Adsorption of polyacrylamide onto Fuller's earth surface

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The adsorption of polyacrylamide onto Fuller's earth surface has been studied at fixed pH (4.0) and ionic strength of the medium. The adsorption isotherms display semi-Langmuirian nature but the kinetic curves show that after a definite time period the exchange phenomenon occurs between the polyacrylamide chain arriving at the interface and those already adsorbed. The adsorption is appreciably affected by the pH, presence of low molecular weight salts, organic solvents, temperature, molecular weight and degree of hydrolysis of the polymer. Various adsorption and kinetic parameters such as the adsorption coefficient, modified Freundlich adsorption isotherm constants, distribution coefficient, rate constants for adsorption and desorption have also been evaluated.

Clay-polymer interactions are involved in several technical areas such as soil stabilization, water treatment, mud formulations for drilling oil wells, injection of water soluble polymers as mobility control agents for improving oil recovery etc. The clays can be considered as the most suitable model adsorbent for any adsorption study as their hydrophilic nature, cation exchange properties and presence of organic moieties offer good opportunities to investigate various unexplored faces of adsorption mechanisms.

In the present study it is proposed to carry out a well organized investigation on adsorption of polyacrylamide (PAM) onto Fuller's earth surface which has been recognised as an adsorbent for selective adsorption of impurities and coloring materials from oils and fats.

Materials and Methods

PAM, used as an adsorbate, was of high molecular weight (about 5×10^7 Da) and supplied by BDH (Prod. 29788, Poole, England). Fuller's earth clay employed as an adsorbent was obtained from the Loba Chemie, India and used as received. The physical characteristics of the adsorbent are as follows: Surface area 120-140 m² g⁻¹; porosity 60-70%; cation exchange capacity 50-200 meq/100 g; mean equivalent diameters of pores 190-200 Å; point of zero charge of the edge face 7.0; and particle size 10 μm. Other chemicals used were of analytical grade quality. Doubly distilled water was used throughout the study.

Adsorption experiments were performed by end-over-end shaking of a well-stoppered boiling test tube containing Fuller's earth (0.1 g) at a fixed pH 4.0 and ionic strength of 2.0 × 10⁻² mol dm⁻³ KNO₃ for 20 min.

Preliminary adsorption experiments indicated (Fig. 1) that the equilibrium adsorption could not be achieved even up to 24 h and a regular variation in the adsorbed amounts of PAM was observed. This unusual behaviour may be attributed to the successive occurrence of flocculation and deflocculation of the Fuller's earth suspensions due to constant agitation. Due to this reason all adsorption experiments were carried out up to 20 min. only.

After shaking for 20 min, the suspensions were centrifuged in an electric centrifuge (Remi, India) and the residual polymer in the supernatants were estimated by the starch-iodide method as described by Scoggins & Miller. In brief, to a mixture of 5 ml of PAM solution and 5 ml of buffer solution (pH-4), were added 1 ml of saturated bromine solution followed by 5 ml of cadmium iodide starch solution which resulted in formation of a blue coloured complex. The absorbance of the resulting solution was recorded on a colorimeter (Systronics, India). All polymer (PAM) determinations were performed in replicate and the results were found to be within 95% confidence limit.

The amount of adsorbed PAM was calculated with the help of mass balance reaction,
Amount adsorbed (mg g\(^{-1}\)) = \frac{(C_o - C_e) V}{m}

where \(C_o\) and \(C_e\) are the initial and equilibrium concentrations (mg per ml) (residual concentration in the present case) of PAM solution respectively, \(V\) the volume of suspensions and \(m\) the amount of adsorbent in g.

### Kinetics of adsorption

For monitoring the progress of the adsorption process, several identical sets were run simultaneously and the amount of adsorbed PAM was determined in each set at different time intervals by the colorimetric method as mentioned above. It is worth mentioning here that for arresting the adsorption process the tubes were simply taken out and centrifuged. The time required for the centrifugation was excluded in the kinetics.

