Adsorption Behavior of Sulfamethoxazole onto an Alumina-Solution Interface

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The adsorption measurements of sulfamethoxazole (SM) onto an alumina surface have been done at room temperature with an object to study the mode of SM adsorption at the solution–alumina interface. It is found that the adsorption isotherm is of the Langmuir type, showing a uni-layer formation of the SM molecules on the alumina surface. The adsorption is pH-dependent and found to increase with increasing pH of the medium. The adsorption is quite sensitive to the presence of Cl^- and $SO_4{}^{2-}$ ions also and shows much interesting variation with increasing concentrations of the added anions. The adsorption also decreases with increasing temperature of the adsorption medium. Various kinetic and adsorption parameters such as the adsorption coefficient, rate constants for the adsorption and desorption, and surface coverage have been evaluated with the help of a proposed kinetics scheme.

The significance of adsorption of low and high molecular weight compounds has been well recognized in various industrial, technological, and biological processes.[1,2] Though extensive experimental investigations have been done to discover the interface behavior of a variety of low molecular weight compounds,[3—6] however, studies pertaining to the adsorption of biologically active compounds at solid–liquid interfaces have been quite limited in number.[7—9] Moreover, the earlier investigations were mainly focused on the study of the conformational aspects of the adsorbed substances and no serious attempts were made to follow the kinetic path of the adsorption process. Thus, looking to the realization of the need for studying the dynamic behavior of the adsorption of compounds of biological significance, this study has been undertaken.

From our research laboratory the results of the adsorption of synthetic polymers and natural biopolymers (proteins) onto the solid surfaces have been published[10—14] and most recently we studied the interface behavior of sulfa drugs, taking sulfanilamide as an example of such drugs.[15] Extending the previous study, we are reporting the results of the adsorption of sulfamethoxazole [4-amino-*N*-(5-methyl-3-isoxazolyl) benzenesulfonamide] onto alumina. The study involves following the kinetic behavior of the adsorption of sulfamethoxazole from its solution onto alumina which has long been known as an effective adsorbent in columnchromatography. For evaluating various kinetic and adsorption parameters of the adsorption process we attempted to apply the adsorption rate expression model to this study as the kinetic scheme has already been applied to many cases.[10—12].

Experimental

Reagents. Adsorbate. Sulfamethoxazole (abbreviated as SM) was obtained from uncoated Septron tablets containing 400 mg of SM and 80 mg of trimethoprim [5-(3,4,5-trimethoxybenzyl)-2,4-pyrimidinediamine].

Adsorbent. The alumina powder was supplied by the BDH (Poole, England) and its specific surface area measured by the BET method using N_2 as an adsorbate was found to be 18.0 m^2 g^{-1}. The zero point charge of the oxide was found to be 9.0 as measured by the usual titration procedure.

4-Methylaminophenol sulfate (Metol) was A.R. grade (Samir Tech, India) and used without further purification. Other reagents used were also guaranteed reagent grade. Fresh solutions of Metol and SM were prepared for each run and conductivity water was used throughout the experiments.

Method. Preparation of SM Solution. A solution of SM was prepared by treating it with 2 drops of 10% v/v hydrochloric acid and diluting to the required volume in a standard flask.

Method of Adsorption. The method to do adsorption consists of shaking a known volume of SM solution of definite concentration containing 200 mg of alumina for about 2 h, which was found to be a sufficient time for an equilibrium to be attained. After the shaking period of adsorption the solution was centrifuged (Remi, India) to obtain a clear supernatent solution. To measure the amount of SM adsorbed, the supernatent solution was analyzed for SM by the colorimetric method (Systronics, India) as described elsewhere in detail.[16]

pH measurements were done in a digital pH meter (Systronics, India) and the pH of the SM solution was varied with 0.1 M sodium hydroxide (1 M = 1 mol dm^{-3}) and hydrochloric acid solution.

The adsorption solution was constantly monitored to maintain a fixed pH during the adsorption process.

Results and Discussion

Concentration Effect. It has been widely reported that on increasing the concentration of adsorbate the extent of adsorption also increases. In this study the effect of increase in the initial concentration of SM solution on the amount adsorbed has been investigated by varying the concentration of SM in the range 2.0 to 20.0 mmol dm^{-3}. The results are shown in Fig. 1, which clearly implies that the amount of SM adsorbed (in mg g^{-1}) increases with increasing concentration. The reason for the observed increase is quite obvious as with increasing concentration of SM solution a greater number of SM molecules will be approaching the interface and consequently the adsorbed mass will increase.

