Research Article

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Removal and Recovery of Brilliant Green and Brilliant Yellow using Mesoporous Aluminophosphate Molecular Sieves from Aqueous Solution

D. Revathi, K. Karthikadevi, C. Kannan*

Department of Chemistry, Manonmaniam Sundaranar University, Abishegapatti, Tirunelveli, TN, India

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*chellapandiankannan@gmail.com

ABSTRACT

Industrial effluents discharged from the dying industry are toxic for living organisms. Mesoporous as well as nanoporous aluminophosphate molecular sieves were synthesized and applied for the removal of Brilliant Green (BG) and Brilliant Yellow (BY) from aqueous solution. The adsorption studies were carried out at various experimental conditions like contact time, initial dye concentration, temperature, pH and adsorption dosage for finding the maximum adsorption. The contact time studies have proved that the adsorption equilibrium was attained at 20 minutes for the adsorption of BG and BY. The dye removal has decreased with an increase in dye concentration of BG and BY. The temperature study has proved that the percentage removal of BG and BY on the adsorbent increased with the increase in temperature. The adsorbent dosage results have shown a significant increase in the amount of dye removal due to an increase in the surface area and active sites of the adsorbent. The negative ΔG value and positive ΔH value for the adsorption of BG and BY on adsorbent were 67.53 $kJmol^{-1}$ and 66.21 $kJmol^{-1}$, respectively. Desorption of dyes with ethanol, followed by calcination, was carried out to regenerate the adsorbent.

Keywords: Dye adsorption; Dye desorption; Industrial effluents; Nanoporous; Mesoporous.

1. INTRODUCTION

Water plays an important role in the world economy, as it functions as a solvent for a wide variety of chemical substances and facilitates industrial cooling and transportation. Approximately 70% of the freshwater used by humans goes to agriculture (Baroni *et al.* 2007). The most important water pollutants are metal ions, dissolved organic compounds and dyes (Jayarajan *et al.* 2011). Industrial effluents discharged from dyeing industries are highly colored with a large amount of suspended organic solids. These effluents are discharged into rivers, making water unfit for domestic, agriculture and industrial purposes (Gharbani *et al.* 2008). Many dyes and their break down products may be toxic for living organisms. It is estimated that about 10-15% of dyes are realized into processing water during this procedure. It is broadcasted that more than 60% of dyes produced worldwide is consumed by textile industries (AL-Degs *et al.* 2007). Dyes can be of many different structural varieties like acidic, basic, disperse, azo, anthraquinone-based and metal complex dyes, among others. Dyes, according to their structures, are classified as anionic and cationic dyes (Wang and Li, 2007). In an aqueous solution, anionic dye carries a net negative charge due to the presence of amine or sulphur containing groups (Royer *et al.* 2009). Several treatment processes are in practice for the removal of dyes from wastewater. Adsorption is more efficient compared to conventional physico-chemical methods for the removal of organic wastes. The dye-adsorbed adsorbent disposal also creates environmental issues. To address all such challenges, an attempt has been made in this work to prepare a reusable $AlPO_4$ adsorbent and use the same as an adsorbent for the adsorption of dyes such as Brilliant Green and Brilliant Yellow.

2. EXPERIMENTAL SECTION`

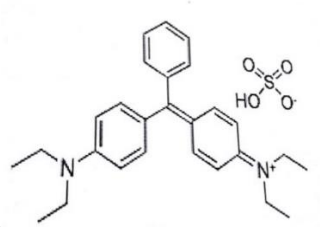
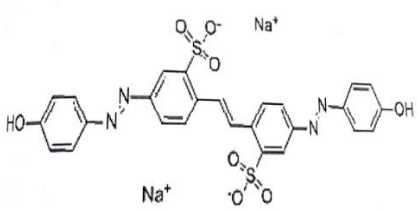
2.1 Materials

The chemicals used in the present work are of pure analytical grade and used directly without further purification. The cationic dye, Brilliant Green (BG) and anionic dye, Brilliant Yellow (BY) were used to study the hazardous dye removal. The properties of BG and BY are listed in Table 1.