### Synthesis of PAMs of varying molecular weight

For preparing PAM of varying molecular weights, thermally induced free radical polymerisation of acrylamide was carried out using potassium peroxydisulphate (KPS) as initiator. The polymerization was carried out for 30 min at 70°C and the polyacrylamide formed was precipitated by adding definite volume of methanol to the reaction mixture. The polymer, so isolated, was dried and dissolved in water and precipitated again. In this way, varying amounts of KPS produced PAM of varying molecular weights. The molecular weights were determined by viscosity measurements as described elsewhere. PAM of molecular weights \(6.8 \times 10^4\), \(17.4 \times 10^4\) and \(41.2 \times 10^4\) were obtained by using \(14.8 \times 10^3\), \(7.4 \times 10^3\) and \(1.4 \times 10^3\) mol dm\(^{-3}\) KPS as initiator, respectively.

### Hydrolysis of PAM samples

For producing partially hydrolysed PAM (HPAM) the method given by Gundiah et al was adopted which involves hydrolysis of PAM (40 g) in alkaline medium under various conditions of temperature \(65°C\) and \(40°C\) and heating time (30 min). The samples so prepared were dissolved to give HPAM solutions of varying acidity. The solutions were titrated potentiometrically against \(0.1\) \(N\) NaOH for determining the degree of hydrolysis of the polymer samples which were found to be 56.8 and 28.1, respectively.

### Results and Discussion

For a better understanding of the PAM-Fuller's earth interaction, it is essential to know how exactly the PAM chains adsorb onto the clay surface. Since the major constituent of the Fuller's earth is montmorillonite, it is reasonable to consider the structure of montmorillonite as representative of Fuller's earth and consider its interaction with the PAM chains.

Montmorillonite crystals have a layer structure formed from a alumina octahedral sheet sandwiched between two inward pointing sheets of silicatetrahedra. The flat cleavage surface is negatively charged from isomorphous replacements between \(\text{SiO}_2\) and \(\text{Al}_2\text{O}_3\); the charge on this face is considered to be independent of \(pH\) as reported elsewhere. Two different functional groups are considered to be present on the edge face, probably from protonation of \(\text{Al}^2\text{O}_3\) and an aluminosilicate. The edge face has a point of zero net charge around \(pH 7\); below this \(pH\) the charge is positive and above \(pH 7\), the charge is negative.

The adsorption of PAM chains mainly occurs via the H-bonding between the carbonyl group and edge aluminols. It has also been shown that the PAM molecules do not adsorb on basal surfaces. The mechanism of adsorption is depicted in Fig. 2.

### Adsorption isotherms

As the molecular weight of PAM is quite high, very dilute solutions were prepared for studying the effect of concentration on adsorption. When the concentration of PAM solution was increased from 4.0 to \(20 \times 10^{-10}\) mol dm\(^{-3}\), the adsorption increased constantly and finally levelled off, thus indicating the semi-Langmuirian nature of the adsorption process. In order to collect more information on polymer-soil interaction, three types of adsorption isotherms, viz. the Langmuir, Freundlich and modified Freundlich
isotherms were used. These have been frequently employed to investigate the sorption characteristics of bentonite and soils.

Originally derived for the sorption of gases on a solid, the Langmuir isotherm can be approximated to a solid-liquid interface in the following linear form

\[
\frac{C_e}{(mlx)} = \left( \frac{1}{b} \right) C_e + \frac{1}{kb}
\]

where, \( C_e \) is equilibrium concentration of polymer solution (but in the present case the residual concentration was taken after 20 min); \( mlx \), the amount of PAM adsorbed in mg g\(^{-1}\); \( k \), the adsorption coefficient; and \( b \), the amount of PAM adsorbed at saturation in mg g\(^{-1}\).

The Freundlich isotherm has the form

\[
mlx = KC^N
\]

where, \( K \) is the predicted quantities of sorption for one gram of the adsorbent of unit equilibrium concentration (mg g\(^{-1}\)) (residual concentration in the present case), and \( N \) is the measure of nature and strength of adsorption forces and on the distribution of active sites.

If \( N<1 \), bond energies increase with surface density, if \( N>1 \) bond energies decrease with surface density and when \( N=1 \), all surface sites are equivalent.

