

ADSORPTION OF ACRIDINE ORANGE ON SOME METAL OXIDES

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The adsorption studies of acridine orange from aqueous solution were carried out over calcium oxide, magnesium oxide and zinc oxide. The adsorbents were subjected to a few pretreatments and the effect of pretreatment was studied on the extent and mode of adsorption. The adsorption over various pretreated surfaces exhibited three kinds of adsorption pattern, namely, S-type, L-type and H-type. The mode of adsorption is explained on the basis of the adsorption isotherm. The H-type is explained as flatwise adsorption with some ionic micellisation. The L-type has been interpreted as multilayer adsorption (flatwise) with the formation of large ionic micelles. The S-type has been explained as edge on (monodisperse) adsorption. The Freundlich adsorption isotherm are applicable within the limited range of concentration of dye. In few cases, these equations are not applicable due to the complex adsorption mechanism.

Key words: Acridine orange, Metal oxides, Aqueous solution.

Introduction

The adsorption of the cationic dye acridine orange by Nasonite and the colloidal properties of the aqueous solution were investigated by Garfinkel-Shweky (1995) using visible spectroscopy. It was found that organic cations were adsorbed by the mechanism of cation exchange. When small amount of the dye was adsorbed, the dye penetrates into the interlayer space and most of it undergoes metachromasy due to interaction between the aromatic entity and the oxygen plane of the clay. But at greater amounts of acridine orange the metachromasy results from the aggregation of dye in the inter particle space. In excess acridine orange, the clay was gradually peptized. Garfinkel-Shweky and Yariv (1997) observed that the adsorption of cationic dye acridine orange by different monoionic laponites leads to changes in the colloids properties of this synthetic mineral in aqueous solution. The organic cation was adsorbed by the mechanism of cation exchange. Small amounts of adsorbed dye keep the clay in the peptized state with all metallic cations. Greater amount of acridine orange resulted in the neutralization of electric charge of clay, and its flocculation. In excess acridine orange the charge of clay platelets became positive and the clay was peptized. The colloidal properties were studied by the absorbance curves in which the absorbance was described as a function of the degree of saturation with constant clay concentration or with constant dye concentration. In the absorbance curves three regions can be identified. The transition between first and

second or second and third region depend on the exchangeable metallic cation initially present in the clay (Garfinkel-Shweky and Yariv 1995). It has also been found that saturated adsorption amount of the dyes on activated carbon was correlated with the electrostatic forces between charges on the carbon surface and ionic dyes. There exist the electrostatic attractive or repulsive forces between the activated carbon and ionic dyes. The adsorption forces are the sum or difference of dispersion and electrostatic forces. This conclusion was further supported by the kinetic and thermodynamic parameter that was calculated from experimental data (Minguan 1997). The adsorption characteristics of types of dyes in aqueous solutions on 9 types of amorphous oxide gel were examined. The adsorptive ability was affected by the pH of the dye solution and composition of the gel (Motoshi *et al* 1990).

The Surface Enhanced Raman Scattering (SERS) spectra of acridine in Ag solution was studied by Seong *et al* (1991). The presence of halide ions was a pre-requisite for the observation of SERS. Different SERS spectra were obtained using different pH solutions. At neutral pH, acridine was adsorbed on the Ag surface via its N lone pair electrons while in acidic medium it adsorbs as the acridinium-chloride ion pair through the Cl atom. The charge transfer effect appears to play an important role along with the electromagnetic effect. On the other hand, photoreaction readily occurs in a highly basic medium. This was concluded in terms of the competitive adsorption of Cl and O ions on Ag. Nonetheless, the acidity of acridinium ion seemed to be far greater on the surface than

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in the bulk aqueous phase (Seong *et al* 1991). Effect of pH on adsorbed amount of methyl orange was studied by Shimada, *et al* (1992) on Al_2O_3 . Red colored Al_2O_3 showed adsorption of methyl orange. Langmuir type isothermal curve was obtained (Shimada *et al* 1992). Safranin T in aqueous solutions was adsorbed by different samples of silica exhibiting representative S-, L- and H-type isotherms, mostly S-type curves were observed. A typical sigmoid type adsorption behavior was found for preparative layer chromatographic silica sample. The adsorption was inhibited in an alkaline media while acidic media promotes adsorption (Mirza *et al* 1992). Adsorption isotherm of 3,6 diamino acridine on Kaoline clay showed that the dye molecules penetrate into the interlayer space of the alumino-silicate layer of the clay, while in the case of alumina the dye molecules cover only the surface. This shows that dye existed as a monolayer in the adsorbed state. The emission of dye adsorbed on clays was quenched completely even in dilute solution which shows that Al^{+3} of the alumino-silicate layer of the clay might partly be responsible for the quenching of the adsorbed dye (Ramaraj *et al* 1992).