2.2 Synthesis of Mesoporous $AlPO_4$

In a typical synthesis, 7.48 g of aluminium hydroxide was added to 17.5 g of sodium dodecylbenzene sulphonate solution with vigorous stirring. Then 9.8 g of phosphoric acid solution was added to the mixture. The mixture was stirred for 6 h at room temperature. The final gel with a molar composition, Al_2O_3:P_2O_5:0.5 SDBS:300 H_2O, was heated to 150 °C with stirring. This was continued until

Table 1. Physical properties of dyes

Properties	BG	BY
Structure		
Molecular formula	$C_{27}H_{33}N_2HO_4S$	$C_{26}H_{18}N_4O_8Na_2S_2$
Molecular weight	482.64	624.55
Maximum adsorption λ_{max} (nm)	625	397

the precipitation of aluminophosphate mesoporous nano-level molecular sieves. Then the final product was washed repeatedly with distilled water filtered and dried at 120 °C for 3 h. This as-synthesized sample was calcined at 600 °C for 6 h to remove the template, organic contaminants and to activate the active sites of mesoporous aluminophosphate molecular sieves.

2.3 Adsorption Experiment

The mesoporous $AlPO_4$ was activated by heating in an electric Bunsen at 500 °C for 4 h to remove the physically adsorbed species present in the pores and the surface. Then 0.5 g of mesoporous $AlPO_4$ was added with 50 ml of BG and BY solutions, separately. The solutions were agitated at 150 rpm. The concentrations of the solutions were measured spectro-photometrically. To find out the maximum removal of BG and BY over mesoporous $AlPO_4$, the experimental conditions like contact time, initial dye concentration, temperature, pH and catalyst dosage were optimized. The effect of contact time was studied up to adsorption equilibrium time. The effect of pH was studied in the pH range from 2 to 10. The adsorption of BG and BY over mesoporous $AlPO_4$ was studied in the concentration range of 100 - 500 mg/L. The temperature effect of adsorption of BG and BY was studied in the range of 30 - 70 °C. The mesoporous $AlPO_4$ dosage effect was studied in the range of 0.5 - 2.5 g.

The adsorption capacity (mg dye/g adsorbent) of mesoporous $AlPO_4$ was calculated by using the following equation:

$$q = (C_0 - C_e)\ V/W$$

The dye removal percentage (%) was calculated by using the following equation:

$$\text{Dye removal in percentage} = (C_0 - C_e) \times 100/ C_0$$

where, q is the amount of dye adsorbed on mesoporous $AlPO_4$ (mg/g), C_0 and C_e are the initial and final dye concentrations in solutions (mg/l), respectively, V is the volume of solution (L) and W is the adsorbent weight (g).

3. RESULTS AND DISCUSSION

3.1 FT-IR Characterization of Mesoporous $AlPO_4$

To confirm the formation of tetrahedral framework of $AlPO_4$, FT-IR characterization has been carried out. The FT-IR of the calcined sample was shown in Fig. 1.

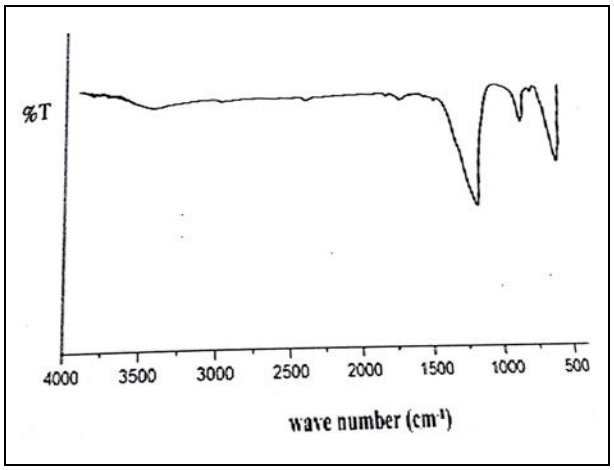


Fig. 1: FT-IR spectrum of calcined mesoporous $AlPO_4$

The asymmetric stretching of tetrahedral framework of $AlPO_4$ was observed near 1106 cm^{-1} and corresponding symmetric stretching was observed around 674 cm^{-1}; the bending modes were positioned near 466 cm^{-1}. These vibrations confirmed the formation

of $AlPO_4$ molecular sieves. The broad peak at 3423 cm^{-1} was due to –OH groups and water molecules present in the molecular sieves.

