Full Length Research Paper

Influence of pH on the uptake of toluene from water by the composite poly (4-vinylpyridinium)-maghnite

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The objective of this study is to investigate the effects of the degree of α ionization on the rate uptake of organic pollutant (toluene) by poly (4-vinylpyridinium)-maghnite. Two-step experiment was carried out where the organophilic maghnite adsorbent was prepared in the first step and toluene was adsorbed on maghnite in the second step. This material organophilic maghnite was prepared by exchanging the organic polycation as poly (4-vinylpyridinium) chloride (PVPS) for sodium (Na$^+$) on the layer surface of clay. This process of wastewater treatment is of interest for the wastes stabilisation in which toluene contaminations occurs. Batch adsorption studies were conducted to evaluate the effects of initial toluene concentration. The results show that the two-step process is an efficient, simple and low cost technological way for the removal of organic pollutants from water.

Key words: Adsorption, organic pollutant, P4VP, maghnite, organoclay.

INTRODUCTION

The development of technological ways for the decontamination of soils and waters polluted by hydrophobic organic compounds encouraged researchers to use polycationic surfactant as potential agents for the enhanced solubilisation and the removal of contaminants from soils and sediments (Fournanis et al., 2001; Zadaka et al., 2009; Liu, 2007). Pollution caused by organic compounds is a common problem faced by many countries and is likely the cause of health hazards, harm to ecology, damage to structures or amenities, and interference with the legal use of water. Organic contaminants include many categories of compounds, of which benzylics are recognised as hazardous chemical pollutants. Many methods are possible to taking away benzylics from effluents that are chemical oxidation, ozonolysis, flocculation, reverse osmosis, adsorption, ion exchange, and biological techniques. Adsorption

techniques are rapidly gaining prominence as a treatment process for providing high-quality effluents that are low in concentration of dissolved organics (Walker et al., 1998). A number of adsorbents, such as activated carbons, peat moss, brown coal, industrial waste, agricultural products, polymers, chitosan, and fly ash, are used for organics removal (Chang et al., 2004). Cost effectiveness, availability, and adsorption properties are the main criteria for choosing an adsorbent to take out pollutants. Some work (Li et al., 2007; Vidal et al., 2009; Breen, 1998, 1999) have shown that changes in smectites polycation could make them sufficientlyhydrophobic and easily allow the retention of aromatic hydrocarbons in water.

The aromatic hydrocarbons benzene, toluene, ethylbenzene and xylene (that is, "BTEX compounds") are of concern as water contaminants resulting from petrochemical spills and leakages. A number of workers (Jiang et al., 2002; Crini, 2005; Durand-Piana et al., 1987; Billingham et al., 1997) also showed that smectite/ polycation complexes can develop a net positive charge (Becker et al., 2000) found that anionic dyes were

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removed from wool dyeing effluent water by bentonite and cationic polyelectrolytes in combination, but not by either of these components alone. A likely interpretation of this result is that attachment of the polycations to the aluminosilicate in appropriate proportions provided a positively charged solid phase for adsorption of anionic dye molecules. These various studies indicate a need for further work to devise principles for the use of smectite–polycation complexes for water pollutant removal. In the present study poly (4-vinylpyridinium)-maghnite with degree of α ionization different were employed for removal of toluene and used as an effective adsorbent in the wastewater treatment.

MATERIALS AND METHODS

Bentonite

The bentonite (maghnite) used in this work comes from a quarry located in Maghnia (West of Algeria) and was supplied by the company "ENOF" (an Algerian manufacture specialized in the production of nonferric products and useful substances). The different chemical elements of the native bentonite were transformed into oxides and analysed by X-ray fluorescence ENOF. Its chemical composition was found to be as follows: 54.90% SiO_2, 1.85% MgO, 27.71% Al_2O_3, 0.08% K_2O, 0.08% CaO, 2.82% F_2O_3, 3.14% Na_2O, 9.4% loss on ignition. These results confirm that the bentonite used consists essentially of montmorillonite, since the ratio SiO_2/Al_2O_3 is equal to 3.77 and thus belongs to the family of the phyllosilicates (Khenifi et al., 2009; Boufatit et al., 2008). These bentonite form stable suspensions in water and have flat platelets or needle-like structures. The Na-exchanged form of bentonite was prepared by stirring samples for 24 h with 1 M NaCl. This was followed by several washes with distilled water and filtration to remove excess NaCl and other exchangable cations from the clay. The clay was then resuspended and filtered until a negative chloride test was obtained with 0.1 M $AgNO_3$ (Gupta et al., 2006).

