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Rate of Adsorption of Complexing Ligands on Granular Activated Carbon

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A study of the rates of diffusion could throw light on the type of diffusion operative in the adsorption process of ligands used in this work by the granular activated carbon. In this work, a series of structurally related ligands based on oxine have been studied which shows that surface diffusion phenomenon is operative.

Key Words: Granular activated carbon, Ligand, Adsorption, Oxine.

INTRODUCTION

The growth in the use of activated carbon as a potential adsorbent for wastewater treatment has been steady and strong. Activated carbon owes its adsorptive properties to its high porosity and large surface area. Adsorption of complexing ligands on F-400 surface[1] was studied as a possible way to the preliminary adsorption characteristics of carbon with respect to copper adsorption . It has been noted by many investigators that organic ligands can play a major role in natural water by complexing trace metal ions[2, 3]. The adsorption of heavy metals on granular activated carbon (GAC) resulted from the development of +ve charges on the surface of carbon and the presence of negative charges on the metal chelates. The functional oxidized groups present on the surface of the carbon particles play a major role in removing metal chelates[4]. The ligands chosen in this work were 8-hydroxy quinoline (oxine) and its derivatives, namely, 2-methyl-8-hydroxy quinoline (meoxine), 8-hydroxy quinoline-5-sulphonic acid (QSA), 7-iodo-8-hydroxy quinoline-5-sulphonic acid (IQSA) and 7-nitro-8-hydroxy quinoline-5-sulphonic acid (NQSA). Their properties as complexing agents for several elements are well known[5].

EXPERIMENTAL

The granular activated carbon selected in this work was of Calgon F-400 grade[1].

The kinetic studies were carried out using a thermostatic bath, temperature maintained at 25 ± 1°C. Each arrangement had a 1 L round bottomed corning flask held in the bath with a clamp fitted with Remi motor stirrers whose speed

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could be regulated. All samples for analysis were withdrawn through the neck of the flask.

Adsorption rate of ligands on GAC

Optimum conditions for maximum adsorption in terms of agitating time, ligand concentration, temperature were established. In a corning 1 L flask, 500 mL of ligand solution was taken, having a concentration chosen from the adsorption isotherm of the ligand corresponding to the value of C_e from the descending portion of the graph (Figs. 1 and 2). This was necessary to allow rapid uptake of ligand during the adsorption process. Solutions were stirred for 30 min so that it was in equilibrium with the thermostat bath. GAC (0.5 g) was then added directly, stirring being continued. It was found that the initial adsorption rate was relatively fast when compared to the entire adsorption period. The samples collected at definite time intervals were analyzed at 350 nm using a visible spectrophotometer. The concentrations were calculated using a Beer's law plot and C_t *vs.* time plot gave a fall in concentration with time (Fig. 3).

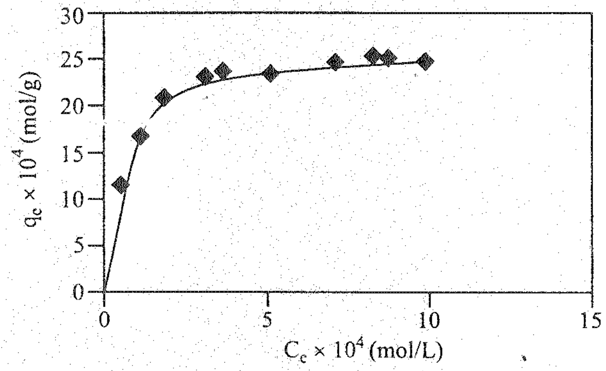

Fig. 1. Adsorption isotherm system: F-400-oxine

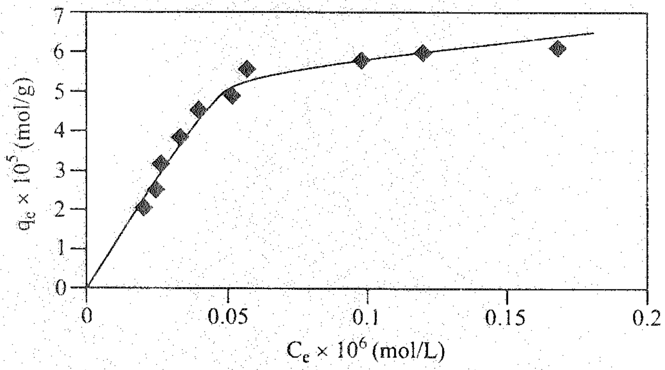

Fig. 2. Adsorption isotherm system: F-400-IQSA

Equation used for calculating q_t, amount of ligand taken up at these time intervals was:

$$q_t = (C_0 - C_t)\, V/d$$

where q_t = ligand concentration on the GAC (mol/g) at that interval of time, C_0 = concentration of the ligand (mol/L) at the initial time, C_t = concentration of the ligand (mol/L) at time t, V = volume of solution (L) taken and d = weight of the GAC (g).