3.2 Adsorption Studies

3.2.1 Effect of Contact time

The effect of contact time has been studied at room temperature (30 °C) for the adsorption of BG and BY on mesoporous $AlPO_4$ up to 30 min (Fig. 2). The very rapid adsorption was observed at 20 min for both cationic and anionic dyes (BG and BY), and further increase in contact time did not register a significant increase in adsorption percentage. This was due to the attainment of the adsorption equilibrium of BG and BY dyes on nanoporous $AlPO_4$ molecular sieves. Though both dye structure and charge were different, they were adsorbed rapidly; this indicated that the pore size and active sites were sufficient to accumulate different types of dye molecules.

3.2.2 Effect of pH

The effect of pH was studied in the pH range from 2 to 10 for the adsorption of dyes (Fig. 3). The pH of the solutions was adjusted by using 0.1 N NaOH and/or 0.1 N HCl. The adsorption of BG increased gradually with increase in pH and reached a maximum at pH =10; adsorption of BY decreased gradually with an increase in pH up to 10. The low adsorption of BG at low pH may be due to the repulsive force with the nanoporous aluminophosphate. Hence, the adsorption decreased in acidic pH. When pH increased above 7, the surface of the nanoporous aluminophosphate occupied negative charge and hence the adsorption of cationic dye, BG, increased and reached maximum at pH = 10 and the adsorption of anionic dye BY decreased. Above pH = 7, the surface of the adsorbent became more basic; hence it repelled the anionic dye.

3.2.3 Effect of Concentration

The BG and BY adsorption on nanoporous $AlPO_4$ were studied in the concentrations range of 100 – 500 mg/L, at room temperature (Fig. 4). The adsorption capacity of nanoporous $AlPO_4$ was found to be maximum at 100 mg/L; further increase in concentration decreased the adsorption of BG and BY on the adsorbent. The initial concentration provided an important driving force to overcome all mass transfer resistance of the dye molecule between the aqueous and solid phases. When increasing the concentration of dye solution, the surface area and active sites were saturated, and hence adsorption decreased with the increase of dye concentration.

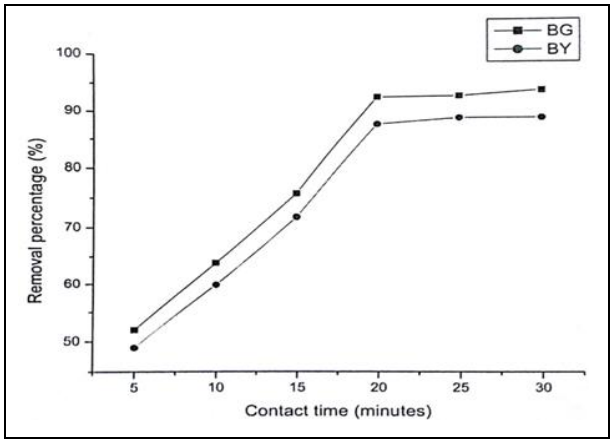


Fig. 2: Effect of Contact time on adsorption of BG and BY over mesoporous $AlPO_4$

Concentration: 100 mg/L, Temperature: 30 °C, Adsorbent dosage: 0.5 g

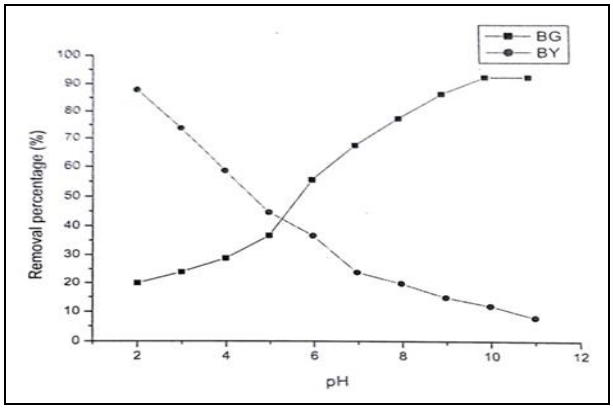


Fig. 3: Effect of pH on adsorption of BG and BY over mesoporous $AlPO_4$

Contact time: 20 min, Concentration: 100 mg/L, Temperature: 30 °C, Adsorbent dosage: 0.5 g