Due to the complex nature of soil, the exchange of solute on soil adsorption sites is known to be a heterogenous process with the assumption that the exchange surface is heterogenous and each exchange site adsorbs individually according to the Langmuir isotherm. According to the equation derived by Spotsite using statistical mechanics. According to the proposed equation,

\[
S_1 = \frac{S_{max} X(a_1/a_2)^\beta}{1 + \alpha(a_1/a_2)^\beta}
\]

where, \( a = Aa_2/ S_{max} \); \( a_1 \) and \( a_2 \) are activities of solute 1 and 2 in solution respectively; \( S_{max} \) is the maximum available exchange sites or cation exchange capacity; \( S_1 \), the amount of solute 1 sorbed; and \( A, \beta \) are the empirical constants.

Equation (3) reduces to the Freundlich isotherm when \((a_1/a_2)^\beta << 1\), i.e., when the adsorbing solute (solute 1) is in trace quantities. However, without limiting the sorbing solute to trace quantities, Eq. (3) is a modified form of the Freundlich isotherm, transferring it as follows:

\[
\log S_1/(S_{max} - S_1) = \beta \log C + \log (A/S_{max})
\]

where activities have been replaced by concentrations. By plotting a graph between \( \log S_1/(S_{max} - S_1) \) versus \( \log C \), \( A \) and \( \beta \) can be determined.

**Distribution coefficient**

The adsorption can also be quantified in terms of distribution coefficient, \( K_d \), defined as the ratio of equilibrium concentration of the sorbed species to the equilibrium concentration of the species in solution. The constant \( A \), given as \( A = S_{max} K_d \), is a measure of the weighted average distribution coefficient and the parameter \( \beta \) describes the spread of the distribution coefficient about the average distribution coefficient (\( K_d \)).

When the amount of adsorbed PAM is plotted against the residual concentration of PAM solution (after 20 min.), a semi-Langmuirian adsorption isotherm is obtained (Fig. 3). As can be judged from the shape of the curve a high slope is obtained which implies a greater affinity of the adsorbate for the adsorbent. This high affinity is further supported by a large value of the adsorption coefficient calculated in accordance with the linearized Langmuir equation.
Thus, to explain the kinetic results the adsorption (Eq. 1). The constants N, A, β and K_d have been calculated as 0.4222, 1.1256 x 10^{-2}, 2.4137 and 1.66 x 10^{-3}, respectively. A value of N<1 implies that bond energies increase with surface density. This may be because due to greater crowding of molecules at the interface, the strength of bond between the adsorbate and adsorbent increases. A high value of K_d suggests a favourable distribution of polymer molecule towards the soil surface. Similarly, the value of β, being greater than one indicates a higher spread of distribution coefficient. The empirical constant, A represents a measure of the weighted average distribution coefficient.

Kinetics of adsorption

Polymer adsorption consists of the following three steps, (i) diffusion of incoming chains from bulk solution to the surface; (ii) adsorption of polymer chains onto the surface, and (iii) conformational changes in the surface layer.

The dynamics of adsorption is typically shown by the plot drawn between the adsorbed amount and time. In most of the cases, the adsorbed mass gradually increases constantly up to a certain time limit and then finally levels off indicating a saturated adsorption. In the present case, the adsorption of PAM, (Fig. 1) shows that the adsorbed amount fluctuates periodically with time and does not show equilibrium adsorption in the whole time span of 24h. In fact, there is a regular repetition of the preceding pattern. Thus, to explain the kinetic results the adsorption process up to only 30 min has been considered as shown in Fig. 4. It is observed that (i) initially up to 8 min. the adsorption occurs quite rapidly with an almost constant rate and then slightly decreases up to 12 min; (ii) after 12 min. the adsorption decreases up to 16 min. where it passes through a minimum followed by an increasing adsorption.

These results are quite unusual and rarely reported in the sense that there is a decrease in the adsorbed amount between 12 to 16 min. To analyse the results, both qualitatively and quantitatively, we have divided the curve into four regions, viz., region I up to 8 min., region II from 8 to 12 min., region III from 12 to 16 min. and region IV beyond 16 min.

Region I (up to 8 min.)

