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Removal of Anionic Dye from Aqueous Solution by using Nanoporous Aluminophosphate Molecular Sieves

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Abstract

In the present investigation, the hazardous anionic dye, orange G (OG) is removed from aqueous solution by using nanoporous aluminophosphate molecular sieves through adsorption. The adsorption studies are carried out at different experimental conditions such as contact time (upto 30 minutes), dye concentration (100-500 mg/L), pH (2-11), temperature (30°C-70°C) and adsorbent dosage (0.5g–2.5 g) for optimizing the maximum removal of OG. The experimental data are analyzed by adsorption isotherms, adsorption kinetics and adsorption thermodynamics. Adsorption of OG increased with increase of temperature. The thermodynamic reports revealed that the adsorption of OG over nanoporous aluminophosphate molecular sieves is spontaneous and endothermic.

Keywords: *Adsorptive removal; Aluminophosphate; Mesoporous; Nanoporous;Orange G.*

1. INTRODUCTION

The environmental pollution problems are threatening the human being day by day. Particularly the pollution of water bodies frightening the peaceful future of all living systems. Hazardous dyes pollution is the main environmental concern. From the total productions of dyes, 15% are lost as dye effluent during dye production and dying process (Zollinger, 1991). The dye molecules are common water pollutants and a very small amount in water is highly visible and can be toxic (Lee *et al*. 1999). So many physico-chemical methods such as coagulation, flocculation, biosorption, photodecomposition, ultrafiltration and adsorption (Babel *et al*. 2003; Galindo *et al*. 2000; Robinson *et al*. 2001; Kannan *et al*. 2013) are reported for dye effluent treatment. Among these methods, adsorption is an efficient method for dye effluent treatment (Fu *et al*. 2001 ; Karthikeyan *et al*. 2012). The dye effluent treatment by using alumina (Kannan *et al*. 2008), Silica (Kannan *et al*. 2011) and bio materials (Hasine Kas¸g¨oz, 2005; Gutierrez-Segura *et al*. 2009; Antonio *et al*. 2008; Namasivayam *et al*. 1992; Namasivayam *et al*. 1998; Namasivayam *et al*. 1994; Namasivayam *et al*. 2001; Chen *et al*. 2001; Robinson *et al*. 2002; Shukla *et al*. 2002) are reported. In the present investigation nanoporous aluminophosphate molecular sieve is used for the removal of anionic dye from aqueous solution. The nanoporous materials are classified as three types. They are, 1. Microporous (< 2 nm) 2. Mesorporous (2 nm – 50 nm) 3. Macroporous (> 50 nm). In the present investigation, large pore mesoporous aluminophosphate molecular sieve is used for adsoption study.

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2. MATERIALS & METHODS

The mesoporous aluminophosphate ($AlPO_4$) molecular sieve is used as an adsorbent for the removal of hazardous dye study. The synthesis and characterization of $AlPO_4$ is given in our previously reported article (Kannan *et al*. 2013). The Orange G (OG) dye is used as adsorbate. The structure of OG is given in Fig.1 and the properties of OG is given in Table 1.

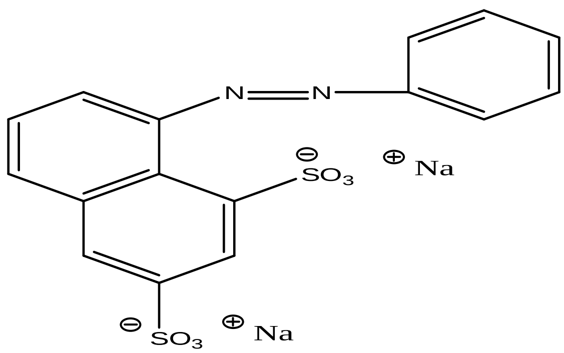

Fig.1: Chemical structure of Orange G

Table 1. Details of OG dye

Molecular formula	Molecular weight	Maximum absorption	Make
$C_{16}H_{10}N_2Na_2O_7S_2$	452.38	480 nm	Loba chemie pvt ltd

3. RESULTS & DISCUSSION

Adsorption studies

The effect of removal of OG on mesoporous $AlPO_4$ through adsorption at different parameters such as contact time, pH, dye concentration, temperature and adsorbent dosage are optimized for maximum adsorption.

