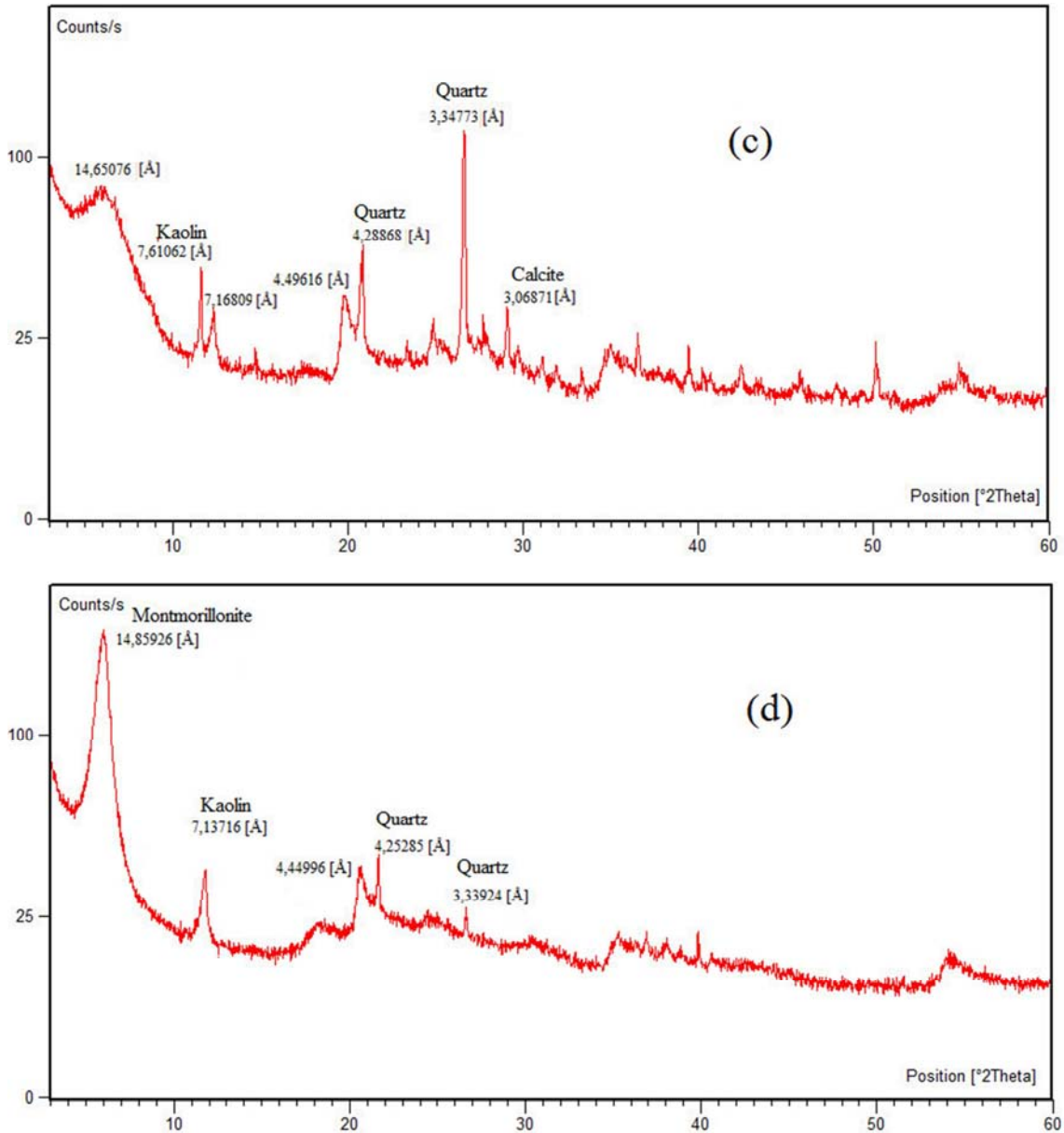
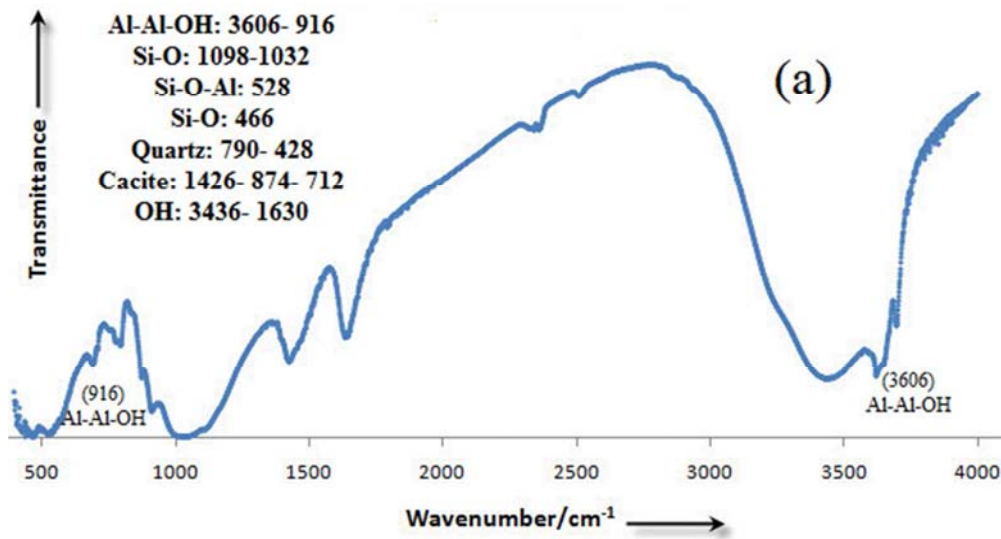