Preparation of poly (4-vinylpyridinium)-maghnite

The solutions of Poly(4-vinylpyridinium) chloride salts (P4VPS) with degree of α ionization different equal to 0.10, 0.25, 1.00 and 1.50 were prepared by adding 0.25 g P4VP for concentrations of different solution for hydrochloric acid (HCl) equal to 0.2, 0.5, 2 and 3 M. An amount of 2.5 g of Na-maghnite per 30 mL aqueous solutions of P4VP chloride salt was contacted for 24 h. The solids were washed with distilled water to remove excess salt, separated, and dried at 80°C. The P4VP–Maghnites were named P4VPS-Mag 1, 2, 3 and 4. The values of degree of α ionization mentioned in the Table 1 are calculated from the following equation: α is degree of ionization defined as the report of number of mole of the HCl in it of the monomer 4-vinylpyridine (4VP).

$$\alpha = \frac{n_a(HCl)}{n_b(4VP)}$$

Adsorbate

The toluene used in this study was an analytical grade reagent of 99% purity from the Aldrich.

Adsorption experiments

Preliminary adsorption experiments were performed at 25°C to determine the influence of pH on the uptake of toluene from water by the composite poly (4-vinylpyridinium)-maghnite. Batch adsorption experiments were conducted in 10 ml centrifuge tubes with 0.1 g of organo-maghnite combined with a 5 ml solution containing an appropriate concentration of a solute (250 and 500 ppm). After centrifugation, the concentration of the supernatant was determined. Toluene uptake by organo-maghnite was calculated from the difference between the quantity of toluene added and the quantity remaining in the equilibrium solution after 24 h of contact. The amount of toluene was determined by measuring of the absorbance at 271 nm in a Unicam Ultraviolet UV1 spectrophotometer. The amount of species adsorbed by surfactant-modified bentonite, q_e (mg/g), could be calculated as

$$q_e = \frac{V(C_0 - C_e)}{W}$$

(Rawajfih et al., 2006).

Where C_0 and C_e (mg/l) are the initial and final concentrations of toluene, respectively, V the volume of toluene solution and W is the weight (g) of organo-maghnite adsorbent.

Instrumentation

The distance between the layers of the organo-maghnite, the basal spacing d_{001}, was determined by X-ray diffraction analysis. X-ray diffraction (XRD) measurements were performed using an Inel automatic diffractometer (Detector CPS 120 and Source XRG 3000) with a Cu tube source (λ = 1.54 Å); generator tension was 50 kV at a current of 20 mA. Scans were taken from 2θ = 1.0 to 10, step size = 0.1 and scan time per step of 10 s using the high-resolution mode (Witthuhn et al., 2005). The d_{001} spacing of clay particles was calculated according to Bragg's law

$$d = \frac{\lambda}{2\sin\theta}$$

Thermogravimetric analysis, (TGA), was performed on a TA instruments 2950 unit under a flowing nitrogen atmosphere at a scan rate of 10°C per minute from 20 to 800°C (Chigwada et al., 2006).

RESULTS AND DISCUSSION

Characterization of organophilic maghnite

It appears, in Figure 2, that the preparation of the P4VP with HCl gives an organic phase slightly fixed on maghnites. The reaction with the HCl creates a positive load on nitrogen of polymer (P4VPS), which induces an increase in average dimensions polymers chains; this is due to the internal electrostatic repulsions. This effect makes it difficult to penetrate the polymer between the layers. The examination of these results shows that the amount of intercalated polymer P4VP are found between 6 to 10% by weight of maghnite, for an initial report P4VP/BC 10%. However, if we compare these values for α different degree, we find that the ratio between the

Table 1. A physicochemical characteristic of the different supports P4VPS – Maghnite and their sorption capacities toluene at 250 ppm and 500 ppm in batch tests.