The work with clean metal surfaces has emphasised the complexities that undoubtedly occur when metal powders chemically deposited metal films, oxides of metals and non metals are used as adsorbents. This more complicated surface phenomenon cannot therefore be restricted. In this recent study we have investigated the behavior and the extent of adsorption of acridine orange on some inorganic metal oxides. The adsorption of acridine orange at room temperature was found to be suitable for surface area measurements on a wide variety of solids, including carbon, cement, fibres, organic pigments etc. This work will provide the guideline to the chemists for the adsorption of dyes on some organic and inorganic solids.

Experimental

Chemically pure grade solid acridine orange from E-Merck (Germany) was used without purification. Ethyl alcohol was distilled and used whenever required. Water was doubly distilled and used for the preparation of solution as well as for washing glassware. Sodium hydroxide and conc. HCl was used for preparing 0.1 N solution for washing metal oxides. The stock solutions of dye were prepared by dissolving an appropriate amount of the dye in the solvent followed by making up the volume up to mark. For adsorption purposes, further test solutions, ranging from 1-10 ppm for acridine orange, was prepared. The adsorption studies were carried out with acridine orange over various adsorbents namely calcium oxide, magnesium oxide and zinc oxide for

investigations. In a series of adsorption experiments, calcium oxide, magnesium oxide and zinc oxide were used as such without further treatment called as "fresh" calcium oxide, magnesium oxide and zinc oxide. In third series of adsorption experiments, these adsorbents were used after washing with 0.1 N HCl solution followed by heating at 200°C in the muffle furnace for 1-2 h and subsequently cooling gradually to room temperature called as "washed". All these solids were placed in desiccator (CaCl_2) to avoid contact of moisture with the adsorbents.

Adsorption studies. To study adsorption phenomenon the following procedure was adopted. Prepared test solution ranging in concentration from 1 ppm to 10 ppm in 100ml measuring flasks. Weighed 1g adsorbent in a series of 50 ml measuring flasks. Then to each flask added test solution from above series, made the volume up to the mark. The flasks were then tumbled for about half an hour and then kept stationary under thermostating condition away from light for a period of an hour. The amount of solute adsorbed was calculated from the difference in initial reading (without adsorbent) and final concentration of the solution measured absorptiometrically on the spectrophotometer at λ_{max} 490 nm (Mirza *et al* 1995). The absorbance of the sample should be according to Beer-Lambert law. The amount of the adsorbate removed by adsorption (x) was determined by subtracting final concentration (C_e) of solution from initial concentration (C_o) and amount of the adsorption per gram of the adsorbent (x/m) was calculated by dividing x with amount of adsorbent taken (usually 1g). Plotting x/m against C_e directly proved the applicability of the Freundlich adsorption isotherm.

Results and Discussion

The results obtained from the adsorption studies of acridine orange on various adsorbents such as calcium oxide, magnesium oxide and zinc oxide are discussed in the following sections.

Three major types of adsorption isotherms regarding adsorption from solution of acridine orange on different metal oxides have been classified by Giles *et al* (1964). These are discussed as H-type, L-type and S-type. The S-type (Figs 1,3 and 7) is initially convex to the solution concentration and then a plateau. The H-type (Fig 6) adsorption isotherm starts with positive value against the equilibrium concentration, usually, a sharp rise on vertical axis. In such isotherms the solution has high affinity for the adsorbent. The L-type (all other figures) adsorption isotherm is initially concave to the solution concentration and then plateau. In L-type adsorption isotherm, initially it is like H-type, then a plateau, fol-

Table 1
Mode of adsorption and monolayer capacities of acridine orange on metal oxides

Adsorbent	X/m (mono)	X/m (max)	Isotherm type	Monolayer/Multilayer	Figure
Fresh MgO	1.29	6.46	S-type	Multilayer	1
MgO washed in 0.1N HCl	Multilayer	2	8.44	L-type	
MgO washed in 0.1N Na OH	Multilayer	3	9.4	S-type	
Fresh CaO	1.13	7.45	L-type	Multilayer	4
CaO washed in 0.1N Na OH	Multilayer	5	8.56	L-type	
Ca O washed in 0.1 N HCl	Monolayer	6	6.6	H-type	
Fresh ZnO	0.4	6.63	S-type	Multilayer	7
ZnO washed in 0.1N NaOH	Multilayer	8	3.34	L-type	
ZnO washed in 0.1 N HCl	Multilayer	9	1.36	L-type	