Figure 1. X-ray diffraction analysis of bentonites: Crude (a), purified (b), activated (c) and purified-activated (d) bentonite.



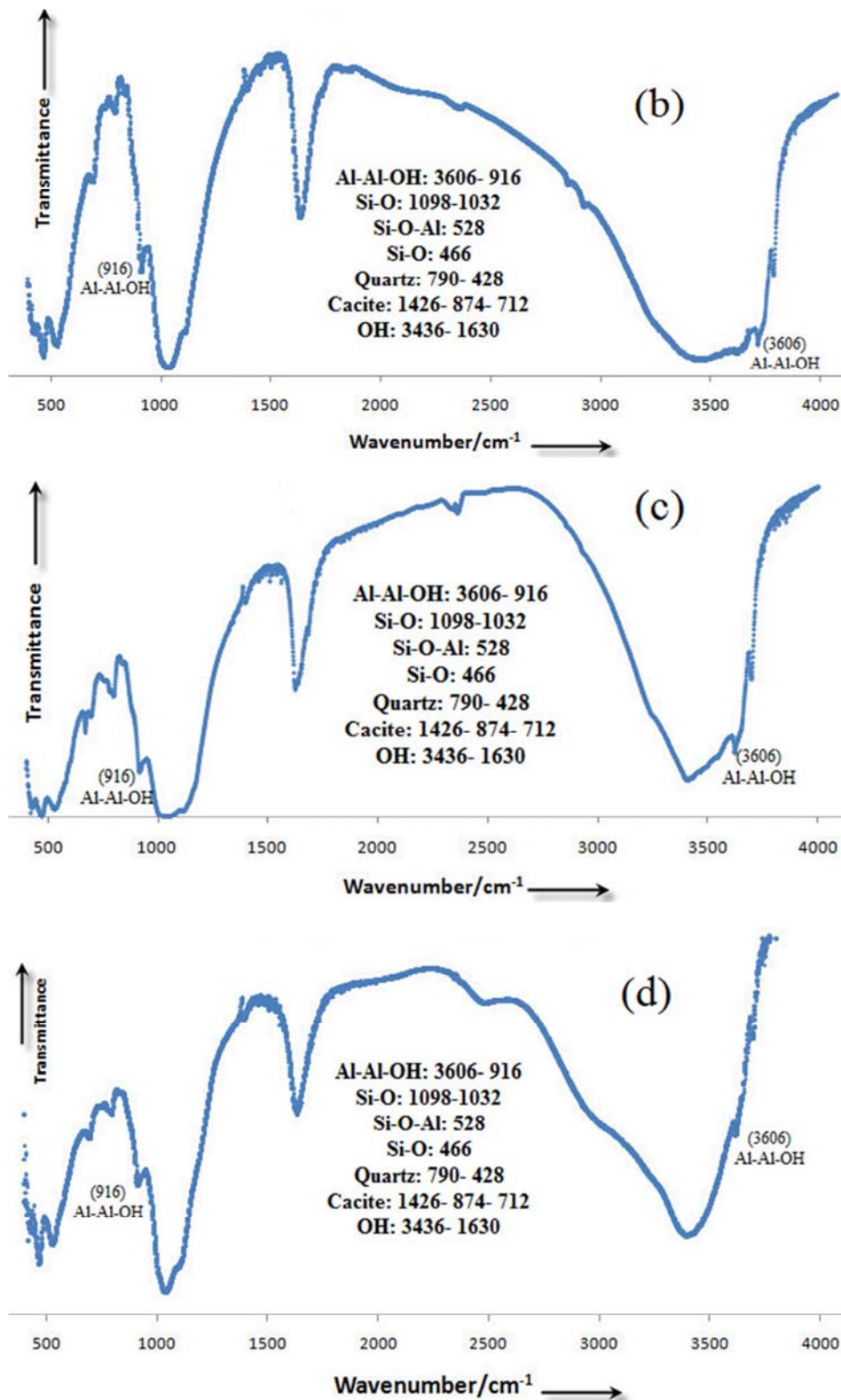


Figure 2. Infrared Spectroscopy of bentonites: Crude (a), purified (b), activated (c) and purified-activated (d) bentonite.

2.3. Batch Adsorption of Magnesium and Cadmium from Phosphoric Acid Experiments

The experiments were carried out by batch techniques. Adsorption experiments were carried out in mechanically agitated beakers containing 100 ml of phosphoric acid with

various amounts of bentonite from 0.1 to 12g. The vessel was immersed in a water bath controlled at different temperatures.

The content was agitated with a constant stirring rate of 200 rpm, because above this value, the agitation has little effect on the adsorption process [18, 19, 20]. At preset times, after shaking, the bentonite was separated from the

supernatant, aqueous samples (2 ml) were taken, and the concentration was analyzed. The batch adsorption lasted 180 min. The pH values were measured by a Taccussel digital pH meter during the experiments. The amount of adsorbed magnesium and cadmium was determined from the difference between the initial and final concentrations in aqueous solution using an atomic absorption spectrometer (novAA 400, Analytik Jena)

3. Results and Discussions

The effect of bentonite amount, temperature, contact time and equilibrium pH on the adsorption of magnesium and cadmium has been investigated and the results are reported in Figures 3–6.

3.1. Effect of Bentonite Amount

To study the influence of the mass of the bentonite on the adsorbability of impurities contained in H_3PO_4 pretreated, the tests shall be conducted at the laboratory scale with masses of bentonite in the range 0.1 to 12 g maintaining the other fixed parameters.

The change in mass of bentonite has a positive effect on yields fixation of impurities in the range 0.1 to 12 g. The results presented in Figure 3 reveal that the adsorption of magnesium and cadmium increases with an increase of amount of bentonite; this is explained by the increase of the specific surface of bentonite as a function of its mass [17]. The optimal value of the mass of bentonite is advanced to 5g.

