

Adsorption of cationic polyacrylamide onto sepiolite

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Abstract

The adsorption of PAM onto sepiolite from aqueous solutions has been investigated systematically as a function of some parameters such as calcination temperature of sepiolite, pH, ionic strength and temperature. The adsorption of cationic polyacrylamide (PAM) increases with pH from 5.50 to 11.00, temperature from 25 to 55 °C and ionic strength from 0 to 0.1 mol L⁻¹. The sepiolite sample calcined at 200 °C has a higher adsorption capacity than the other calcined samples. Adsorption isotherms of PAM onto sepiolite have been determined and correlated with common isotherm equations such as Langmuir and Freundlich isotherm models. The Langmuir isotherm model appeared to fit the isotherm data better than the Freundlich isotherm model. The physical properties of this adsorbent are consistent with the parameters obtained from the isotherm equations. The zeta potentials of sepiolite suspensions have been measured in aqueous solutions of NaCl and different PAM concentrations and pH. From the experimental results: (i) pH strongly alters the zeta potential of sepiolite, (ii) sepiolite has an isoelectric point at about pH 6.6 in water and about pH 8 in 250 mg L⁻¹ PAM concentration, (iii) PAM changes the interface charge from negative to positive for sepiolite. Effect of temperature on adsorption has been quantified by calculating various thermodynamic parameters such as Gibbs free energy, enthalpy and entropy. The dimensionless separation factor (R_L) has shown that sepiolite can be used for adsorption of PAM from aqueous solutions.

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1. Introduction

The use of polymers to control the stability and flocculation behavior of colloidal suspensions is of great technological importance. They are widely used in various industrial products and processes, such as paints, coatings, ceramics, pesticides, pharmaceuticals, cosmetics, cement, and drilling fluids, to modify the rheology and control the stability of systems. On the other hand, clay suspensions are very powerful adsorbents that are much cheaper than common adsorbents like activated carbon to remove polymers from industrial wastewaters. The adsorption and interaction of non-ionic polymers and cationic surfactants with clay components have been widely investigated [1–4]. However, studies on the cationic polyelectrolyte and clay interaction are scarcer. Cationic polymers stabilize clay through electrostatic interactions with negatively charged clay surfaces. PAM, the cationic polymer discussed in this paper, is used in

water treatment, food packing, adhesives, paper manufacture, film formers for gelatin capsules, etc. Positively charged PAM is believed to bind to negatively charged sites on mineral surfaces [5–7]. Through this binding action, the PAM solution induces clay stabilization, making clay particles to stick readily to one another to form aggregates [8]. Owing to alterations in particle surface physicochemical properties after polymer coating, wettability of clay particles coated with polymers differs from that of uncoated particles [9–13].

Some investigators have studied sorptive properties of PAM with clays. These include adsorption of an anionic PAM onto two kaolinitic soils, a sandy loam Worsham (Typic Ochraquults), and a sandy clay Cecil (Typic Hapludults) [14], electrokinetic properties and structure of adsorbed layers of PAM at Fe₂O₃–polymer solution interface [15], adsorption of C-PAM on silica surfaces [16], sulfonate group surface concentration on the various membranes and its effect on the adsorption of a cationic polyacrylamide onto Perfluorosulfonate ionomer membranes (PFSIs) [17], the adsorption of C-PAM on the cellulosic fibres [18], the adsorption of PAM onto negatively charged smectite particles [19] adsorption of cationic, anionic and hydrophobically modified polyacrylamides on silica surfaces

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[20], and interactions of polyacrylamide polymer with bentonite in aqueous systems [21]. In our previously paper, adsorption of a cationic PAM onto kaolinite was investigated [22].

Sepiolite, as an adsorbent, may be a good alternative to these systems. Sepiolite is a natural hydrated magnesium silicate clay mineral, $(\text{Si}_{12})(\text{Mg}_8)\text{O}_{30}(\text{OH}_6)(\text{OH}_2)_4 \cdot 8\text{H}_2\text{O}$. Structurally it is formed by blocks and channels extending in the fibre direction. Each structural block is composed of two tetrahedral silica sheets and a central octahedral sheet containing magnesium. Due to the discontinuity of the external silica sheet a significant number of silanol ($\text{Si}-\text{OH}$) groups are present at the surface of these minerals [23]. Some investigators have studied sorptive and electrokinetic properties of organic compounds, cationic surfactants and metal ions with sepiolite. These include adsorption of thiram from aqueous solution on active carbon and sepiolite [24], the infrared study of the thermal treatment of sepiolite and palygorskite saturated with organic acids [25], the removal of reactive blue 221 and acid blue 62 onto sepiolite from aqueous solutions [26], the adsorption mechanism of cationic surfactants onto acid- and heat-activated sepiolites [27], the adsorption of acid red 57 from aqueous solutions onto sepiolite [28], and the spectroscopy of rhodamine 6G adsorbed on sepiolite from aqueous solutions [23]. As can be seen above, only a limited number of studies on the use of sepiolite as an adsorbent have been found in the literature.