Adsorption Isotherm. One of the most significant parameters of an adsorption investigation is the adsorption isotherm, which is commonly obtained by plotting a graph between the adsorbed amount (mg g^{-1}) and equilibrium concentration of the adsorbate. The usefulness of the parameter lies in the fact that it not only provide a quantitative idea of the adsorption process but also highlights various probable modes of the adsorption.[17] In this investigation the adsorption isotherm obtained is shown in Fig. 2. Looking to the shape of the adsorption isotherm it is clear that the isotherm belongs to L2, i.e. the Langmuir type, of isotherm, which is a widely reported isotherm in most of the adsorption studies.

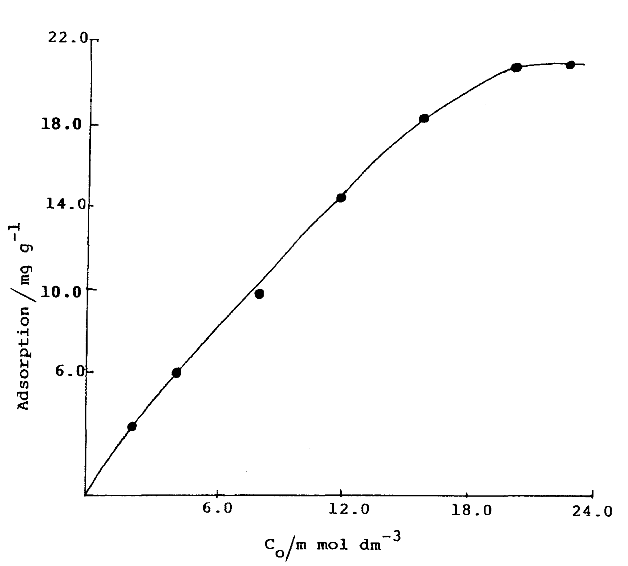


Fig. 1. Effect of the initial concentration of the sulfamethoxazole (SM) solution on its adsorption onto alumina at pH 5.8 and ionic strength at 0.001 M KNO_3.

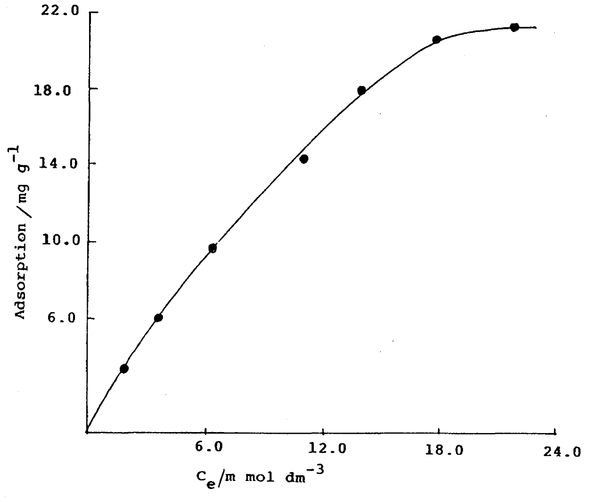


Fig. 2. Amount of SM adsorbed (in mg g^{-1}) versus the equilibrium concentration of the SM solution (mmol dm^{-3}).

When we analyze the slope of the isotherm, it becomes clear from the initial curvature that as more sites on the alumina surface are filled it becomes increasing difficult for an interface-approaching molecule to find a vacant site available for adsorption. As the initial slope is not very steep it also suggests that the rate of adsorption is slow and the adsorbing SM molecules do not have much affinity for the alumina surface.

Now we explain how the adsorption of SM molecules on the alumina surface occurs. Since the adsorption experiment is done at pH 5.8, which is quite below the zero point charge (ZPC) of alumina (9.0) obviously several protonated hydroxy groups ($AlOH_2^+$) must be present on the surface of alumina along with some AlOH groups. Also the SM molecules will also be present in their protonated form, i.e.