					Rate of retention of toluene			
					C_0 = 500 ppm		C_0 = 250 ppm	
Sample	α	pH solution	P4VPinter (%)	d_{001} Å	q_e (mg g^{-1})	% of uptake toluene/ at C_0	q_e (mg g^{-1})	% of uptake toluene/ at C_0
Maghnite	0.00	-	0.0	13.8	-	-	-	-
P4VPS-Mag 1	0.10	3.8	8.6	14.7	0.1	0.4	2.45	19.6
P4VPS-Mag 2	0.25	2.5	9.5	14.8	1.05	4.2	3	24
P4VPS-Mag 3	1.00	1.2	9.6	15.0	2.9	11.6	4.7	37.6
P4VPS-Mag 4	1.50	0.5	7.1	15.0	4.15	16.6	5.85	46.8

minimum amount of P4VPS inserted for α ≈ 0.7-1 and the minimum amount of P4VPS inserted for α ≥ 1.5 exceeds 25%. This finding shows the importance of the parameter ionization on the exfoliation of maghnite by the P4VPS. The spacing interlayer of maghnite is $d_{(001)}$ = 1,38 Å. Maghnite modified by cationic polymer such as poly(4-vinylpyridinium) salt (P4VPS) gives organophilic clay. As it is shown in Table 1 the canionics polymers were intercalated in the interlayer space of the maghnite and the spacing increased gradually with to increase degree of α ionization (to increase rate of quarterisation P4VP) (Figure 3). The addition of P4VPS with low degree of α ionization equal 0,1, the spacing was around 14.7Å, Table 1, indicated that low rate quarterisation N$^+$ from P4VP is accommodated in the interlayer. Subsequent addition of P4VPS with increase degree of α ionization (α = 1, 5) into the layers led to an increase in $d_{(001)}$ spacing up to around 15.0 Å, (Table 1). Polycations are adsorbed via coulombic interactions between the cationic groups on the polymer and the negatively charged clay surface.

It is generally accepted that there is instantaneous collapse of the polycation onto the clay surface and that few loops are formed. The amount of species adsorbed by surfactant-modified bentonite, q_e (mg/g), could be

$$q_e = \frac{V(C_0 - C_e)}{W}$$

calculated as where C_0 and C_e (mg/l) are the initial and final concentrations of toluene, respectively; V the volume of dye solution and W is the weight (g) of organobentonite adsorbent. Degree of α ionization (quaternisation for P4VP by various concentrations of HCl).

$$\alpha = \frac{(C_{HCl} \times V_{HCl}) \times M_{4VP}}{m_{P4VP}}$$

Where C_{HCl} (mol/l) Concentration of HCl, V_{HCl} (L) Volume of HCl, M_{4VP} (g/mol) molecular weight of monomer 4-vinylpyridine, m_{P4VP} (g) weight of polymer poly(4-vinylpyridine).

The effect of the ionisation's degree of P4VP on toluene's adsorption by organophilic maghnite

Figure 4 shows the influence of degree of α ionization of P4VPS on the percentage removal of toluene on organophilic maghnite (P4VPS-Maghnite). It was reported that natural maghnite do not show adsorption capacity for toluene, because the contribution of physical adsorption of toluene by surface silicate layers is negligible (Jock-Churchman, 2002).

Hence, the adsorption increment of toluene showed by the sodium-exchanged maghnite, can be attributed to the presence of the hydrophobic sites on the surface developed by siloxane groups of the intercalated poly(4-vinylpyridinium) cations. These results encourage us to continue the measurements lower concentration for toluene. Indeed, the use of these supports for the decontamination of drinking waters will require a total retention of the pollutants starting from the much diluted solutions. In our case, we use these tests to measure the capacities retention of our organophilic supports. For P4VPS-Mag 4 containing only 7,1% of P4VP and obtained with a value of α = 1,5, the rate of retention is maximum whatever the concentration initial C0 toluene (Table 1).