3.1 Effect of contact time

The effect of contact time has been carried out at room temperature (30 °C) for the adsorption of OG on mesoporous $AlPO_4$ upto 30 minutes. The very rapid adsorption is observed at 20 minutes Fig.2 and further increased of contact time not much increase the percentage of adsorption. This is due to the attaining of equilibrium adsorption.

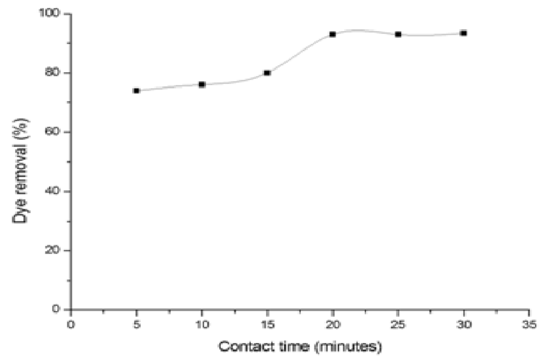

Fig. 2: Effect of contact time for adsorption of OG on mesoporous $AlPO_4$

(Dye concentration: 100 mg/L, Temperature: 30 °C, pH: 2, Adsorbent dosage: 0.5 g)

3.2 Adsorption kinetics

In order to examine the controlling mechanism of the adsorption process, pseudo"second order kinetic equation is used to test the experimental data. The pseudo second order kinetic model is based on adsorption equilibrium capacity and can be expressed as,

$$t/Q_t = 1/kQ_e^{\,2} + 1/Q_e t \qquad ..eq.1$$

Where,

k is the rate constant pseudo"second order adsorption (g m^{-1} min^{-1}), Q_e is the amount of dye adsorbed per unit mass of the adsorbent at equilibrium (mg g^{-1}), Q_t is the amount of dye adsorbed per unit mass of the adsorbent at time t (mg $g^{"1}$) and t is time in minutes. The slope and intercept of (t/Q_t) versus t are used to calculate the pseudo"second order rate constant 'k' and Qe. The kinetic plot is shown in Fig.3. The linear regression coefficient (R^2) value is very close to 1 (Table 2) indicated that the adsorption of OG on mesoporous $AlPO_4$ is fitted with the pseudo-second order kinetics.

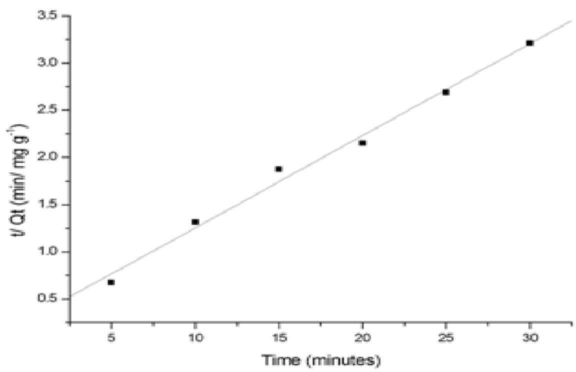

Fig. 3: Pseudo second order kinetic plot of adsorption of OG on mesoporous $AlPO_4$

Table 2. Pseudo Second order kinetic data

Dye	Q_e	K	R^2
OG	9.8726	0.0791	0.9996

3.3 Effect of pH

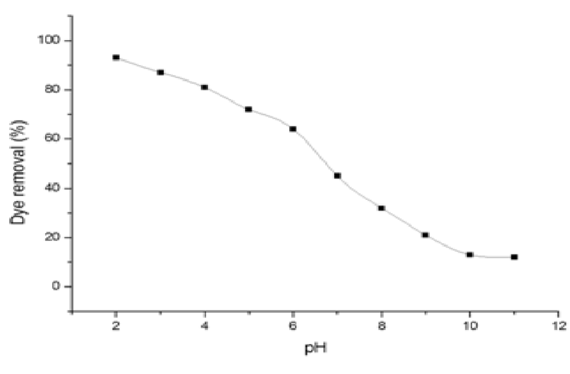

Fig. 4: Effect of pH of adsorption of OG on mesoporous $AlPO_4$
(Contact time: 20 minutes, Dye concentration: 100mg/L, Temperature: 30°C, Adsorbent dosage: 0.5g)