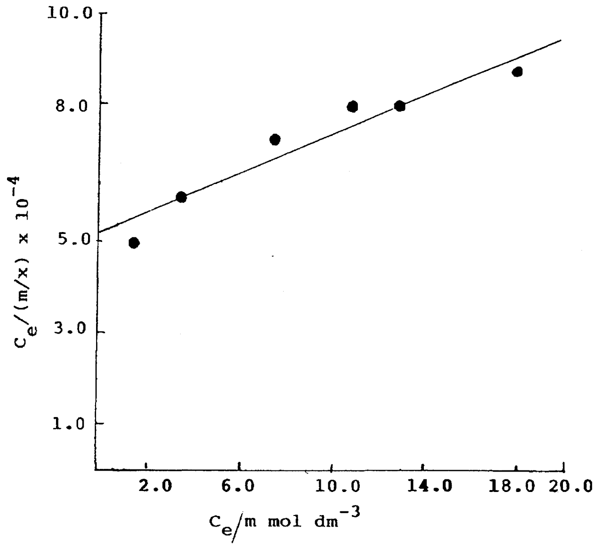


Fig. 3. Plot of $C_e/(m/x)$ versus the equilibrium concentration C_e.

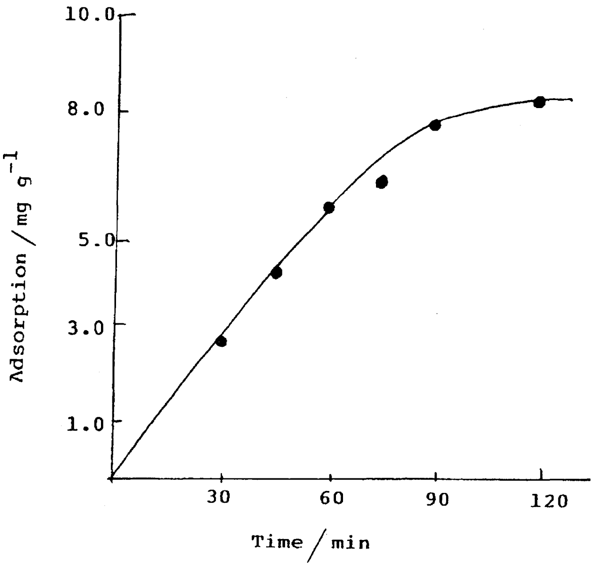


Fig. 4. Variation of the amount of SM adsorbed with time at fixed [SM] = 7.9 mmol dm^{-3}, [Al_2O_3] = 0.2 g, pH = 5.8, [KNO_3] = 1.0 mmol dm^{-3} and temperature = 25±0.2 °C.

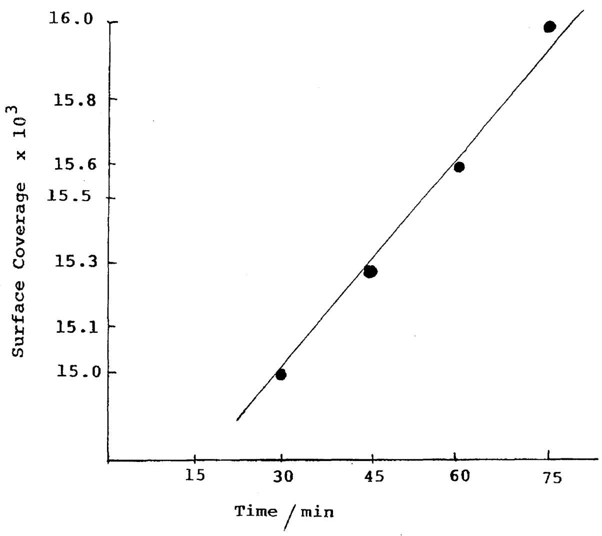


Fig. 5. Variation of surface coverage (θ) with time at fixed $[\mathrm{SM}]=7.9\ \mathrm{mmol\,dm^{-3}}$, $[\mathrm{Al_2O_3}]=0.2$ g, pH=5.8, $[\mathrm{KNO_3}]=1.0\ \mathrm{mmol\,dm^{-3}}$ and temperature $=25\pm0.2$ °C.