This observation shows that the pH, system with a proton H$^+$ is directly related to the polar nature of space and organophilic interlayer where is the adsorption of toluene. In Figure 5, the retention of toluene by the studied supports increases on the one hand with the reduction in the initial toluene concentration, and on the other hand with the increase in the degree of α ionization. The observation of this result is that the load factor of adsorbed polymer salt P4VPS modifies the electrostatic state of space interlayers, place of the adsorption of the toluene molecule. Indeed, the screening charges of maghnite by quaternised P4VP make space interlayers less polar and thus favorable to the adsorption of the absorbent molecule. The P4VP cannot, in any case, be solely responsible for the retention of as much more support high in P4VP retain amounts considerably lower in toluene.
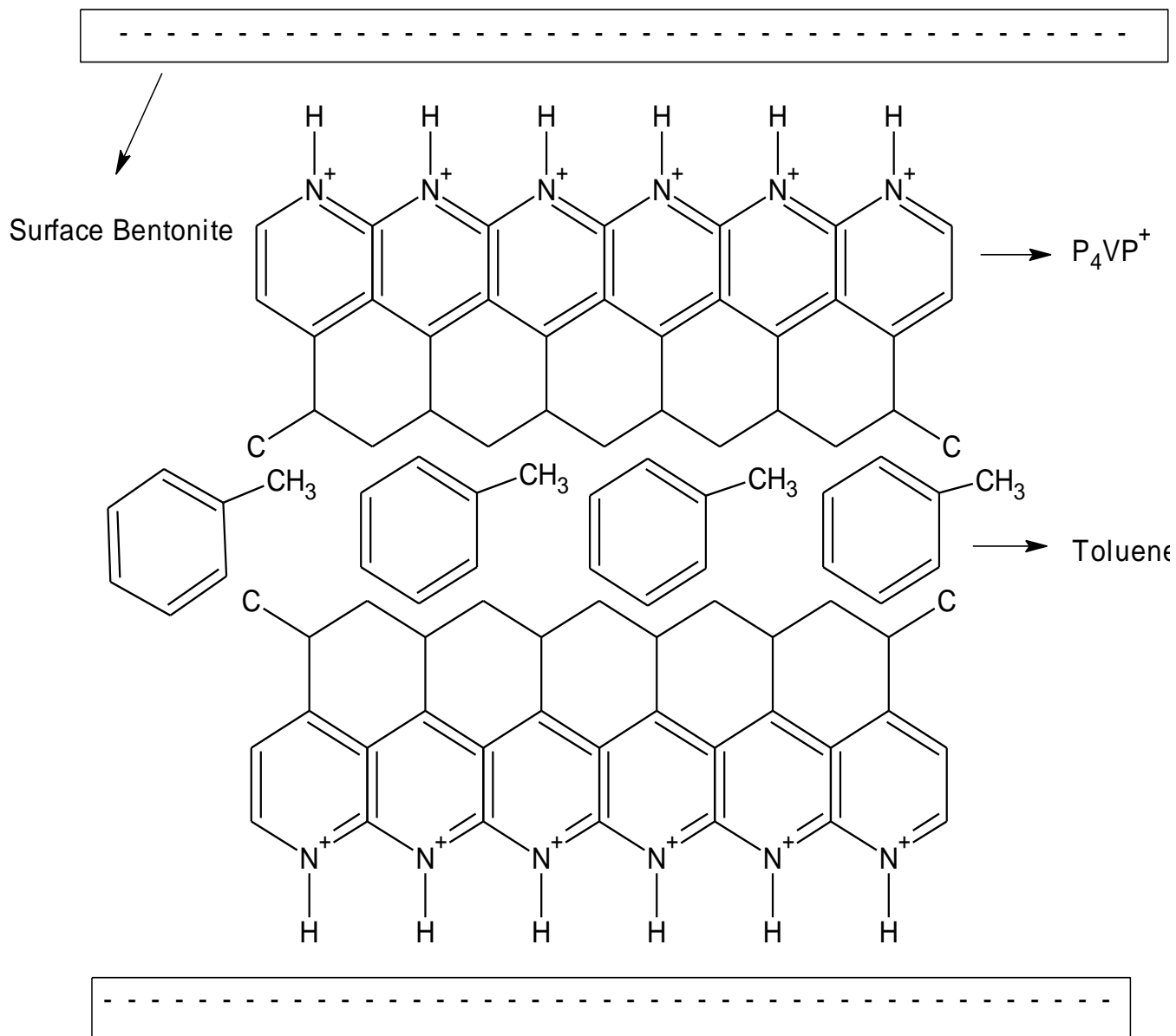
Figure 1. Proposed microstructures in the interlayer of P4VPS-Mag.