Polyacrylamides (PAM) are among the most commonly used polymers in industry [29]. The present study have been determined the factors controlling the adsorption of PAM onto sepiolite. The effects of calcination temperature of sepiolite, solution pH, ionic strength, and temperature on PAM adsorption have been evaluated, and parameters for Langmuir adsorption isotherm have been reported. The results obtained have been applied to a batch design for the adsorption of PAM from aqueous media by using sepiolite. Particle surface chemistry characterization was achieved by determining the zeta potential as a function of sepiolite suspension conditions, such as different PAM concentrations and pH.

2. Materials and methods

2.1. Materials

Sepiolite sample was obtained from Aktaş Lületaşı Co. (Eskişehir, Turkey). The chemical composition of the sepiolite determined by XRF is given in Table 1. X-ray measurements

Table 1
Chemical composition of sepiolite

Constituent	Percentage present (%)
SiO_2	53.47
MgO	23.55
CaO	0.71
Al_2O_3	0.19
Fe_2O_3	0.16
NiO	0.43
LoI	21.49

LoI: loss of ignition.

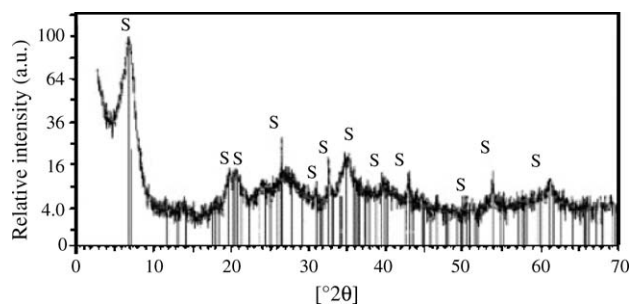


Fig. 1. X-ray diffraction patterns of sepiolite.

were performed using a Philips X-ray diffractometer employing nickel-filtered $\text{Cu K}\alpha$ radiation. The X-ray powder diffraction pattern of sepiolite has been given in Fig. 1. By comparing the d values obtained in this study and taken from JCPDS chart, the results have shown that this structure belongs to sepiolite. Cationic polyacrylamide (PAM), molecular weight $6.5 \times 10^6 \text{ g mol}^{-1}$, charge density 150 C g^{-1} and cationicity of 19% has been used. PAM was provided by Cytec industries Inc., West Paterson, NJ. The chemical structure of cationic PAM is shown in Fig. 2. Brilliant Yellow ($\text{C}_{26}\text{H}_{18}\text{N}_4\text{O}_8\text{S}_2\text{Na}_2$) was purchased from Acros used for the determination of PAM.

2.2. Purification and calcination of sepiolite

The sepiolite sample was treated as follows before use in the experiments: the suspension containing 10 g L^{-1} sepiolite was mechanically stirred for 24 h; after waiting for about 2 min the supernatant suspension was filtered through filter paper. After cleaning the sample mechanically of the visible impurities, it was ground and sieved to obtain $75 \mu\text{m}$ size fraction. Then, it was dried at 105°C , and used in further experiments. Calcinated sepiolite samples have been prepared in the temperature range of $105\text{--}700^\circ\text{C}$ with a Nuve MF-140 furnace for 3 h.

2.3. Cation exchange capacity, density, and surface area

The cation exchange capacities (CEC) of the various sepiolite samples were determined by the ammonium acetate method, the densities by the pycnometric method. The specific surface area of the sepiolite was measured by BET N_2 adsorption by Micromeritics FlowSorb II-2300 equipment. The results obtained are summarized in Table 2.

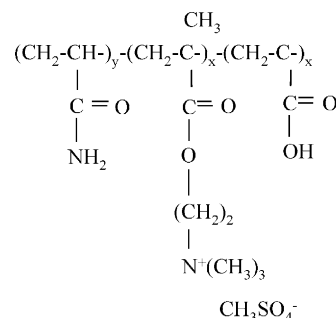


Fig. 2. The chemical structure of cationic PAM.

Table 2
Some physicochemical properties of sepiolite

Temperature (°C)	Cation exchange capacity (meq 100 g ⁻¹)	Density (g mL ⁻¹)	Specific surface area (m ² g ⁻¹)
105	25.0	2.5	342
200	24.5	2.7	357
300	26.0	2.6	321
500	27.0	2.5	295
700	25.0	2.3	250