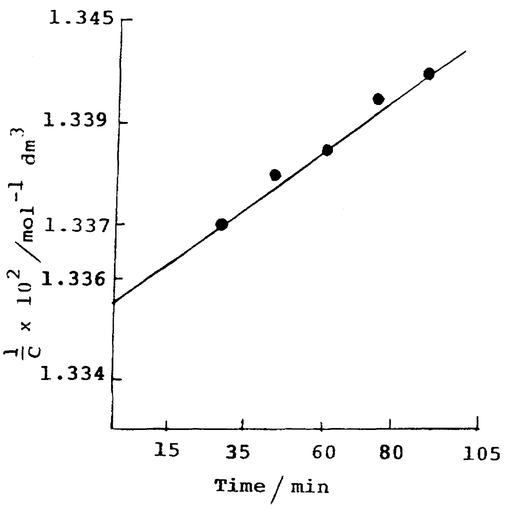


Fig. 6. Plot of $1/C$ versus time for the evaluation of k_1.

$H_3\overset{+}{N}$-⌬-SO_2NHR. Now it can clearly be seen that the driving forces for adsorption of SM molecules are mainly H-bonding forces operating between the AlOH group of alumina and $H_3\overset{+}{N}$-group of SM.

From this discussion it is clear that the adsorption of SM on alumina takes place via either protonated amino groups or sulfonamide groups. It is therefore obvious that in both the cases a vertical type of orientation will be acquired by adsorbed SM molecules. Furthermore, this vertical adsorption is also supported by the fact that a flat type of adsorption of SM molecules would require a surface area of 34 Å²/molecule of SM (from Fig. 2) which in no way may be justified.

One more point that deserves much attention is the fact that the initial slope reflects the rate of change of site availability with increase in solute adsorbed. As more solute is taken up, there is usually progressively less chance that an approaching SM molecule will find a suitable site on which it can be adsorbed, i.e. to cause adsorption of a given amount of solute the external solution concentration must be raised by ever increasing amounts. This applies to the normal L type of curves in otherwise case the isotherm would be an S type one.

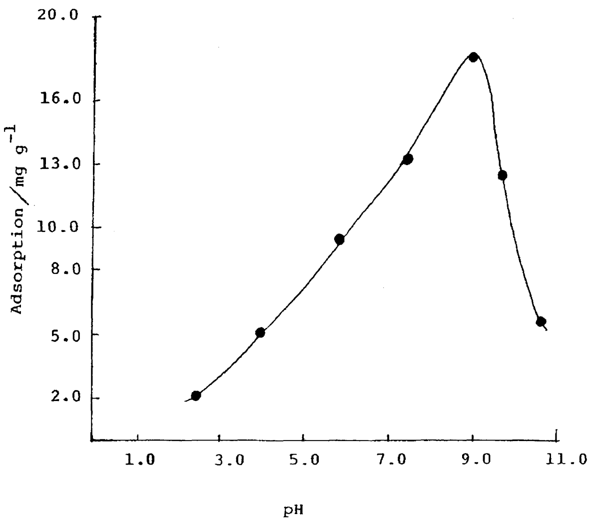


Fig. 7. Effect of varying pH of the SM solution on its plateau adsorption at fixed $[\mathrm{SM}]=7.9\ \mathrm{mmol\,dm^{-3}}$, $[\mathrm{Al_2O_3}]=0.2$ g, $[\mathrm{KNO_3}]=1.0\ \mathrm{mmol\,dm^{-3}}$ and temperature $=25\pm0.2$ °C.

Adsorption Coefficient. The evaluate numerically of the value of the adsorption coefficient K $(=k_1/k_2)$ a plot has been drawn between $C_e/(m/x)$ and C_e, which according to the Langmuir isotherm equation yields a straight line from the intercept and slope of which the value of the adsorption coefficient K is calculated. Such a plot is shown in Fig. 3 and the adsorption coefficient has been calculated to be 0.49×10^{2} $\mathrm{dm^3\,mol^{-1}}$.

Kinetics of the Adsorption Process. The kinetic path of the adsorption of SM molecules onto the alumina surface has been studied by monitoring the residual concentration of the adsorbate solution at different times. The progress of the reaction is depicted in Fig. 4, which clearly indicates that the rate of the adsorption process is almost constant up to 90 min and then starts decreasing. After about 2 h the adsorption rate levels off, thus indicating a saturation in the adsorption of SM. Now with the help of the adsorption plots, various adsorption parameters shall be evaluated.

Surface Coverage (θ). The fraction of the surface occupied by the adsorbate molecules is commonly termed the surface coverage (θ). The surface coverage by the SM molecules at various times has been calculated according to the following equation (details given elsewhere).[10)]

$$\theta=\frac{C_0-C}{C_0+k'}, \qquad (1)$$

where C_0= initial concentration of the SM solution,
C = residual concentration of SM in the supernatent solution after adsorption at different times,
k'= a constant $(=k_2/k_1)$.