In this region the rate of the adsorption process is almost constant, i.e., linear, and such a behaviour has often been exhibited by end functionalized large chains. In the initial stages, the soil surface is bare and the kinetics of adsorption is governed by the diffusion of the chains from the bulk solution to the surface. All the chains that arrive at the interface are considered to be immediately adsorbed. The mass transport can be interpreted as a Fickian diffusion. The diffusion constant D can be calculated with the help of the equation

\[ q = \frac{2}{\pi} \cdot C_0 \cdot \sqrt{D \cdot t} \]  \hspace{1cm} (5)

where \( q \) is the adsorbed mass and \( C_0 \) being the concentration of the polymer solution. From the plot drawn between \( q \) and \( \sqrt{t} \), the diffusion constant, \( D \), has been calculated as 2.4 x 10^{-16} \text{ cm}^2 \text{ min}^{-1}. In this constant adsorption rate region, the kinetic scheme proposed by Bajpai et al. can also be applied to evaluate the rate constants for adsorption (\( k_1 \)) and desorption (\( k_2 \)). According to the proposed scheme, the following equation can be given

\[ \frac{1}{C} = k_1 t + \frac{1}{C_0} \]  \hspace{1cm} (6)

where the term have their usual meaning.

A plot drawn between \( 1/C \) and \( t \) gives the value of \( k_1 \) as 38.8 x 10^{-2} \text{ min}^{-1}. Also, once both \( k_1 \) and \( k \) are known, \( k_2 \) can be calculated and was found to be 1.33 x 10^{-10} \text{ mol dm}^{-3} \text{ min}^{-1}. 

Fig. 3—A plot showing the variation of adsorbed amounts (mg g\(^{-1}\)) of PAM with the equilibrium concentration of PAM solution at fixed pH = 4.0, [KNO\(_3\)] = 2 x 10^{-3} \text{ M}, Temp = 27 ± 0.2°C, Fuller's earth = 0.1 g.
Region II (8-12 min.)

In this region the rate of adsorption is lowered. This may be because in region I a surface layer of adsorbed polymer is formed on the soil surfaces which provides an energy barrier to those chains which arrive from the bulk to the interface. According to Ligoure and Leibler, the situation can be considered by a simplified model where the adsorbed amount approaches exponentially an residual adsorbed amount $q_e$ with time, introducing a characteristic penetration time $T$.

$$q = q_e [1 - \exp(-t/T)] \quad \ldots (7)$$

Equation (7) suggests that the adsorption process has an exponential nature now, and the penetration rate may be obtained from the slope of $\ln(q_e-q)$ as a function of time. For the system under study, the penetration constant has been calculated as $21.7 \times 10^{-2}$ min$^{-1}$.

Region III (12-16 min.)

This region is an entirely new feature observed in adsorption of proteins$^{20}$ and polymers$^{21}$. The decrease in the adsorbed mass with time can be mainly attributed to the fact that for rearrangement in the surface layer there is an exchange between the surface bound polymer layer and the free solution$^{22}$. As the process of exchange begins, a larger number of polymer chains gets detached from the surface and move into the bulk than the chains coming from the bulk to the interface. This obviously results in a fall in the adsorbed amount of polymer and, therefore, the kinetic curve moves down beyond 12 min. as shown in Fig. 4.

Region IV (beyond 16 min.)

After a certain time period, the rate of detachment of polymer chain is dominated by the new adsorbing chains and, therefore, the adsorbed mass begins to rise. Similar type of behaviour has also been noticed by Forantz et al.$^{23}$ who observed that there was an overshoot in the polystyrene adsorbed the invading and detaching chains "worm" their way in and out of the surface layer by the sequential attachment and detachment of adsorbed segments. The whole mechanism can also be modelled as shown in Fig. 5.

Effect of pH

Effect of pH in adsorption investigations where a charged macromolecule adsorbs on a charged surface has created much interest in recent past not only because of the chemistry involved but also due to the practical utility of the subject$^{24}$. In the present case, however, with varying pH of the suspension, the charge on the fuller's earth surfaces varies due to the presence of aluminols and silanols whereas the PAM
Since aluminols have greater tendency to form H-bonds then protonated aluminols, adsorption of PAM will take place via the H-bond formation between the carboxyls of the PAM and aluminols of the edge face. On increasing the pH, the number of unprotonated aluminols decreases and, therefore, the adsorption increases. Such a strong specific interaction between the PAM and aluminols have also been reported elsewhere.