2.4. Batch adsorption and desorption of PAM

Adsorption experiments were carried out by shaking 0.1 g sepiolite samples with 50 mL aqueous solution in a series of 250 mL polyethylene flasks. Each polyethylene flask was filled with 50 mL of a PAM solution of varying concentrations (25–450 mg L⁻¹) and adjusted to the desired pH, ionic strengths and temperature. At the end of the adsorption period, the solution was centrifuged for 15 min at 5000 rpm and then the concentrations of the residual PAM, C_e , were determined with the aid of a Cary |1E| UV–vis spectrophotometer (Varian). A preliminary experiment revealed that about 8 h is required for PAM to reach the equilibrium concentration. The result is shown in Fig. 3. The maximum wavelength of Brilliant Yellow solution (2.5×10^{-5} mol L⁻¹) is 400 nm, the maximum wavelength of solution that involved PAM-Brilliant Yellow complex is 510 nm; therefore the measurements were made at the wavelength $\lambda = 510$ nm. In order to construct a calibration plot, 4.5 mL of 2.5×10^{-5} mol L⁻¹ solution of Brilliant Yellow, 0.5 mL of the PAM solutions were placed in 25 mL flasks, respectively. The absorbance was linear for the range 25–450 mg L⁻¹. The correlation coefficient was found to be 0.9915. All procedures above were carried out at 25 °C. Blanks containing no PAM were used for each series of experiments. Suspensions of the sepiolite-PAM mixture were centrifuged after adsorption process. The

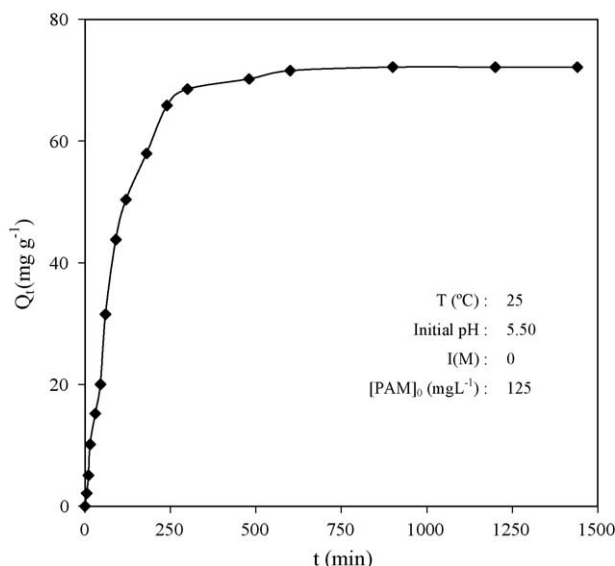


Fig. 3. The effect of time on the adsorption of PAM on sepiolite.

Table 3

The final pHs of the PAM-adsorbed sepiolite suspensions at different initial pHs

Initial pH	5.50	8.00	9.00	11.00
Final pH	7.19–7.68	8.32–8.61	8.72–9.12	9.25–9.64

supernatant was used to determine the concentration of PAM remaining in solution. Color complexation of the supernatant involved using a Brilliant Yellow solution [22] and pink solution formed was quantified using UV–vis spectroscopy at 510 nm against a series of standards. It was assumed that the amount of PAM depleted from solution had adsorbed onto sepiolite surface.

The effect of pH was observed by studying the adsorption of PAM over an initial pH range of 5.50–11.00. The pH of the solution was adjusted with NaOH or HCl solution by using an Orion 920A pH-meter equipped with a combined pH electrode. The pH-meter was standardized with NBS buffers before every measurement. The final pHs of the PAM-adsorbed sepiolite suspensions at different initial pHs are given in Table 3. The sorption studies were also carried out at different temperatures, i.e., 25, 35, 45, and 55 °C, to determine the effect of temperature and to evaluate the sorption thermodynamic parameters. A thermostated shaker bath was used to keep the temperature constant. The amounts of PAM adsorbed were calculated from the concentrations in solutions before and after adsorption [30]. The amount of PAM adsorbed (Q_e) (mg g⁻¹), onto sepiolite was calculated from the mass balance equation as follows [31]:

$$Q_e = (C_0 - C_e) \frac{V}{W} \quad (1)$$

where C_0 and C_e are the initial and equilibrium liquid-phase concentrations of PAM (mg L⁻¹), respectively, V the volume of PAM solution (L), and W is the mass of sepiolite sample used (g).

For the desorption study, after the sepiolite-polymer suspensions were equilibrated in a similar manner to the described adsorption experiments, some of suspensions were centrifuged and sepiolite samples were taken away from suspensions, then the PAM-adsorbed sepiolite samples were added to the solutions without PAM at different conditions such as, pH, ionic strength and etc. in 250 ml polyethylene flasks. The mixtures were shaken for 8 h and amounts of PAM that transferred to the solution were determined like adsorption experiments. According to the experimental data of desorption in Table 4, this adsorption process is irreversible which is in agreement with literature [32].

2.5. Zeta potential measurements

The zeta potential of sepiolite suspensions was measured using a Zeta Meter 3.0 (Zeta Meter Inc.) equipped with a microprocessor unit. The unit automatically calculates the electrophoretic mobility of the particles and converts it to the zeta potential using the Smoluchowski equation. The Smoluchowski's equation, the most elementary expression for zeta potential gives a direct relation between zeta potential and electrophoretic mobility

$$\zeta = \frac{4\pi V_t}{D_t} EM \quad (2)$$

Table 4

Desorption of PAM from sepiolite (initial PAM concentration is 250 mg L^{-1} , T : 25°C)

pH	I (M)	Adsorbed PAM to surface (Q_e) (mg g^{-1})	Desorbed PAM from surface (Q_d) (mg g^{-1})	Desorbed PAM from surface (%)
5.50	0	115.40	4.36	3.78
8.00	0	119.87	1.81	1.51
9.00	0	122.30	11.69	9.58
11.00	0	124.95	17.62	14.11
5.50	0.001	119.87	2.71	2.26
5.50	0.01	122.60	15.36	12.53
5.50	0.1	124.51	10.50	8.43

where EM is electrophoretic mobility at actual temperature, V_t is viscosity of the suspending liquid, D_t is dielectric constant, π is constant and ζ is the zeta potential [33,34].