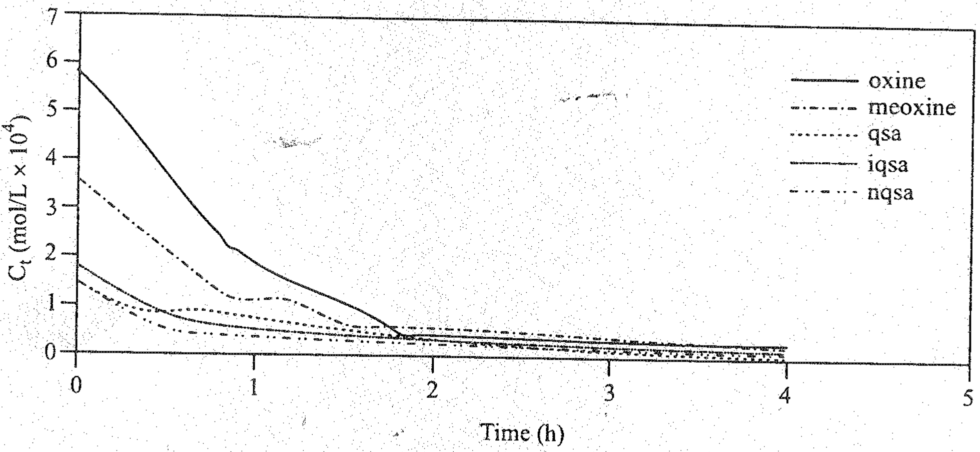

Fig. 3. Kinetics of removal of ligand from solution

For each value of C_t obtained, a corresponding value of C_e from the adsorption isotherm was obtained which gave the value for $\bar{q}^*$ (ligand concentration on the GAC obtained from the adsorption isotherm).

A plot of $\bar{q}^*$ and $\bar{q}$ *vs.* time indicated the approach to equilibrium concept in the process (Fig. 4).

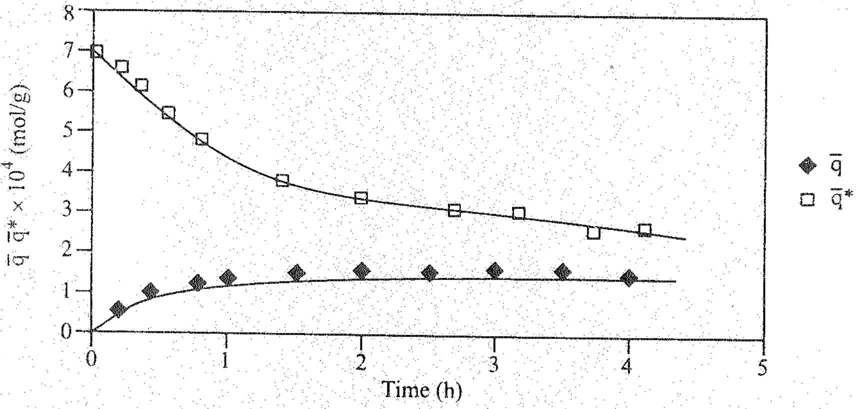

Fig. 4. Adsoption phase approach to equilibrium system: F-400-NQSA

The difference between the values of $\bar{q}^*$ and $\bar{q}$ at any interval of time is the driving force operating during the process leading to adsorption on the GAC.

Also a plot of $d\bar{q}/dt$ *vs.* $(\bar{q}^{*2} - \bar{q}^2)/2\bar{q}$ gave the quadratic driving force (QDF) plots[7] (Figs. 5 and 6).