The OG is adsorbed well on mesoporous $AlPO_4$ at pH 2. The percentage of adsorption of OG decreased with increase of pH Fig. 4. It is due to the surface of the $AlPO_4$ is surrounded by positively charged protons. The attractive force between this proton and the negative charge present in OG increased and hence the percentage of adsorption is high at low pH. When increase the solution pH from 2 to 11, the negatively charged ions surrounded the surface of $AlPO_4$, and it results the repulsion with negatively charged OG. So, the percentage of adsorption is decreased.

3.4 Effect of Dye concentration

The adsorption of OG dye on mesoporous $AlPO_4$ is studied between the dye concentration ranges 100 mg/L - 500 mg/L at room temperature is shown in Fig.5. The adsorption percentage is maximum at 100 mg/L and further increased of dye concentration decrease the adsorption percentage is due to the saturation of active sites present on $AlPO_4$ molecular sieves.

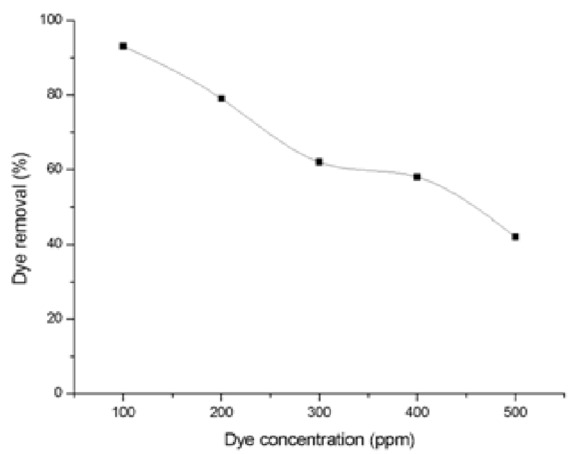

Fig. 5: Effect of dye concentration of adsorption of OG on mesoporous $AlPO_4$
(Contact time: 20 minutes, Temperature: 30 °C, pH: 2, dsorbent dosage: 0.5 g)

3.5 Adsorption Isotherm Studies

3.5.1 Langmuir and Freundlich adsorption isotherms

Adsorption data at different concentrations are measured for the adsorption OG and applied to Langmuir and Freundlich adsorption isotherm equations. The Langmuir equation is represented as

$$C_e / Q_e = (1/Q_{max}K_L) + (C_e/Q_{max}) \qquad ..eq.2$$

Where,

Q_e is the equilibrium concentration of dyes on the adsorbent (mg g^{-1}), C_e is the equilibrium concentration of dyes in solution (mg L^{-1}), Q_{max} is the monolayer capacity of Adsorbent (mg/g), and K_L is the Langmuir adsorption constant. A plot of C_e/Q_e Vs C_e is a straight line with slope $1/Q_{max}$ and the intercept $1/Q_{max}K_L$ (Fig. 6). The correlation coefficient (R^2) values are very close to 1 for OG, indicated that the adsorption process follows the Langmuir adsorption isotherm. The monolayer adsorption capacity of mesoporous $AlPO_4$ for OG is 23.07 mg/g Table 3.