The zeta potential measurements were carried out as a function of pH, and PAM concentrations. In this procedure, 0.1 g sepiolite was transferred to a 250 mL polyethylene flask to which 50 mL of an aqueous solution was added yielding a final sepiolite concentration of 2 g L^{-1} . The sepiolite particles were dispersed by a thermostatic shaker bath. After shaking 8 h, the samples were allowed to stand for 5 min to let larger particles settle. An aliquot taken from the supernatant was used to measure the zeta potential. The average of 10 measurements was taken to represent the measured potential. The applied voltage during the measurements was generally varied in the range of 50–150 mV.

3. Results and discussions

3.1. Effect of thermal activation on the adsorption

The presence of channels of molecular dimensions determines that sepiolite can be considered as an adsorbent with a uniform microporosity constituted by the channels and an appreciable non-microporous surface due to the small size of the fibers. The thermal behavior of sepiolite has been the subject of several publications in the literature [35,36]. It has been stated that the structural changes of sepiolite with increasing temperature affect the specific surface area and adsorption capacity. Sepiolite has structurally four water molecules coordinated to magnesium. The loss of these water molecules with increasing temperature will affect specific surface area and adsorption capacity of sepiolite. It has been stated that water molecules coordinated to magnesium lose until 500°C . After losing four water molecules coordinated to magnesium, the structure folds. The folding of the structure is associated with a decrease in the adsorption properties since the channels become narrower and the superficial slots sinter. A further increase in temperature produces the dehydroxylation of the structure and leads to the formation of clinostatite. In this way, the changes observed in the adsorption isotherms on both natural sepiolite dried at 105°C and the sepiolite subjected to a heat treatment can be interpreted on the basis of only the reduction of porosity upon the heat treatment. The results obtained in order to investigate the changes taking place in the specific surface area of sepiolite in the calcination

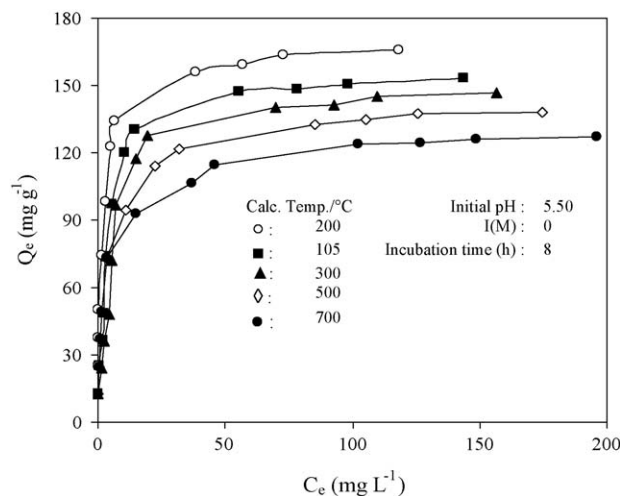


Fig. 4. Adsorption of PAM on calcinated sepiolite.

temperature range of 105 – 700°C have been shown in Table 2. As can be seen in Table 2, the specific surface area of sepiolite has increased until 200°C and then continuously decreased with increasing calcination temperature. Thermal treatment produces a maximum specific surface area of $357 \text{ m}^2 \text{ g}^{-1}$ at 200°C . This result is generally in line with the reported literature [28,37]. The decrease in the specific surface area of sepiolite may be a result of the removal of most of the micropores and the folding of structure due to heating the sample.

Furthermore, it has been seen from Table 1 that sepiolite has about 21.49% loss on ignition. This result is in a good agreement with Balci's results [38], which used thermal gravimetric analysis (TGA) method to determine the percent weight loss for sepiolite. He said that (i) the removal of hygroscopic water from the external surface and zeolitic water from the voids of the structure was completed up to 220°C with a 8.7% weight loss for the untreated sepiolite sample, (ii) the first part of the bound water was evolved from the structure with a 5.4% weight loss up to 450°C , (iii) the remaining part of bound water began to leave the structure at higher temperatures (about 750°C) and was accompanied by an 8.5% additional weight loss, (iv) the removal of structural water molecules (hydroxyl groups) was completed at 1.5% weight loss up to 850°C [39,40].

Fig. 4 shows the adsorption of PAM onto calcinated and natural sepiolite samples. As can be seen in this figure, the amount adsorbed of PAM on sepiolite has increased until 200°C calcination temperature and then decreased the amount adsorbed of PAM with increasing activation temperature. After 200°C calcination (Table 2), the decrease in the amount adsorbed of PAM with increasing activation temperature has been reduced as a result of decrease in surface area.