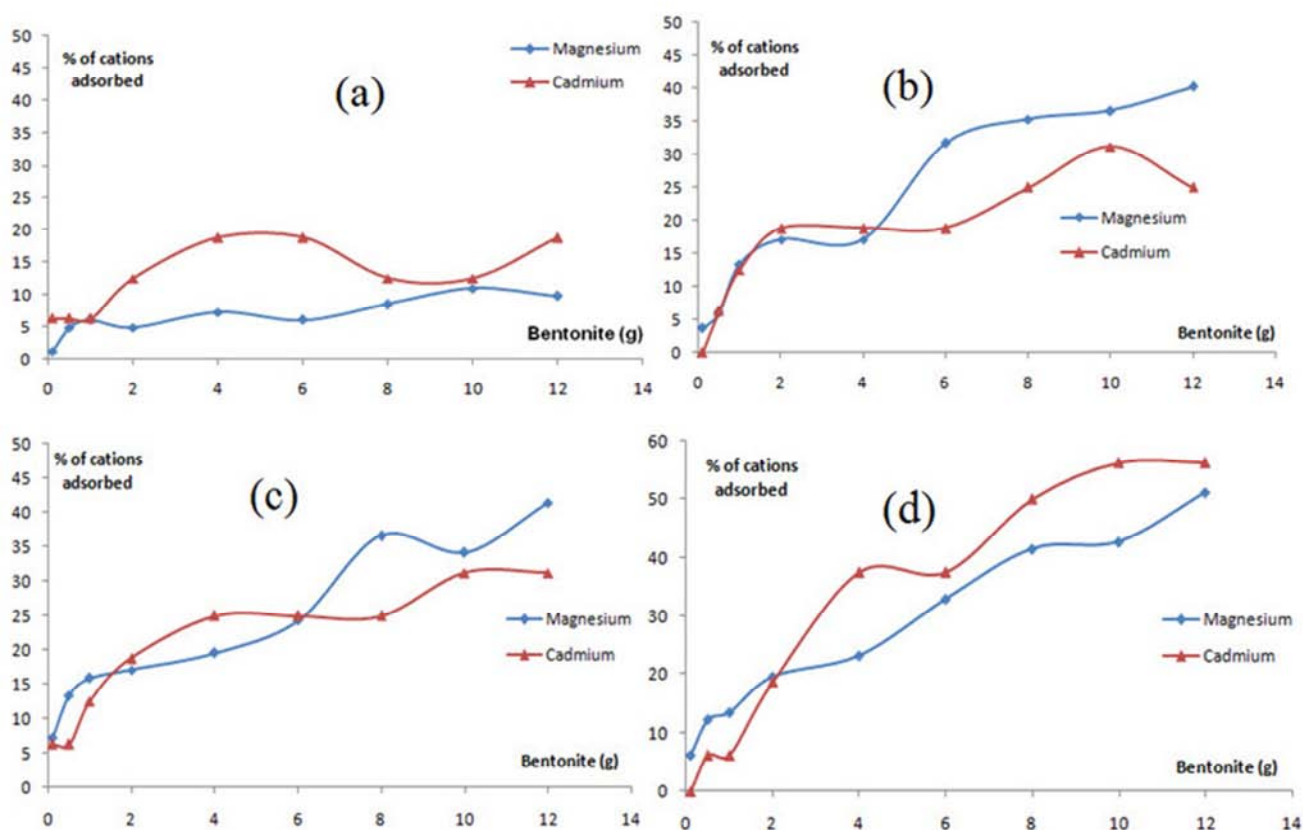


Figure 3. Effect of bentonite amount on magnesium (II) and cadmium (II) adsorption onto bentonite: Crude (a), purified (b), activated (c) and purified-activated (d) bentonite.

3.2. Effect of Temperature

The effect of temperature on the adsorbability of impurities must be studied between 20 and 100°C, keeping other parameters fixed, equilibrium pH to 1.78, mass of bentonite to 5 g and contact time of 15 min. The results obtained in Figure 4 show a decrease in yield with increasing temperature. This observation could be explained by the fact that, low temperatures favor the adsorption.