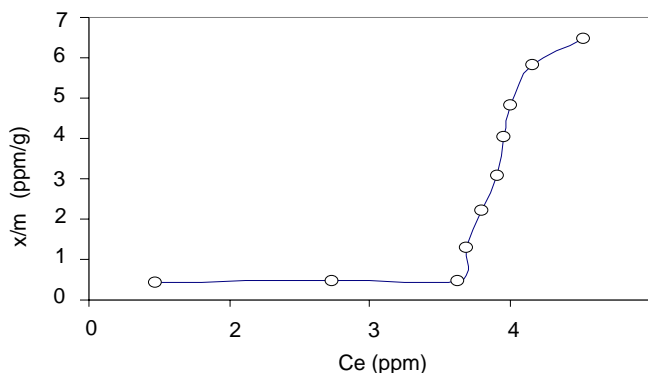


Fig 1. Adsorption of acridine orange on fresh MgO.

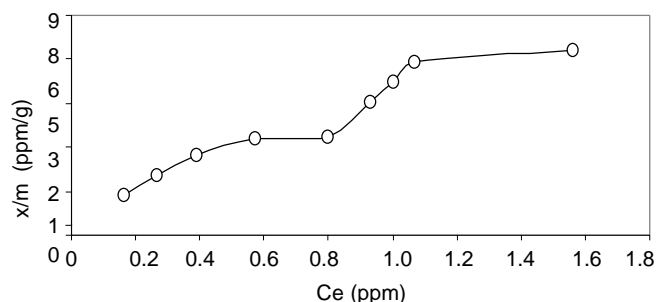


Fig 2. Adsorption of acridine orange on washed MgO in 0.1 N HCl solution.

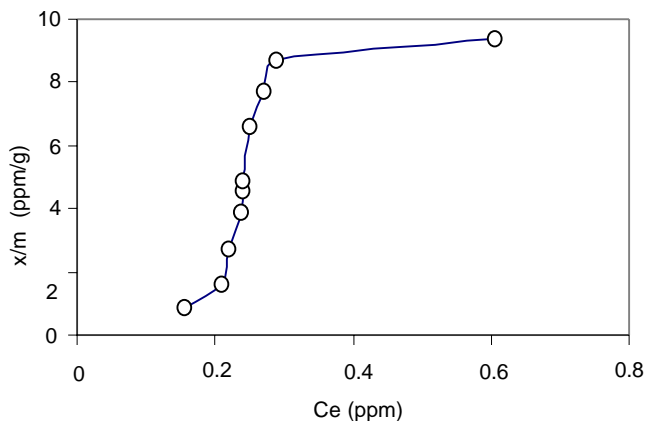


Fig 3. Adsorption of acridine orange on washed MgO in 0.1 N NaOH solution.

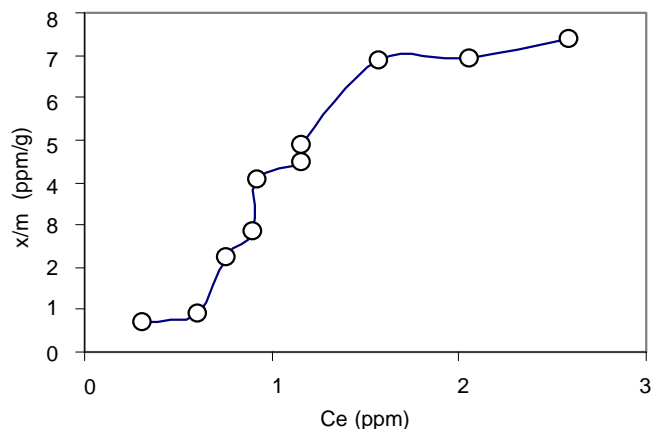


Fig 4. Adsorption of acridine orange on fresh CaO.