3.2. Effect of pH on the adsorption

To study the influence of pH on the adsorption capacity of sepiolite for PAM, experiments were performed using various initial solution pH values, changing from 5.50 to 11.00 (Fig. 5). The curves in this figure clearly show that the adsorption capacity

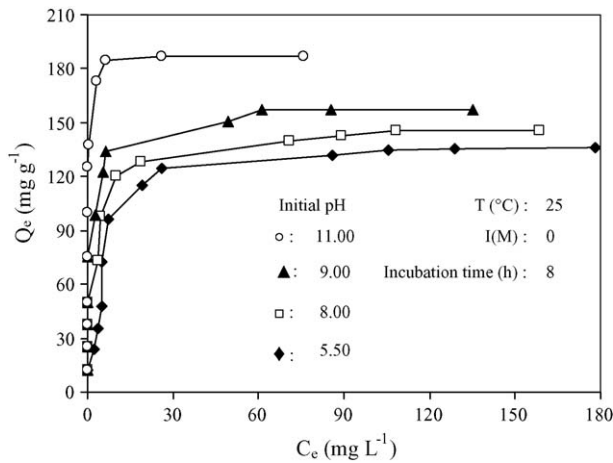
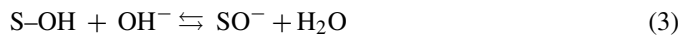


Fig. 5. The effect of solution pH on the adsorption of PAM onto sepiolite.

of sepiolite samples increase with increased pH. The sepiolite has a pH_{IEP} at pH 6.6 and exhibits negative zeta potential value at the pH range 6.6–10.00 (Fig. 6). As the pH of the PAM solution becomes higher (Eq. (3)), the association of PAM cations with negatively charged sepiolite surface can more easily take place as follows (Eq. (4)):



where S denotes the surface.

Adsorption depends usually directly on electrokinetic behavior of oxide as determined by the amount of H^+/OH^- adsorption. At pH values higher than zero point of charge (pH 6.6), the association of PAM cations with more negatively charged sepiolite surface because of increasing SO^- groups can be more easily take place. Some parts of the sepiolite surface are positive at acidic pH where Eq. (5) takes over

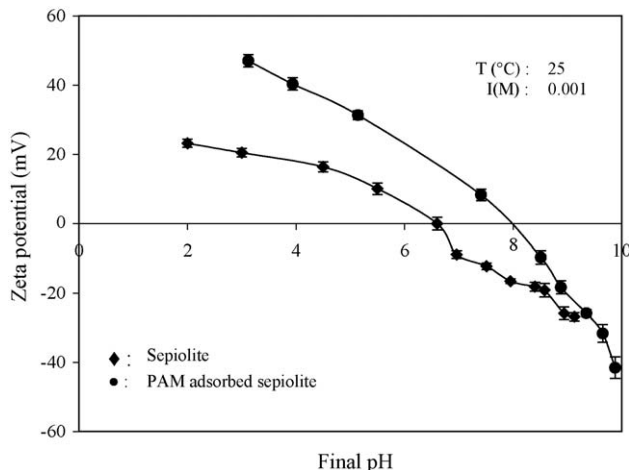


Fig. 6. The effect of pH on the zeta potential of sepiolite and 250 mg L^{-1} PAM adsorbed sepiolite.

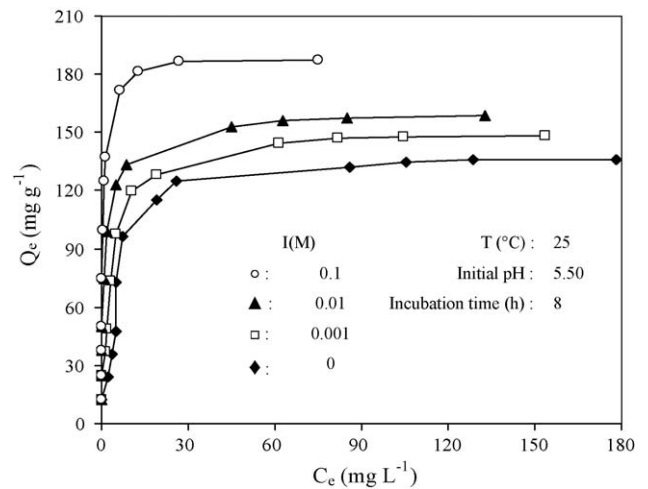


Fig. 7. The effect of ionic strength on the adsorption of PAM onto sepiolite.

Thus, interaction of positive charged PAM with sepiolite at lower pHs should be decrease and as a result, adsorption capacity should decrease.

3.3. Effect of ionic strength on the adsorption

Since sodium chloride is often used as a stimulator in adsorption processes, we tested the effect of ionic strength (NaCl) on adsorption of PAM onto sepiolite. The result is shown in Fig. 7. It indicates that the higher the NaCl concentration, the higher the adsorption capacity. The adsorption capacity values (Q_m) at NaCl concentrations 0.001, 0.01, 0.1 M are about 151.5, 158.7 and 188.7 mg g^{-1} , respectively, higher than that of solutions free of NaCl.