Effect of pH

The pH is the most important factor affecting the adsorption process. To study the influence of pH on the adsorption capacity of P4VPS-Maghnite, experiments were performed using various initial pHs varying from 0, 5 to 3, 8. The uptake of toluene decreased with increasing pH (Figure 6). It was observed that the adsorption is highly dependent on the pH of the solution, which affects the surface charge of the adsorbent and the ionisation's degree and speciation of the adsorbate. The quaternised polymer is adsorbed on the surface of maghnite; it associated with a surface of the clay negative charges in order to compensate for its positive loads N^+. The

observation of this result is that if quaternised the polymer load factor increases, the polarity of interlayers spaces decreases more and more, and by consequence the toluene retention becomes important. For poly(4-vinylpyridinium)-maghnite (P4VPS-Mag), the attractive forces to organic solutes were composed of the affinity of exposed siloxane surfaces and adsorbed N^+ from polymer, and adsorption toluene as described in Figure 1.

Conclusion

This paper deals with the removal of toluene from aqueous solution by two-step; first step organo-maghnite
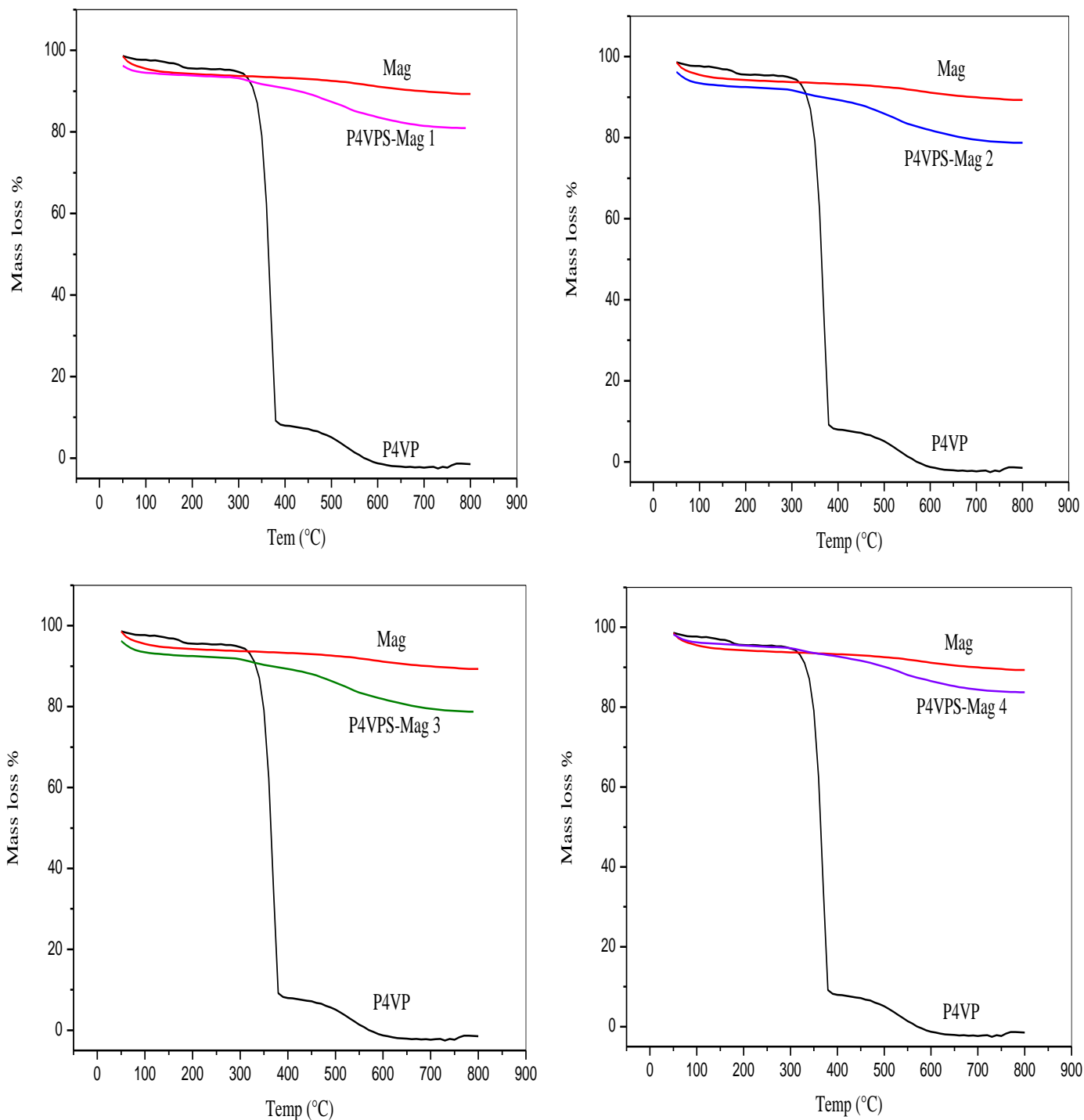
Figure 2. TGA curves for P4VP, Mag and P4VPS– Maghnite.