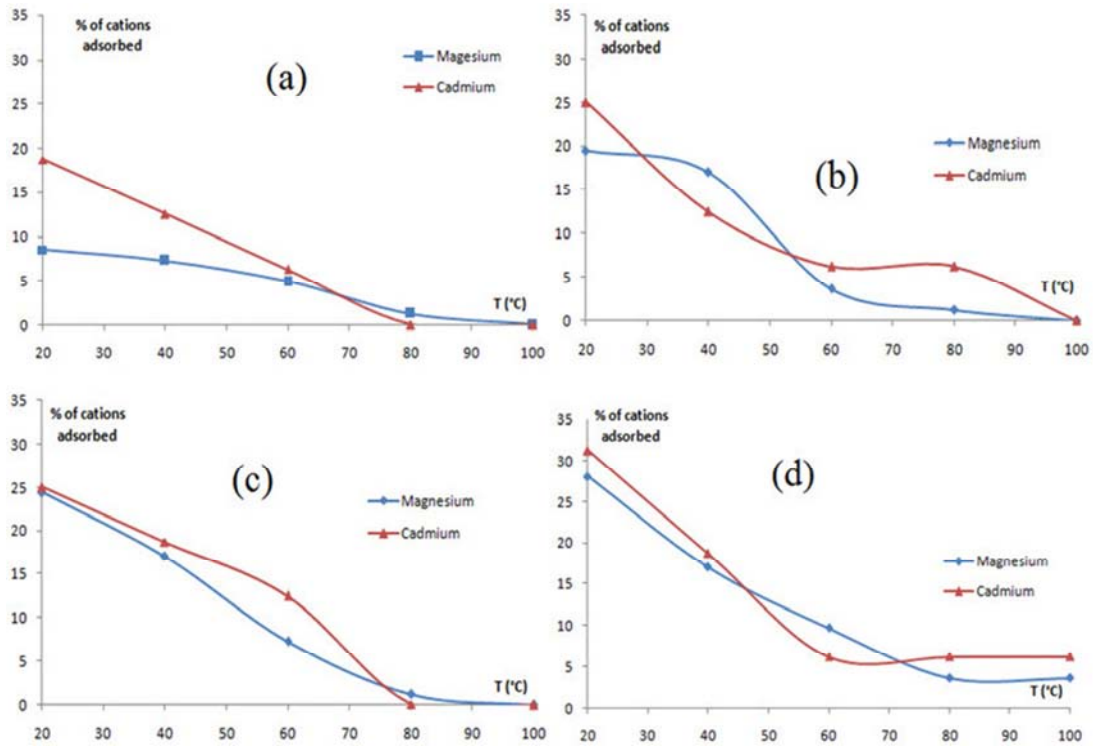


Figure 4. Effect of temperature on magnesium (II) and cadmium (II) adsorption onto bentonite: Crude (a), purified (b), activated (c) and purified-activated (d) bentonite.

3.3. Effect of Contact Time

The effect of contact time on the determination of impurities was studied between 5 min and 180 min, keeping the other parameters fixed, equilibrium pH 1.78, the mass of bentonite to 5 g, the temperature at 20 °C and stirring speed 200 rpm. The results are shown in Figure 5 reveal that the adsorption of magnesium and cadmium increases with an increase of contact time.

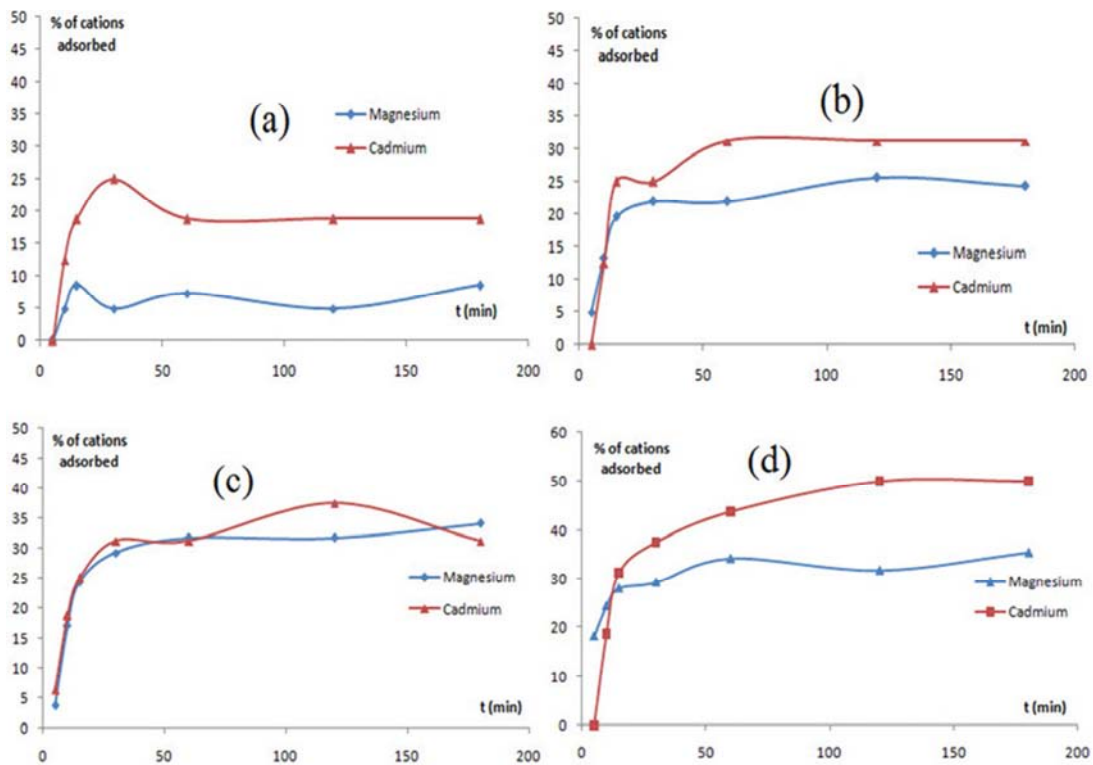


Figure 5. Effect of contact time on magnesium (II) and cadmium (II) adsorption onto bentonite: Crude (a), purified (b), activated (c) and purified-activated (d) bentonite.

3.4. Effect of Equilibrium pH

The influence of pH on the removal of Mg^{2+} and Cd^{2+} ions by bentonite was investigated. In the present work, the adsorption of Mg^{2+} and Cd^{2+} was studied in the pH range 1–3 with a constant clay amount of 5 g/100 mL of phosphoric

acid solution, a shaking time of 15 min and temperature at 20°C. The results presented in Figure 6 reveal that the adsorption of magnesium and cadmium increases with an increase in solution pH and the highest yields adsorption of impurities are obtained in the pH range between 1.5 and 3.