The presence of NaCl in the solution may have two opposite effects. On the one hand, since the salt screens the electrostatic interaction of opposite charges of the oxide surface and the polyelectrolyte molecules, the adsorbed amount should decrease with increase of NaCl concentration. On the other hand the salt causes an increase in the degree of dissociation of the polyelectrolyte molecules by facilitating the protonation [32,41]. The amount adsorbed increases as the dissociated PAM ions free for binding electrostatically onto the solid surface of oppositely charged increase.

The latter effect seems to be dominant on the adsorption capacity of the surface. Furthermore, as the salt concentration increases, a coiled structure for more neutral PAM polymer may be obtained resulting an increase in the concentration of polymers in the adsorbed layer by decreasing the electrostatic repulsions between ionised PAM molecules.

3.4. Zeta potentials of PAM-loaded sepiolite

Fig. 8 shows the variations of zeta potential as a function of adsorbed PAM concentration at initial pH 5.50, for which the final pH of the suspensions changes in the range of 7.19–7.68 (see Table 3). The zeta potential increases with an increase in adsorbed-PAM concentration, for pH values examined. Sepiolite is slightly negatively charged in this pH range, the adsorption

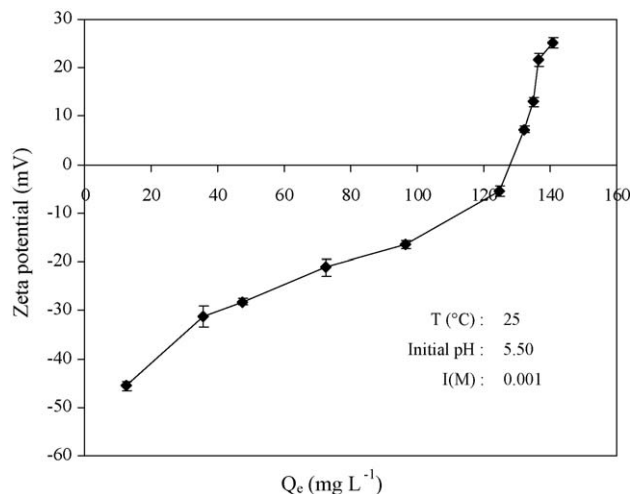


Fig. 8. The variation of the zeta potential of PAM-adsorbed sepiolite at the different Q_e values.

of a large amount of positively charged PAM onto the surface of sepiolite gives rise to a reversal in zeta potential. As more positively charged PAM is attached onto the particle surface, the zeta potential becomes more positive. Similar observations have also been earlier observed for adsorption of ionic and non-ionic polyacrylamide on kaolinite and bentonite [42–44].

3.5. Adsorption isotherms

The analysis of the isotherm data is important to develop an equation which accurately represents the results and which could be used for design purposes. The adsorption curves were applied to both the Langmuir and Freundlich equations. The widely used Langmuir isotherm has found successful application to many real sorption processes and is expressed as in the linear form [45]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K} + \frac{C_e}{Q_m} \quad (6)$$

Table 5
Isotherm constants for cationic PAM adsorption onto sepiolite

Calcination temperature (°C)	Adsorption temperature (°C)	I (M)	pH	Langmuir isotherm			Freundlich isotherm			R_L
				Q_m (mg g ⁻¹)	K (L mg ⁻¹)	R^2	n	K_F	R^2	
Natural	25	0	5.50	140.84	0.16	0.9968	3.02	31.13	0.7277	0.926–0.034
Natural	25	0.001	5.50	151.52	0.41	0.9994	3.89	49.45	0.8264	0.978–0.075
Natural	25	0.01	5.50	158.73	1.34	0.9997	7.37	88.92	0.8836	0.985–0.086
Natural	25	0.1	5.50	188.68	4.08	0.9999	8.09	123.16	0.8360	0.967–0.067
Natural	25	0	8.00	147.06	0.69	0.9993	6.82	74.51	0.8101	0.977–0.008
Natural	25	0	9.00	158.73	1.62	0.9997	9.71	99.90	0.8494	0.984–0.004
Natural	25	0	11.00	188.68	17.67	0.9999	14.95	150.67	0.8890	0.997–0.002
Natural	35	0	5.50	158.73	0.44	0.9993	4.42	60.25	0.8141	0.978–0.016
Natural	45	0	5.50	188.68	1.77	0.9993	6.45	109.98	0.8033	0.998–0.007
Natural	55	0	5.50	196.08	10.20	0.9999	32.79	176.35	0.6363	0.999–0.002
105	25	0	5.50	156.25	0.31	0.9989	5.43	29.51	0.9718	0.999–0.022
200	25	0	5.50	166.67	0.89	0.9993	4.24	31.11	0.9963	0.999–0.009
300	25	0	5.50	151.52	0.17	0.9976	4.05	27.42	0.9305	0.999–0.036
500	25	0	5.50	138.89	0.31	0.9994	9.52	18.25	0.9859	0.999–0.018
700	25	0	5.50	128.21	0.29	0.9992	9.87	12.74	0.9891	0.999–0.017