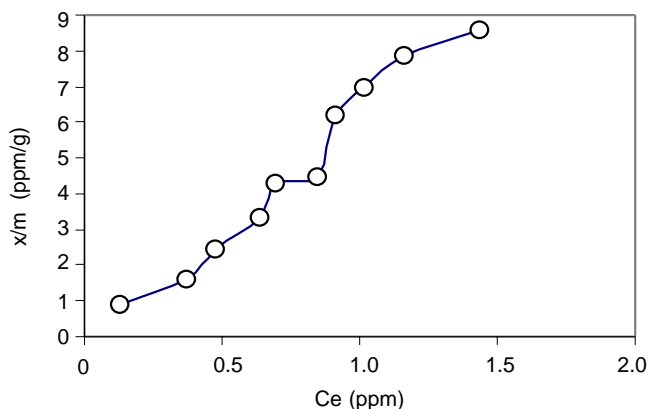


Fig 5. Adsorption of acridine orange on washed CaO in 0.1N NaOH solution.

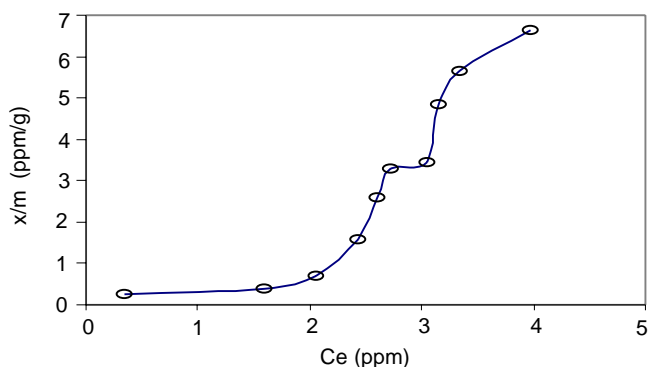


Fig 7. Adsorption of acridine orange on fresh ZnO.

lowed by another rise and possibly another plateau. The initial rise in adsorption depends upon the number of adsorption sites available. The plateau signifies the completion of monolayer i.e., saturation of surface and further adsorption takes place only on new surface developed. The length of the plateau in an isotherm indicates a high energy to be overcome before additional adsorption can occur on new sites. The start of a plateau indicates a monolayer completion. Further rise in an adsorption isotherm signifies the multilayer formation. The L-type isotherms are very commonly observed in the present studies. The isotherms are related with the mode of adsorption, orientation of adsorbed species, adsorption affinity monolayer or multilayer formation. The adsorption data like isotherm monolayer capacity, possibility of multilayer formation for acridine orange is shown in Table-1.

The monolayer adsorption capacity was determined from the plateau (Brunaur's point) on the isotherm. The results indicate that the metal oxides surface treated with sodium hydroxide possess an increase in adsorption capacity as compared to those of acid treated surfaces. This trend has been observed overall in metal oxides. This may be attributed due to acid-base interaction of the adsorbate with the adsorbent.

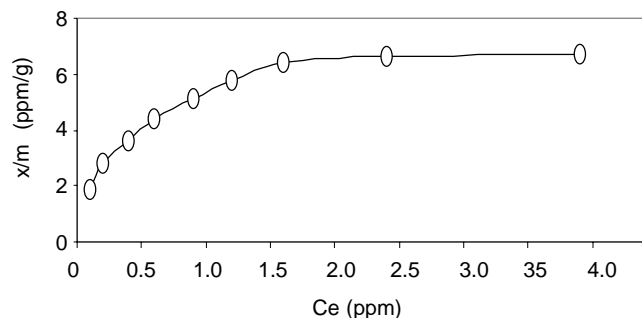


Fig 6. Adsorption of acridine orange on washed CaO in 0.1N HCl solution.

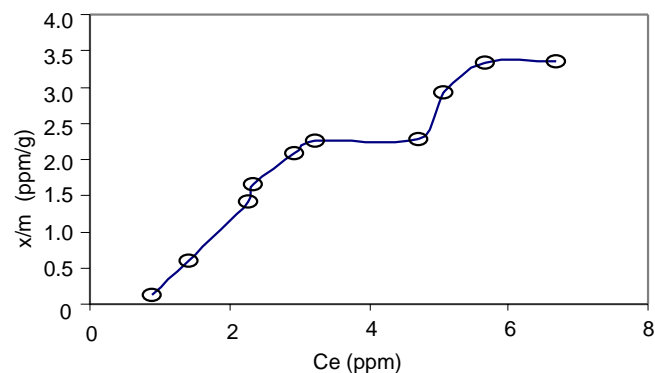


Fig 8. Adsorption of acridine orange on ZnO in 0.1 N NaOH solution.