With the help of this equation, θ values at different times have been calculated and are shown in Fig. 5. As the proposed kinetic scheme is applicable up to the time at which the rate of adsorption is constant, the θ values have been calculated up to 90 min, since until that the plot drawn between the adsorbed amount and time is almost straight (Fig. 4). It is clear from Fig. 5 that surface coverage (θ) increases with increasing time of the adsorption which is quite obvious also since as the time goes on the fraction of the alumina surface gets progressively occupied by the SM molecules and, therefore, the surface coverage increases.

Calculation of k_1 and k_2. To calculate the rate constants for adsorption (k_1) and desorption (k_2) we take up the following equation (for details see Ref. 10),

$$\frac{1}{C}=\frac{k_1}{C_0}\cdot t+\frac{1}{C_0} \tag{2}$$

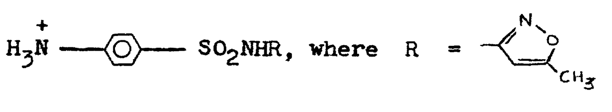
where C and C_0 have the same meaning as in Eq. 1.

It is clear from Eq. 2 that a plot between $1/C$ vs. t should yield a straight line, from the slope and intercept of which k_1 may easily be calculated. The plot so drawn is shown in Fig. 6 and the value of k_1 as calculated from Eq. 2 has been found to be 1.23×10^{-6} s^{-1}. Once the value of both K and k_1 is known, it is quite simple to evaluate k_2, which in the present case has been found to be 2.50×10^{-8} mol dm^{-3} s^{-1}.

pH Effects. The role of pH is quite significant in deciding the rate of any physical or chemical process. In studies pertaining to the adsorption of substances onto polar surfaces such as alumina the pH factor becomes much more important since a small variation in the pH of the solution does bring about a large change in the electrostatic charge profile of the system on which the driving forces of adsorption are fundamentally dependent. In fact, a change in the pH of the adsorption medium affects the electrostatic charges over the adsorbate and adsorbent species which in some way influences the adsorbed amount.

In this study the effects of pH on the adsorption of SM onto alumina have been studied by varying the pH of the adsorption medium from pH 2.6 to 10.4. The results are depicted in Fig. 7, which clearly indicate that the adsorbed amount increases with increasing pH of the medium. The results observed may be explained as below:

When we consider the state of affairs of the electrostatic charges at pH 2.6 of the SM solution it is found that the SM molecules are present in the protonated form as shown below,



and alumina contains $-\mathrm{AlOH_2}^+$ type of groups on its surface. Obviously, one has to preclude the possibility of electrostatic interactions as the driving forces of adsorption because of the like charges of both the adsorbate and adsorbent molecules. Therefore, under this situation it is likely to think of the H-bonding type of forces between the SM molecules and alumina surface as the driving forces for the adsorption. The schematic representation of the formation of H-bonding may be shown as

$$\mathrm{AlOH}+\mathrm{H_3}\overset{+}{\mathrm{N}}\text{-⌬-}\mathrm{SO_2NHR}\rightarrow \mathrm{AlOH}\cdots\mathrm{H_3}\overset{+}{\mathrm{N}}\text{-⌬-}\mathrm{SO_2NHR} \tag{3}$$

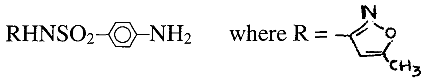
Some authors[18,19] have also postulated an interaction of surface hydroxyls and $\mathrm{H_3}\overset{+}{\mathrm{N}}$–groups in a somewhat different way,

$$\mathrm{AlOH}+\mathrm{H_3}\overset{+}{\mathrm{N}}\text{-⌬-}\mathrm{SO_2NHR}\rightarrow \mathrm{AlO^-}\cdots\mathrm{H_3}\overset{+}{\mathrm{N}}\text{-⌬-}\mathrm{SO_2NHR}+\mathrm{H^+} \tag{4}$$

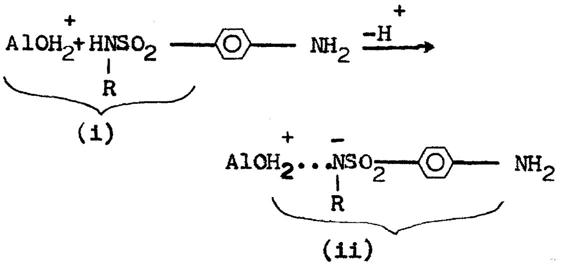
Here it is worth mentioning that since fewer unprotonated surface hydroxy (AlOH) groups are present at pH 2.6, very low adsorption results therefrom. It has also been noticed that almost no adsorption takes place below pH 2.6 as the whole alumina might be in the protonated forms and, therefore, both 1 and 2 type of interactions could not be considered.