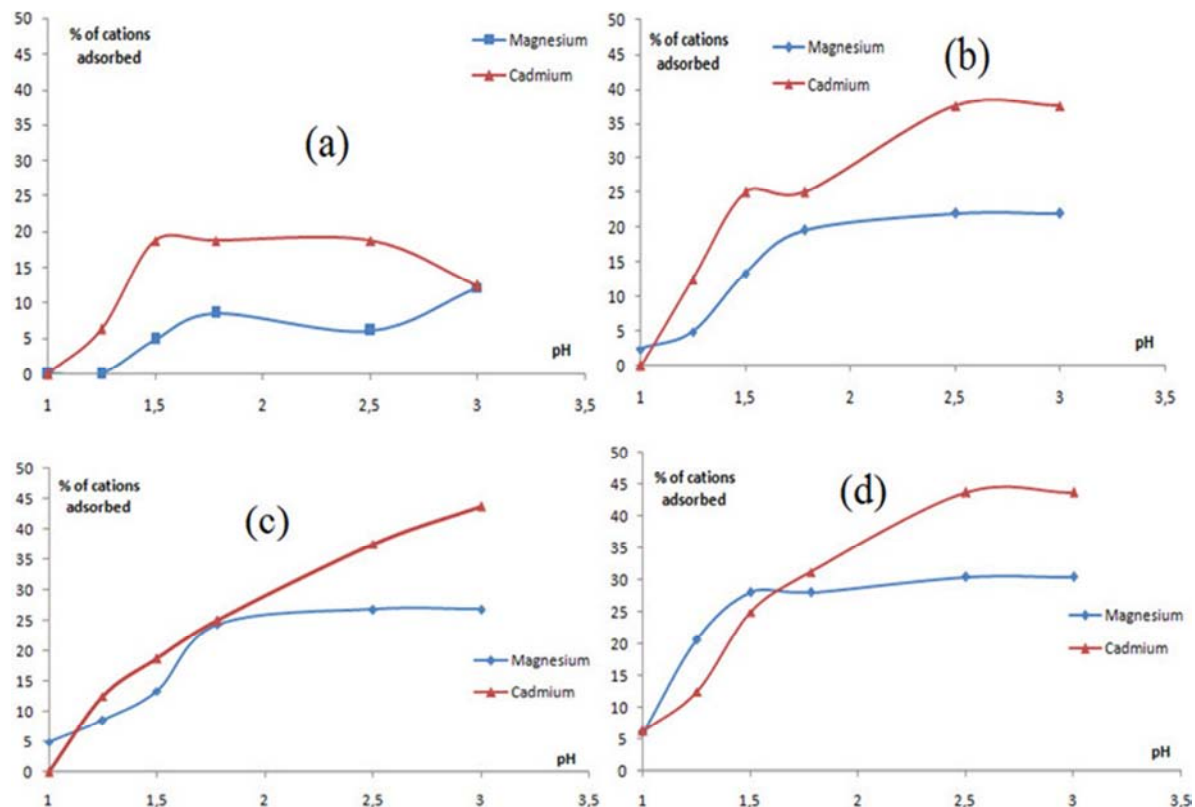


Figure 6. Effect of equilibrium pH on magnesium (II) and cadmium (II) adsorption onto bentonite: Crude (a), purified (b), activated (c) and purified-activated (d) bentonite.

4. Conclusions

The obtained results of magnesium (II) and cadmium (II) adsorption onto bentonite showed that the purified-activated bentonite WTPa has a highest cation exchange capacity, then it is the best in the study of adsorption of magnesium and cadmium from industrial phosphoric acid, because the purified-activated bentonite is pure and positively charged at the same time but the industrial phosphoric acid presents other impurities that may prevent the elimination of magnesium and cadmium such as organic matter.

The effect of the adsorbent bentonite amount, temperature, contact time and pH solutions was determined and specific conditions were determined and it was observed that the maximum removal of magnesium (II) (>50%) and cadmium (II) (>55%) was observed at pH: 1.78; temperature: 20°C, contact time: 15 min and at an amount of bentonite WTPa equal to 12 g. the temperature was found to have an inverse effect on adsorption of magnesium (II) and cadmium (II) and The contact time and the pH were found to have a positive effect on adsorption of magnesium (II) and cadmium (II).

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