(ii) When pH of the solution becomes equal to the \( \text{pH}_{\text{ZPC}} \) of the Fuller's earth, the number of unprotonated aluminols become maximum and, therefore, the adsorption also reaches at its maximum value.

(iii) However, when pH is raised beyond 7.0, the number of aluminols goes on decreasing and this obviously results in a decreasing adsorption.

It is worth mentioning here that amide groups react only with aluminols, they do not interact with H-bonded silanol groups. Similar type of pH dependence has also been reported elsewhere.

**Salt effect**

Salts play a key role in influencing the adsorption on a charged surface as their presence in the system exerts multiple effects on adsorbate-adsorbent interaction. In a system containing a macromolecule and charged surfaces, the ions present can either bind to the macromolecular functional groups, adsorb preferentially on the surface or cause screening of coulombic potential produced due to macro ion and charged surfaces.

In the present work, the effect of anions have been investigated by adding sodium salts of chloride, sulphate and phosphate to the adsorption system in the concentration range 0.005 to 0.1 M. The results are shown in Fig.7 which clearly reveal that the adsorption appreciably decreases with increasing salt concentration and the order of effectiveness in causing depression is found to be \( \text{PO}_4^{3-} > \text{Cl}^- > \text{SO}_4^{2-} \).

The observed decrease in adsorption may be explained by the fact that at pH 4.0 the aluminols of edge-face are present in protonated form (AlOH\(^+\)), and, therefore, the anions may preferentially get adsorbed onto the edge-face, occupying the active sites on the clay surfaces. This obviously prevents the PAM chains from adsorption decreasing the adsorption.

The sequence of effectiveness of added anions is also justified as the chloride ions being smaller in size than sulphate ion can easily diffuse from the solution.
to the edge-faces of the Fuller's earth and get adsorbed. The sulphate ions being bigger in size and do not diffuse easily towards the surface. Therefore, they bring about a lower depression on the adsorption. However, the phosphate ions although largest in dimension exhibits greatest effectiveness. The reason for the observed behaviour of phosphate is that this anion is known to interact with hydroxyl groups and thus get adsorbed on edges and on aluminium hydroxide basal surface of the clay preventing PAM d.  

Solvent effect

Presence of organic solvents has particular relevance in the present study as the Fuller's earth is quite well known for its adsorption tendency toward organic molecules.

In the present study various aliphatic alcohols were added (10% v/v) to the PAM-Fuller's earth suspensions. It was noticed that the added alcohols exert almost no effect on the adsorbed mass of PAM. The reason for such an abnormal behaviour may be that the added alcohols displace the water molecules already adsorbed at active sites of the clay surfaces and thus get preferentially adsorbed. It is notable here that the alcohols molecules do not exhaust those active sites where the PAM chains are adsorbed and this is because of the fact that the PAM molecules show much greater affinity towards adsorption onto the clay surfaces (as evident by a very large value of adsorption coefficient) and, therefore, they are not replaced by the alcohol molecules. Thus, the added alcohols have no effect on the adsorption of PAM.

Addition of dioxane to the adsorption system has resulted in a drastic fall in the adsorbed amount as shown in Fig.8. It is observed that, the adsorption remains almost unaffected when the dioxane is added up to 8% (v/v). However, upon further increasing the added proportion of dioxane (above 8-10%), the adsorption suddenly falls and thereafter also the decrease in the adsorption continues. The reason for the observed results is that when dioxane is added (upto 8% v/v) the amount may not be sufficient to affect the amount of PAM adsorbed. However, when the concentration of dioxane exceeds 8%, the molecules of dioxane compete with those of PAM for adsorption and are adsorbed preferentially because of their polar nature. Thus, due to the preferential adsorption of dioxane molecules the adsorption of PAM is adversely affected.