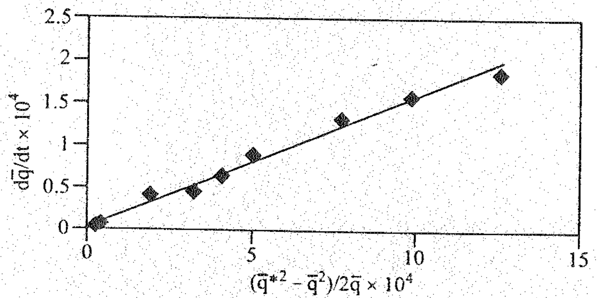

Fig. 5. Quadratic driving force plot system: F-400-MeOxine

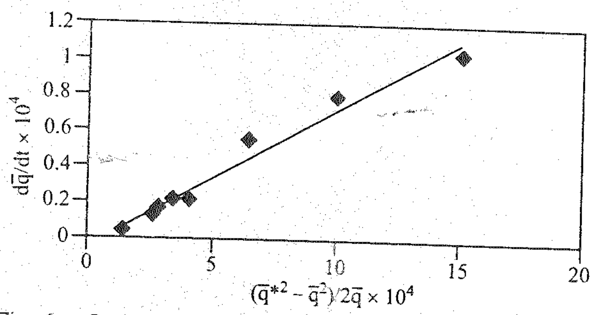

Fig. 6. Quadratic driving force plot system: F-400-NQSA

RESULTS AND DISCUSSION

The results obtained in the present work have been subjected to the Langmuir and Freundlich models and were found to fit well and therefore have been considered in the present investigation to explain the adsorption processes. Batch technique was effectively used to get reliable data on kinetic studies.

In the present investigation, the quadratic driving force (QDF) equation as proposed by Vermeulen[6], has only been used to obtain the values of the diffusion coefficient (D). The QDF expression is as given below:

$$d\bar{q}/dt = \pi^2 D/a^2[(\bar{q}^{*2} - \bar{q}^2)/2\bar{q}]$$

For computing the values of D, firstly the adsorbent phase concentration q_t was computed as a function of time using the equation

$$q_t = (C_0 - C_t)\ V/W$$

where, C_0 = initial concentration of the adsorbate in mol/L, C_t = concentraton of the adsorbate at time t in mol/L, V = volume of solution in L, and W = weight of adsorbate in g.

Secondly, the value of $\bar{q}^*$ in equilibrium with $C_e = C_t$ is determined from the corresponding adsorption isotherm. The difference $(\bar{q}^{*2} - \bar{q}^2)/2\bar{q}$ was then calculated for the desired intervals of time. All $d\bar{q}/dt$ values are calculated by using a polynomial equation program developed. On plotting $d\bar{q}/dt$ *vs.* $(\bar{q}^{*2} - \bar{q}^2)/2\bar{q}$, the slope gave $(\pi^2 D)/a^2$ and knowing the radius of the particle the value of D can be obtained (average particle diameter for calculations was taken as 0.15 cm). Data for some ligands are given in Table-1 and a few representative cases in Figs. 1–6.

TABLE-1
DIFFUSION COEFFICIENT DATA FOR LIGANDS ON F-400 GAC

Ligands	System F-400-ligands	
	K	$D \times 10^8$
Oxine	0.0484	3.0681
MeOxine	0.0167	1.0586
QSA	0.3143	19.9234
IQSA	0.0109	0.6909
NQSA	0.0735	4.6592

K = slope from QDF plot. D in cm^2/sec.

A critical analysis of the values of diffusion coefficient (D) clearly speaks of surface diffusion phenomena operating in the processes in the present investigations. These values were obtained from the QDF plots used in the present work. The value of 19.92×10^{-8} for QSA is unusually high compared to the other ligands and this could be, because of the fact that QSA is highly soluble in aqueous medium and has a smaller cross-sectional area, helped in diffusing readily into the pores and once adsorbed could readily undergo surface diffusion on the GAC. However, the other three ligands namely MeOxine, IQSA and NQSA once adsorbed would find steric factors hindering surface diffusion owing to substituents and hence their values are lower than that of QSA. In the case of oxine, the value is abnormally low which could be ascribed to its lower solubility in water as compared to QSA and further it had to be prepared in a 5% solution in methanol which is likely to affect the diffusion on the surface. The magnitude of diffusion coefficient values all speak of surface diffusion phenomena operative in the present cases and in such situations ligand geometry has been shown to affect the whole process.

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