Now upon increasing the pH of the adsorption medium the positive charges over alumina and the SM molecules decrease, which results in a greater interaction between the two, thereby increasing the extent of adsorption. Now let us consider the possible mode of interaction between the SM molecules and protonated alumina in the alkaline range, specifically at pH 7.0.

At pH 7.0 the SM molecule is present in the solution as an uncharged species, i.e.,



However, when the SM molecule comes near an $\mathrm{AlOH_2}^+$ group on the alumina surface the interaction between the protonated aluminol (i.e. $\mathrm{AlO\overset{+}{H}_2}$) and SM is thermodynamically favored & this results in expulsion of an acidic H from the SM molecule to generate a negatively charged SM as shown below,



It can be seen that species (ii) due to electrostatic attraction between $\mathrm{AlOH_2}^+$ and $\mathrm{SM^-}$, is more stable than species (i).

Beyond pH 7.0, i.e. in the alkaline range, the SM molecules bear a net negative charge but on the other hand a positive charge is still retained with the alumina surface unless the pH reaches 9.0, which is the zero point charge of alumina. Obviously an electrostatic attraction begins to operate as shown below and causes a steep rise in the adsorption.

$$\mathrm{AlOH_2}^+ +\mathrm{R\bar{N}SO_2}\text{-⌬-}\mathrm{NH_2}\rightarrow \mathrm{AlOH_2}^+\cdots\mathrm{R\bar{N}SO_2}\text{-⌬-}\mathrm{NH_2} \tag{5}$$

It is also clear that in this pH range the orientation of SM molecules after adsorption will be inverted, directing amines group of the molecule outwards. As the pH of the adsorption

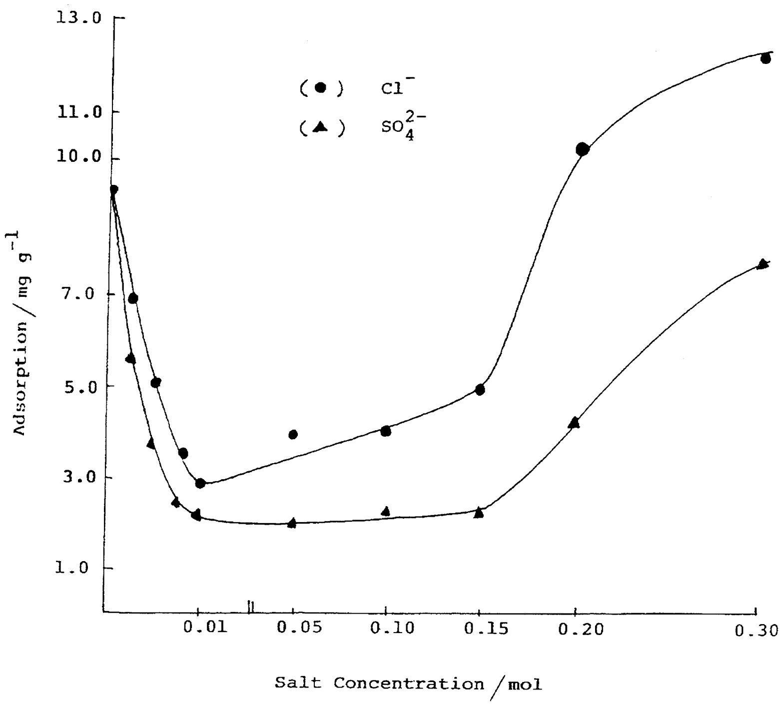


Fig. 8. Effect of addition of salts on the plateau adsorption of SM at fixed [SM]=7.9 mmol dm^{-3}, [Al_2O_3]=0.2 g, pH=5.8 and temperature=25±0.2 °C.

medium becomes equal to the zero point charge of alumina (9.0), the alumina surface acquires a zero charge and at this point also the following interaction may be considered to exist.