(poly(4-vinylpyridinium)-maghnite) which is a simple bentonite exchanged with polycationic poly(4-vinylpyridinium) salt (P4VPS) and the second step is the adsorption of the pollutant toluene by organo-maghnite. The results of this study indicate that the method improves greatly the adsorption behaviour of toluene and could be quickly removed from water by P4VPS-Maghnite. The maximum uptake of toluene occurred at higher degree of α ionization because of the high rate quaternisation polymer P4VP. These results indicate the interest of the degree of ionization α consideration in the preparation of organo-maghnite based P4VPS. This
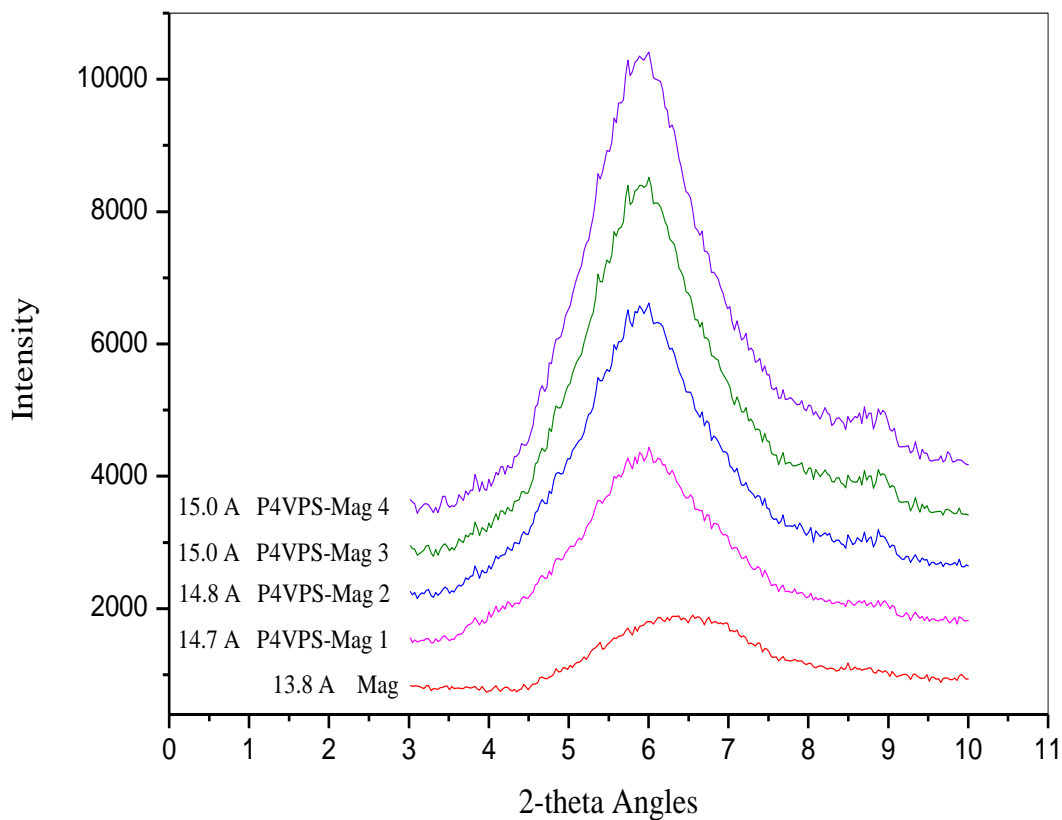
Figure 3. X-ray diffraction patterns of curves Maghnite and P4VPS – Maghnite.
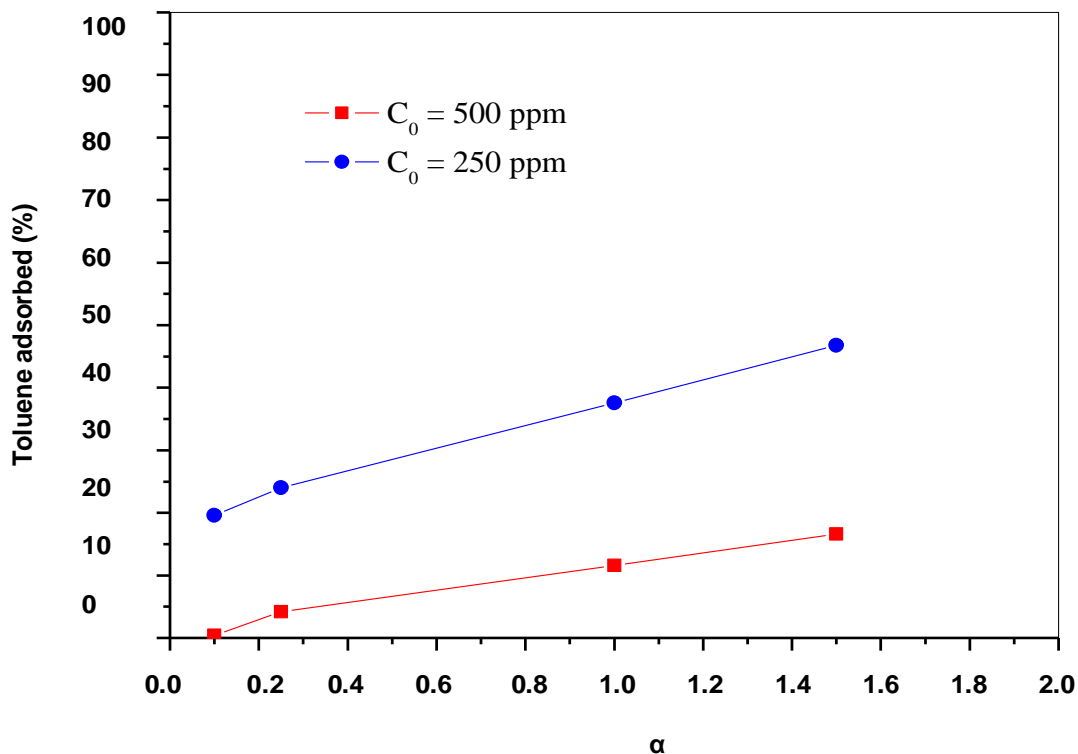