where Q_m (mg g⁻¹) is the maximum amount of PAM per unit weight of sepiolite to form a complete monolayer coverage on the surface bound at high equilibrium PAM concentration C_e , and K is the Langmuir constant related to the affinity of binding sites (L mg⁻¹). Q_m represents a practical limiting adsorption capacity when the surface is fully covered with PAM molecules and assists in the comparison of adsorption performance. Q_m and K are calculated from the slopes and intercepts of the straight lines of plot of C_e/Q_e versus C_e .

The Freundlich isotherm is given as [46]:

$$Q_e = K_F C_e^{1/n} \quad (7)$$

in logarithmic form

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (8)$$

where K_F is roughly an indicator of the adsorption capacity and $(1/n)$ of the adsorption intensity. K_F and $(1/n)$ can be determined from the linear plot of $\ln Q_e$ versus $\ln C_e$. Parameters of the Langmuir and Freundlich isotherms were computed in Table 5. As seen in Table 5, Langmuir isotherm fits quite well with the experimental data (correlation coefficient $R^2 > 0.99$), whereas, the low correlation coefficients ($R^2 < 0.98$) show poor agreement of Freundlich isotherm with the experimental data. Langmuir-type isotherm of adsorption is valid when (i) the adsorbent is homogeneous, (ii) both surface and bulk phases exhibit ideal behavior, and (iii) the adsorption film is monomolecular. When adsorption follows the Langmuir equation, a plot of C_e/Q_e versus C_e should be a straight line [22,45,46]. Table 5 presents the correlation coefficient results for the Langmuir isotherm, which fits a very good correlation between the model predictions and the experimental data, giving the correlation coefficients for Langmuir isotherm in the range of 0.996–0.999.

3.6. Effect of temperature on the adsorption

The effect of temperature on the adsorption isotherm was studied by carrying out a series of isotherms at 25, 35, 45 and

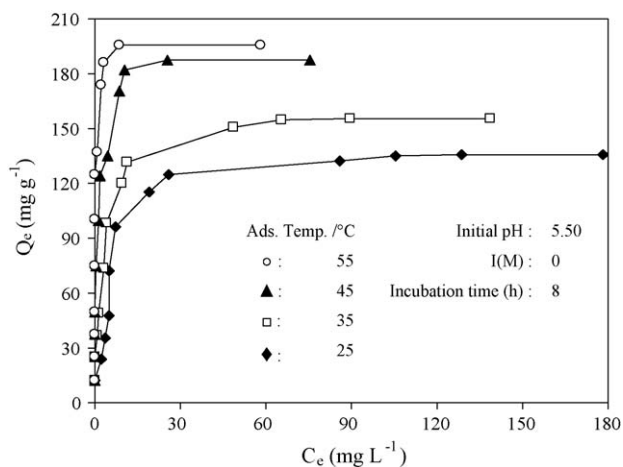


Fig. 9. The effect of temperature on the adsorption of PAM onto sepiolite.

55 °C for the sepiolite and shown in Fig. 9. The adsorption capacity of sepiolite for adsorption of PAM increases with increasing temperature, which is typical for the adsorption of most organics from their solutions. The effect of temperature is fairly common and increasing the temperature must increase the mobility of the large PAM cation. Furthermore, increasing temperature may produce a swelling effect within the internal structure of the sepiolite enabling large PAM to penetrate further. The R_L values at different temperatures were also determined (Table 5), and were less than unity.

The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor, R_L , which is defined as

$$R_L = \frac{1}{1 + KC_e} \quad (9)$$

The value of R_L indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). Here, R_L obtained are listed in Table 5. There are two values of R_L in Table 5 for minimum and maximum C_e values. The fact that all the R_L values for the adsorption of PAM onto sepiolite are in the ranges of 0.005–0.999 shows that the adsorption process is favorable [47].

The isotherm data obtained at different temperatures are also well fitted by the Langmuir equation. Temperature dependence of K can be used to determine the isosteric enthalpy of adsorption, ΔH° . The enthalpy at a fixed surface coverage ($\theta = Q_e/Q_m$)

$$\left(\frac{\partial \ln K}{\partial T} \right)_\theta = - \left(\frac{\partial \ln C_e}{\partial T} \right)_\theta = \frac{\Delta H^\circ}{RT^2} \quad (10)$$

A plot of $-\ln C_e$ against $1/T$ should be a straight line. Fig. 10 shows typical isosteres and reveals an approximately linear relationship. The value of ΔH° calculated at a specific coverage fraction of 0.5 is 24.3 kJ mol⁻¹.