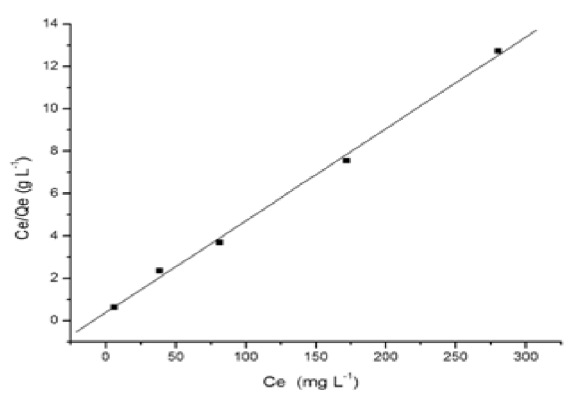

Fig. 6: Langmuir adsorption isotherm plot of adsorption of OG on mesoporous $AlPO_4$

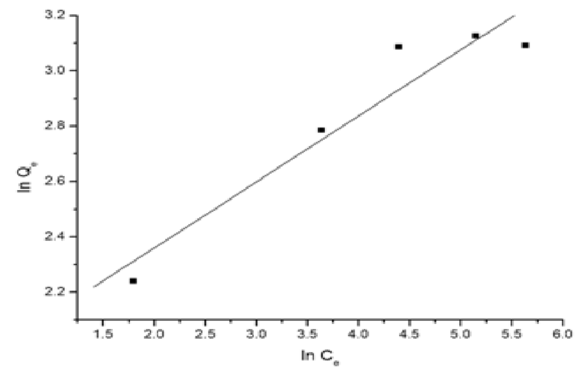

Fig. 7: Freundlich adsorption isotherm plot of adsorption of OG on mesoporous $AlPO_4$

Table 3. Langmuir Adsorption isotherm data

Dyes	Q_{max} (mg/g)	K_L	R^2
OG	23.07	0.1117	0.9986

The Freundlich equation is represented as

$$\ln Q_e = \ln K_F + (1/n) \ln C_e \qquad ..eq.3$$

Where, K_F and 1/n are the Freundlich constants indicated the adsorption capacity and adsorption intensity respectively. The plot of $\ln Q_e$ vs $\ln C_e$ gave a straight line Fig. 7 with the intercept $\ln K_F$ and the slope 1/n. The R^2 value is low, when compared to Langmuir adsorption isotherm and it is indicated that the adsorption followed the Langmuir adsorption isotherm Table 4.

Table 4. Freundlich Adsorption isotherm data

Dye	1/n	n	$\log K_F$	K_F	R^2
OG	0.238376	4.20	0.817892	6.5749	0.9557

3.6 Effect of temperature

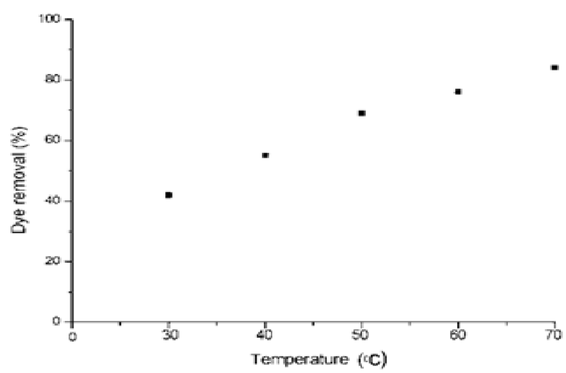

Fig. 8: Effect of temperature of adsorption of OG on mesoporous $AlPO_4$
(Contact time: 20 minutes, dye concentration: 500 mg/L, pH: 2, Adsorbent dosage: 0.5 g)

The effect of temperature for the removal of OG on mesoporous $AlPO_4$ is studied in the range of 30 °C to 70 °C is shown in Fig.8. The adsorption increases with increase of temperature indicated that the adsorption process is endothermic. This may due to increase of interaction between adsorbate and adsorbent and the active sites on the surface and pores of mesoporous $AlPO_4$ is activated. It leads to the increase of percentage of adsorption at high temperature.