Figure 4. The effect of ionisation degree on the percentage retention of toluene.
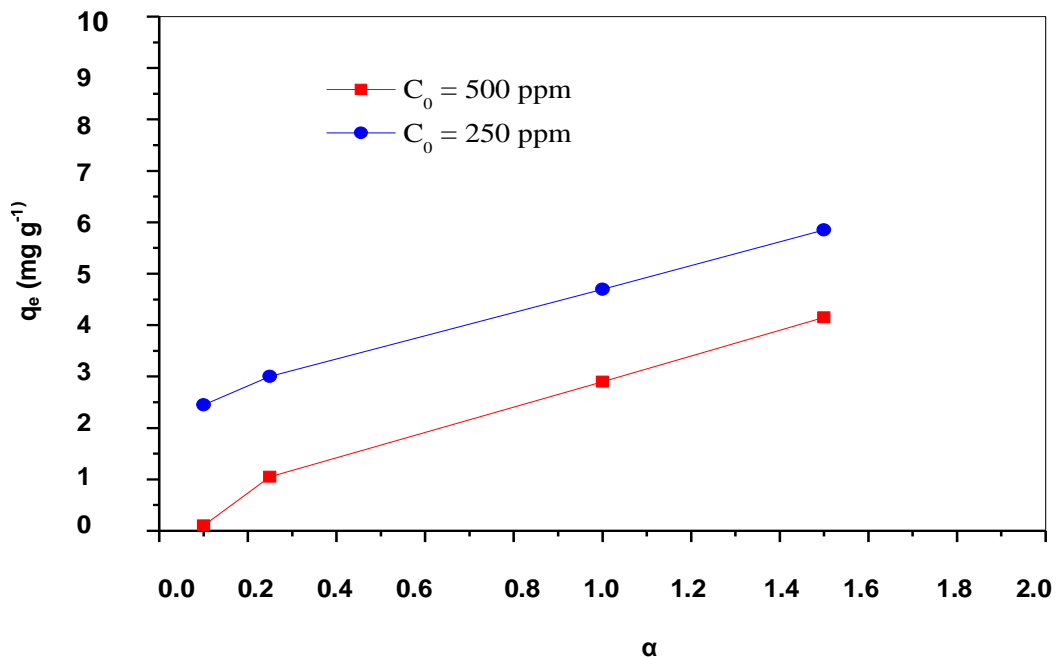
Figure 5. The effect of ionisation degree on the retention of toluene.