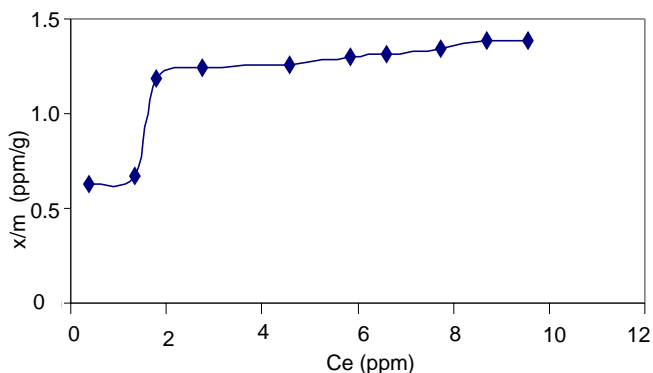


Fig 9. Adsorption of acridine orange on washed ZnO in 0.1N HCl solution.

This is an interesting case because the basic dye shows the reverse case as was observed in our previous paper (Mirza *et al* 1988). This is due to the fact that metal oxides itself shows some interaction with the acridine. In case of fresh metal oxides, the adsorption capacity is less because there is repulsion between basic dyes and the solid oxides, whereas, in case of ZnO the situation is different because ZnO is not a basic in nature. But in case of base treated substances there is some type of interactions develop between solid metal oxides and the basic solution. In this regard there is greater interactions between the metal oxides and acridine dye. On the other hand when solid surface treated with HCl, then there

is strong force of attraction between solid surface and acid molecule appears and weak interactions between acid treated surface and dye occurs. Thus comparing to NaOH treated surface, the adsorption capacity in acid treated surface is further decreased. This anomalous behavior is due to the fact that repulsion occurs between oxide surface and dye molecules, as seen by metal oxides and acridine, both have some basic properties. Therefore as compared to acid or base treated substances adsorption is less in case of fresh metal oxide. But on the other hand if the metal oxides are treated with NaOH then metal oxides show some type of acidic behavior and more interaction with basic dyes. It is also clear that adsorption of dye on the surface of these oxides are less as compared to the acid treated dyes as well as base treated. Thus the adsorption of dyes on ZnO is less as compared to MgO and CaO due to the transition nature of the metal.

References

- Grafinkel-Shweky D, Yariv S 1995 Adsorption of cationic dye acridine orange by different monomeric laponites. *Colloid Polym Sci* **273** (5) 453-463.
- Grafinkel-Shweky D, Yariv S 1997 Metachromasy in claydye systems: The adsorption of acridine orange by Nasonite. *Minerological Society* **32** (4) 653-663.
- Giles C H, Nakhwa S N, Smith D 1960 A system of classification of solution adsorption isotherms and its use in diagnosis of adsorption mechanism and in measurement of specific surface areas of solids. *J Chem Soc* 3973-3993.
- Minguan D J 1997 Adsorption of cationic and anionic dyes on activated carbon. *Colloid Interface Sci* **198** (1) 6-10.
- Mirza M L, Wadood A, Iqbal J, Nawaz S 1995 Sorption of acridine orange on cellulose. *J Res Sci* **7**(1-2) 13-16.
- Mirza M L, Wadood A, Iqbal J, Nisa Q 1992 Sorption behaviour of Safranin-T on silica. *J Nat Sci and Math* **31** (2) 185-191.
- Motoshi N, Yoshio M, Hiroshi S 1990 Adsorption characteristics of amorphous mixed-oxide gels for dyes in aqueous solutions. *Hamamatsu Japan* **432** 81-87.
- Seong T, Kim K, Myung S 1991 Adsorption and surface reaction of acridine in silver sol: Surface-enhanced Raman spectroscopic study. *J Phys Chem* **95**(22) 8844-8849.
- Shimada H, Maru Y, Yasuoka T 1992 Development of teaching materials by using adsorption of methyl orange on alumina in aqueous solution. *KagaKuto Kyocku* **40** (3) 183-185.
- Ramaraj R, Jeyanthi D R, Srinivasan C 1992 Adsorption characteristics and spectroscopic studies of 3, 6, diamino acridine adsorbed on clays. *J Chem Phys Biochem* **30A** (12) 1044-1046.
- Mirza M L, Yasmin N, Iqbal J, Wadood A 1988 Studies on adsorption of Rhodamine-B on silica gel. *J Indian Chem Soc* **LXV** 28-30.