Water–polymer and polymer–polymer interactions were significantly affected by temperature. The adsorption increased markedly with increasing temperature, and this is believed to be due to a breakdown of polymer–water hydrogen bond interactions and concomitant changes of polymer molecular conformation. The polymer chains may be considered more expanded

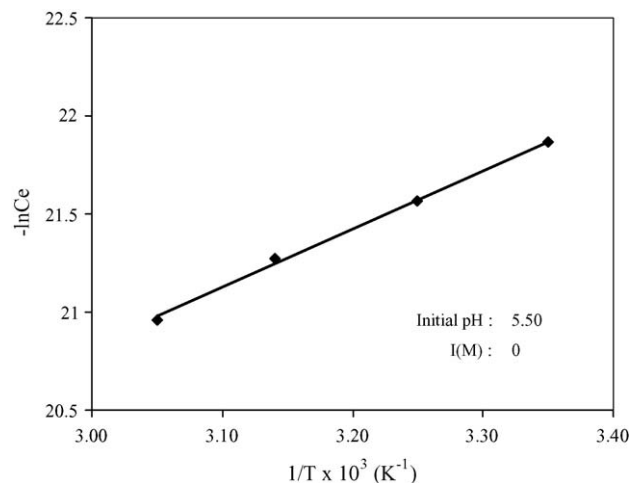


Fig. 10. Plot of $-\ln C_e$ vs. $1/T$ for PAM adsorption onto sepiolite.

in space due to stronger water–polymer interactions via hydrogen bonding at the lower temperature range (25–55 °C). With the disruption of the water–polymer hydrogen bonds at higher temperatures, the polymer–polymer interactions became more favored and led to the formation of a more coiled or contracted conformation [48].

Entropy change of the adsorption process (ΔS°), has been calculated from the intercept of the line in Fig. 10. Gibbs free energy of adsorption (ΔG°), can be found from

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

The values of ΔG° and ΔS° were calculated as -5.6 kJ mol⁻¹ and 100.4 J mol⁻¹ K⁻¹ at 25 °C, respectively. A negative ΔG° the nature of adsorption process for PAM is spontaneous. The reorientation or restructuring of water around nonpolar solutes or surfaces is very unfavorable in terms of entropy, since it disturbs the existing water structure and imposes a new and less ordered structure on the surrounding water molecules. As a result of adsorption of PAM onto sepiolite surface, the number of the water molecules surrounding PAM molecules decrease and thus the degree of the freedom of the water molecules increases. Therefore, the positive values of ΔS° suggest the increased randomness at the solid–solution interface during the adsorption of PAM on sepiolite [49,50].

The data not only indicate that the adsorption of PAM onto sepiolite is not only more favorable at elevated temperatures, but also suggest that the adsorption process is dominated by entropic rather than enthalpic effects since $|\Delta H^\circ| < |T\Delta S^\circ|$.

3.7. Desorption experiments

To establish the nature of PAM adsorption on sepiolite, we have carried out desorption experiments. Table 4 presents the results of desorption studies. It indicates that there is very little (<15%) desorption of PAM. Since major quantity of PAM adsorbed on sepiolite has high affinity. The interaction between PAM and sepiolite seems to be electrostatic. The silicate cleavage face has no adsorption active sites, which can form hydrogen bonding with PAM, whereas, alumina cleavage face is highly

hydrated and energetically stabilized by hydrogen bonding of basal aluminol groups with water molecules impeding any polymer adsorption on this face. Similar observations have also been made earlier for adsorption of ionic and non-ionic polyacrylamide on kaolinite [51,52].

4. Conclusions

The adsorption of PAM with sepiolite was systematically investigated under various conditions:

- The specific surface area of sepiolite has increased until 200 °C calcination temperature, and then continuously decreased with increasing calcination temperature. Thermal treatment produces a maximum specific surface area of 357 m² g⁻¹ at 200 °C. The amount adsorbed of PAM on sepiolite has increased until 200 °C and then decreased the amount adsorbed of PAM with increasing activation temperature.
- Interaction of positive charged PAM with sepiolite at lower pHs decreases and as a result, adsorption capacity decreases.
- The adsorption process becomes more favorable with increasing temperature.
- An increase in the salt concentration results an increase in the concentration of polymers in the adsorbed layer.
- According to the experimental data of desorption in very least amounts of PAM that transferred to solutions were observed.
- The zeta potential increases with an increase in adsorbed-PAM concentration, for pH value examined.
- The Langmuir isotherm model appears to fit the isotherm data better than the Freundlich isotherm model. Adsorption equilibrium correlated reasonably well by Langmuir isotherm.
- The data obtained from adsorption isotherms at different temperatures were used to calculate thermodynamic quantities such as Gibbs free energy, enthalpy and entropy of adsorption. The value of ΔH° calculated at a specific coverage fraction of 0.5 is 24.3 kJ mol⁻¹. The values of ΔG° and ΔS° were calculated as -5.6 kJ mol⁻¹ and 100.4 J mol⁻¹ K⁻¹ at 25 °C, respectively.
- As a result, the sepiolite is an effective adsorbent for PAM from aqueous solution in a commercial system.
- The PAM can be used to disperse the sepiolite in water via the electrostatic stabilization mechanism.

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