3.7 Adsorption thermodynamic study

The thermodynamic parameters, namely free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) have an important role to determine spontaneity and heat change for the adsorption process. The thermodynamic parameters are calculated using the following relations.

$$K_D = q_e/C_e \quad ..eq.4$$
$$\Delta G = -RT \ln K_D \quad ..eq.5$$
$$\ln K_D = (\Delta S / R) - \Delta H / RT) \quad ..eq.6$$

from the equations eq.5and eq.6,

$$\Delta G = \Delta H - TS \quad ..eq.7$$

Where, K_D is the distribution coefficient of the adsorbate, q_e and C_e are the equilibrium dye concentration on mesoporous $AlPO_4$ (mg g^{-1}) and in the solution (mg L^{-1}), respectively. R is the universal gas constant (8.314 J/mol K) and T is the temperature (K). $\Delta H°$ and $\Delta S°$ parameters can be calculated from the slope and intercept of the plot ln K_D vs. 1/T, respectively Fig. 9. Results are summarized in Table 4. $\Delta G°$ values at the temperatures of 30°C – 70°C (303 K - 333 K) are negative Table .5. This indicated that the process is feasible adsorption process and spontaneous. The enthalpy ($\Delta H°$) values are greater than 40 KJ/mol indicated that the adsorption of dye over mesoporous $AlPO_4$ is chemisorption. The positive value of enthalpy indicated that the adsorption process is endothermic. Moreover, the positive value of $\Delta S°$ indicated that the degrees of freedom increased at the solid-liquid interface during the adsorption.

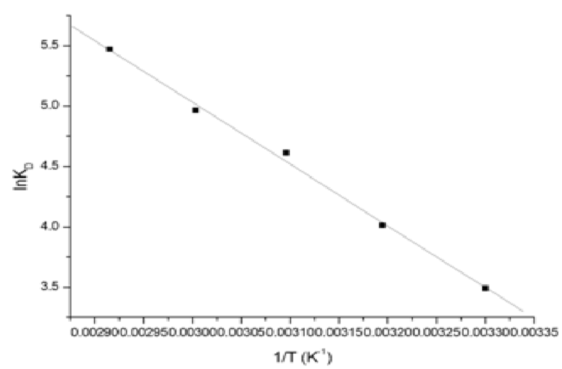

Fig. 9: Thermodynamic plot of adsorption of OG on mesoporous $AlPO_4$

Table 5. Thermodynamic data

Dyes	ΔH (KJ/mol)	ΔS (KJ/mol)	ΔG (KJ/mol)	R^2
OG	40.74	0.1641	-8.997 -10.638 -12.280 -13.921 -15.563	0.9971

3.8 Adsorbent dosage

The effect of adsorbent dosage (0.5 g-2.5 g) of adsorption of OG is studied. The percentage removal is increased with increase of adsorbent dosage (Fig. 10). Since the increase of adsorbent dosage increased the surface area and active sites present on the mesoporous aluminophosphate molecular sieves. Hence, adsorption increased with increase of mesoporous AlPO4 dosage.

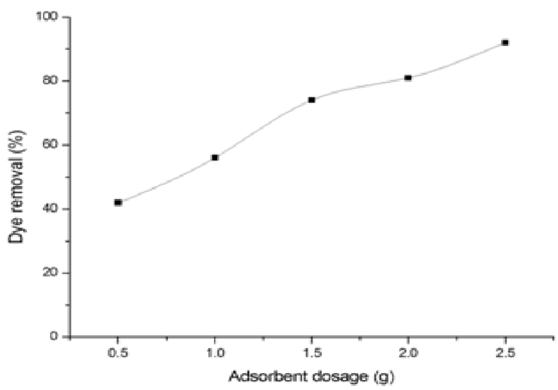

Fig. 10: Effect of adsorbent dosage of adsorption OG dye on mesoporous $AlPO_4$

(Contact time: 20 minutes, Dye concentration: 500 mg/L, Temperature: 30 ºC, pH: 2)

4. CONCLUSION

The environmentally hazardous cationic dye orange G is removed from aqueous solution on mesoporous $AlPO_4$ is investigated to optimize the conditions like contact time, pH, dye concentration, temperature and adsorbent dosage. The removal percentage of OG increased with increase of contact time and temperature indicated that the removal of OG can be achieved at higher temperature. The adsorption of OG on mesoporous $AlPO_4$ obeys the Langmuir and Freundlich adsorption isotherms. The removal of OG is spontaneous and endothermic. These results finally concluded that the mesoporous $AlPO_4$ molecular sieves is best adsorbent for the removal of anionic dye.

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