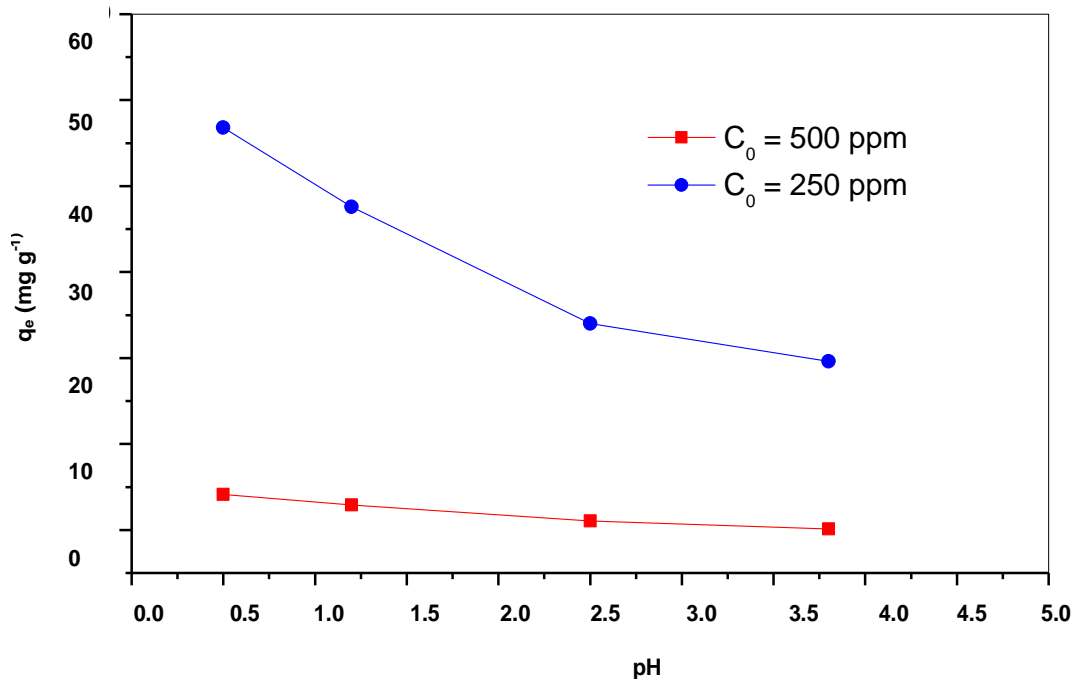## Effect of the pH on the retention of toluene

Figure 6. The effect of the pH on the retention of toluene.

knowledge will be useful in selecting the concentration of P4VPS that will be the most appropriate for application in remediation technologies for organo-bentonite or water

polluted by hydrophobic organic compounds, thus avoiding excessive use of polymer. The findings of this study were useful in determining optimum conditions

(degree of α ionisation for toluene removal both from water on organophilic maghnite (presence of cationic polymer).

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