$$\text{AlOH} + \text{H}_2\text{N-⌬-SO}_2\text{NHR} \rightarrow \text{AlOH}\cdots\text{HNH-⌬-SO}_2\overset{-}{\text{N}}\text{R} \quad (6)$$

$$\text{AlOH} + \text{R}\overset{-}{\text{N}}\text{O}_2\text{S-⌬-NH}_2 \rightarrow \text{AlOH}\cdots\text{R}\overset{-}{\text{N}}\text{O}_2\text{S-⌬-NH}_2 \quad (7)$$

On further increasing the pH beyond 9.0 the surface of alumina acquires a negative charge due to the formation of AlO^- groups on its surface and this results in a fall in the adsorbed amount as an electrostatic repulsion begins to operate between the SM molecules and the alumina surface. Results showing a similar type of pH-dependence of adsorption have also been reported elsewhere.[20)]

Furthermore Fig. 7 also shows that before pH 9.0 the adsorption does not increase as steeply as it falls after pH 9.0. This may be explain by the fact that beyond pH 9.0 some complex type of side processes occur in the adsorption medium due to which the adsorption falls more readily than before pH 9.0, thus making the plot a little more asymmetric in appearance.

Electrolyte Effect. Adsorption studies in presence of electrolytes like NaCl and Na_2SO_4 have been done at pH 5.8 and several interesting results have been obtained as shown in Fig. 8. It is clear from the Figure that in the lower concentration range of added salts (i.e. up to 0.01 M) the adsorption of SM decreases and becomes minimum at 0.01 M concentration of the added anions. However, on further increasing the concentration of electrolytes the adsorption increases continuously, a quite uncommon result.

In the presence of Cl^- and $SO_4{}^{2-}$ ions at the lower concentration (<0.01 M) at the studied pH 5.8, both the alumina and SM will bear a positive charge. In fact there will not be any true competition between the Cl^- ions and SM^+ for getting adsorbed onto the positive alumina surface as the latter are positively charged and, consequently will occupy fewer active sites. On the other hand a major fraction of active sites shall be occupied by the Cl^- alone as being oppositely charged to the alumina surface. Now, when the concentration of electrolytes is further increased i.e. beyond 0.01 M,

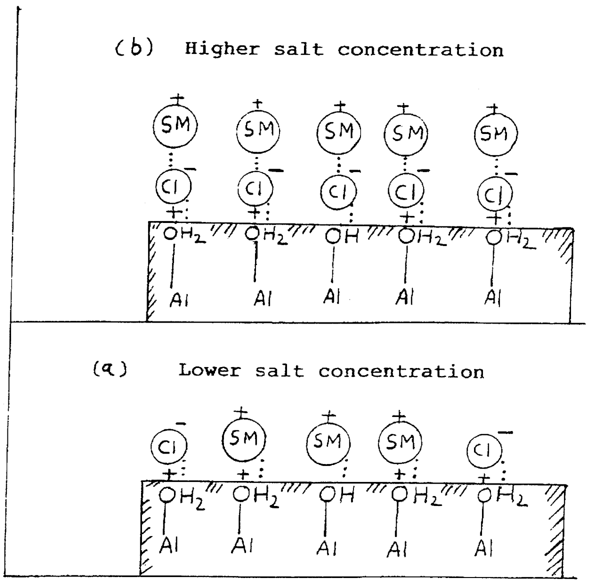


Fig. 9. Schematic representation of the adsorption of SM onto the alumina surface in presence of anions (say Cl^-) at (a) lower and (b) higher concentrations.