Temperature effect

The influence of temperature on the adsorption of PAM was studied by performing the experiments in the temperature range 27°C-55°C. Figure 9 shows that
the rate of adsorption and adsorbed amount increased with increasing temperature. At the same time, it is also observed that as temperature goes on increasing the depth of the valley portion (i.e., decrease in adsorbed mass followed by an increase) goes on decreasing, i.e., the valley portion is more prominent at lower temperature while it appears to become minimum at higher temperature (55°C).

The observed increase in adsorbed mass with increasing temperature can be understood by the fact that as the temperature of the adsorption system rises, the intermolecular forces between the water molecules which were adsorbed at the interlayer portion of the montmorillonite and the active sites become weak facilitating replacement of water by PAM molecules. Thus, the adsorption increases with the increasing temperature. It is also likely that at higher temperature, the viscosity of the PAM solution becomes less and, therefore, the diffusion of PAM molecules will be faster resulting in a greater adsorption.

At higher temperatures diffusion of PAM chains becomes faster and as a consequence there is crowding at the interface. When the exchange phenomenon begins, i.e., new PAM chain arriving at the interface replace the already adsorbed chains, the number of invading chains is consequently greater than that detaching from the interface and as a result the fall in the adsorbed mass is not much as it is at lower temperature, when the diffusion was slow. This is probably the reason why at high temperature, the valley is not deep.

**Effect of molecular weight**

For investigating the effect of molecular weight of PAM on its adsorption, three samples of PAM with varying molecular weights were prepared and their molecular weights determined by viscosity measurement. The results are presented in Fig. 10 which indicates that the adsorption decreases with increasing molecular weight of the polymer. It is also observed that 'valley portions' are not present in the curves, i.e., exchange phenomenon does not occur in the molecular weight range of synthesized polymers. This also suggests that since the adsorption is influenced by molecular weight of the polymer, the PAM chains must be adsorbing in loops and tails predominantly because if the chains had adsorbed majorly with trains then the adsorption would have been almost independent of molecular weight. Now, the greater adsorption of lower molecular weight PAM can be explained by the fact that the lower molecular weight PAM molecules have smaller dimensions and, therefore, they can easily diffuse into the pores of clay and their adsorption is relatively easier as compared to the large molecular weight PAM molecules.
One more remarkable feature is that in this molecular weight range, no exchange occurs between the PAM molecules present in the samples and those already adsorbed. The reason for this behaviour is that the molecular weights of polymers employed for studying the effect of molecular weights are much lower than that used in the study of other parameters. Due to their smaller molecular dimensions, they are firmly held with the clay surfaces as more segments of the chains will be attached directly to the surface. Thus, due to a stronger bonding between the lower molecular weight PAM chains and the surface, the exchange process become less probable.

**Effect of degree of hydrolysis of PAM**

To study the effect of hydrolysis of PAM on its adsorption, two samples of varying degree of hydrolysis were prepared. Figure 11 indicates that the adsorption increases as the degree of hydrolysis of polymers decreases. When degree of hydrolysis increases, a larger number of -CONH₂ groups are hydrolysed to -COOH groups and the polymer molecule becomes partially negatively charged due to limited dissociation of carboxylic groups. Now, due to the negative charges on the polymer molecule they experience a repulsion with the negatively charged basal plane of the clay and, therefore, the adsorption decreases.

**Conclusions**

The adsorption of PAM onto the Fuller's earth surfaces increases with increasing polymer concentration and shows semi-Langmuirian nature. It is found that after a definite time period an exchange occurs between the invading polymer chains and those already adsorbed at the interface. The adsorption becomes maximum at pH 7.0 (the point of zero charge of the fuller's earth) and decreases on both the sides of this pH value. The addition of anions causes depression in the adsorbed mass showing the greatest fall with PO₄³⁻ ion. The adsorption also falls appreciably when dioxane is present in the system in the concentration range of 8% - 20% v/v while alcohols do not affect the adsorption at all. The adsorption also increases with increasing temperature of the adsorption system. It is also noticed that the adsorption decreases with increasing molecular weight and degree of hydrolysis of the polymer. The experimental findings suggest that the adsorption occurs mainly via the hydrogen bonds developed between the carbonyls of the PAM and aluminols of the edge face of the clay.

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