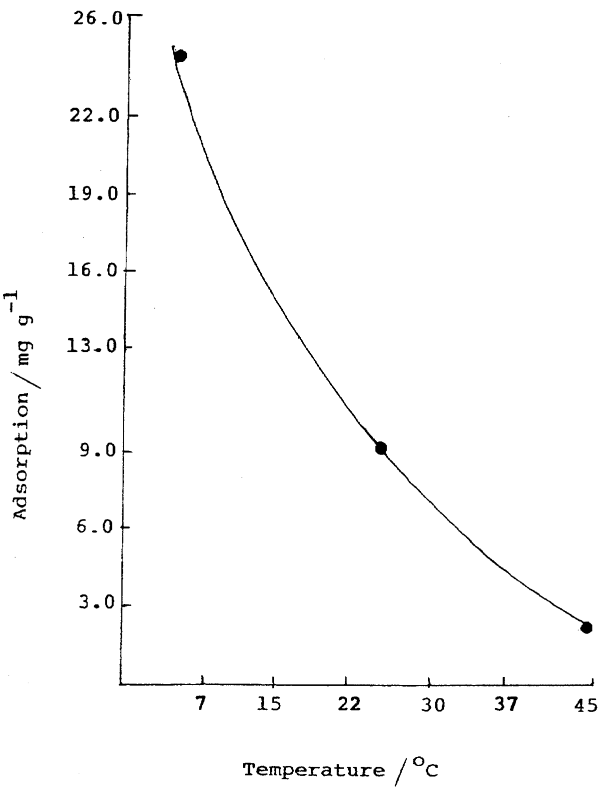


Fig. 10. Effect of temperature (°C) on the plateau adsorption of SM.

the adsorption of SM is found to increase. The increase so observed may be attributed to the fact that once the surface of alumina becomes richly occupied by the Cl^- or SO_4^{2-} ions as a result of their preferential adsorption, the surface of alumina acquires a net negative charge which facilitates the adsorption of the protonated SM molecules. This picture of adsorption naturally results in a bilayer formation on the alumina surface, which is schematically shown in Fig. 9. A similar type of preferential adsorption of Cl^- and SO_4^{2-} ions onto iron oxide has also been shown elsewhere.[21)]

When the adsorption curves for Cl^- and SO_4^{2-} ions are compared it becomes apparent that more depression in adsorption is caused by SO_4^{2-} ions due to their bivalency as compared to the monovalent Cl^- ions. But beyond 0.01 M concentration the increase in the adsorption of SM is rather steep in the case of Cl^- ions, which may be attributed to the fact that the SO_4^{2-} ions due to their larger size cause steric hindrance for the approaching SM molecules, causing a lower increase in the amount adsorbed.

Temperature Effects. The effects of increasing temperature on the adsorption of SM have been studied by adsorption experiments in the temperature range of 5 °C to 45 °C. The results are shown in Fig. 10, which clearly imply that with a rise in temperature the adsorption generally decreases. The greater amount of adsorption at lower temperatures may be attributed to the following facts:

(i) Since the adsorption appears to be physical in nature, the responsible intermolecular forces become prominent at lower temperatures and therefore the adsorption will be greater.

(ii) At lower temperature the possibility of agglomeration of charged SM molecules may not be ruled out as reported by some authors[22—24)] in case of cationic and anionic dyes. Obviously greater adsorption will be observed at lower temperatures therefore.

(iii) A greater escaping tendency of SM molecules from the solid phase to the bulk phase may be considered at higher temperatures, which also explains a greater adsorption at lower temperature.

(iv) The increased solubility of SM at higher temperatures may also significantly curtail the extent of adsorption.[25)]

(v) At lower temperatures the number of active sites on the surface of the adsorbent may also increase as postulated by some authors.[25)] This will obviously results in an increase in the adsorbed amount of SM. A similar type of results have also been reported by other workers.[26,27)]

In several investigations,[28)] however, an increase in the adsorption capacity has been observed which is attributed to either an increase in the number of active sites on the adsorbent or strengthening of the bonds between the adsorbate and adsorbent.

Role of the Substituent (R) Group. When we compare the adsorption of SM with sulfanilamide under identical conditions it is found that in the latter case the adsorption is about 60% more than the former. The reason for the lower adsorption of SM may be the bulkiness of the substituent group, which produces steric hindrance to the alumina surface.

One more point of greater consideration is that due to the electron-withdrawing nature of the substituent group in the SM molecule the negative charge over the SM molecule is rather decreased and this results in a lower adsorption as compared to that of the sulfanilamide molecules.

Conclusions

The adsorption of sulfamethoxazole (SM) onto the alumina surface is characterized by a Langmuir type of adsorption isotherm. The adsorption is much poorer at low pH but increases as the pH of the SM solution increases. After crossing the zero point charge of alumina the adsorption starts decreasing. Similarly the addition of anions to the adsorption medium significantly affects the adsorption. An initial fall in the adsorbed SM is followed by a sudden rise in the adsorption isotherm. The temperature, as usual, has an inverse effect on the adsorption. The bulky substituent group in the SM molecule lowers its adsorption due to the steric hindrance as compared to the sulfanilamide molecule.

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