3.2.4 Effect of Temperature

The effect of temperature for the removal of BG and BY on nanoporous $AlPO_4$ were studied in the range of 303 K to 343 K as shown in Fig 5. The adsorption increased with the increase of temperature from 30 °C to 70 °C, which indicated that the adsorption process was endothermic. This may due to an increase in interaction between adsorbate and adsorbent.

3.2.5 Effect of Adsorbent Dosage

The impact of adsorbent dose (0.5 - 2.5 g) on BG and BY adsorbent has been investigated (Fig. 6). The percentage removal of BG and BY has increased as the adsorbent dose increased; because the surface area and active sites of the adsorbent has grown when the dose was

increased. Hence, adsorption increased with the increase of nanoporous $AlPO_4$ dosage.

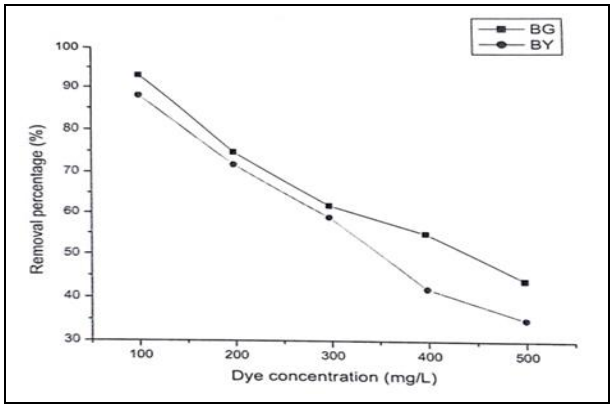


Fig. 4: Effect of Concentration on adsorption of BG and BY over mesoporous $AlPO_4$

Contact time: 20 min, Temperature: 30 °C, Adsorbent dosage: 0.5 g, pH: 10

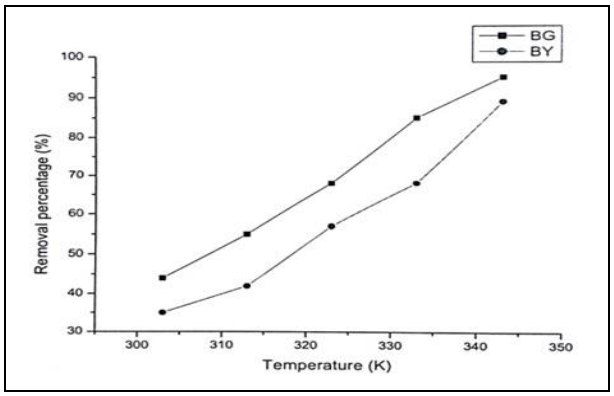


Fig. 5: Effect of Temperature on adsorption of BG and BY over nanoporous $AlPO_4$

Contact time: 20 min, Concentration: 100 mg/L, Adsorbent dosage: 0.5 g, pH: 10

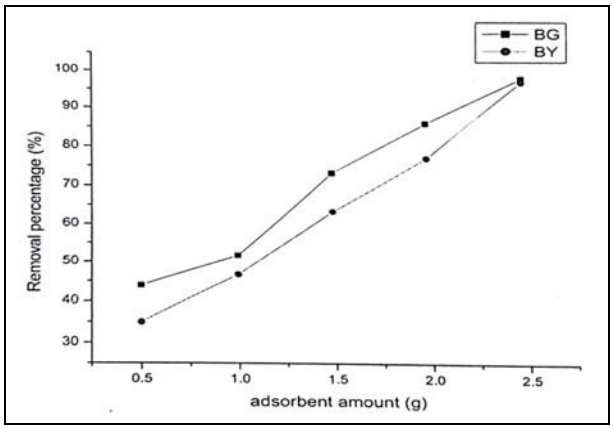


Fig. 6: Effect of Adsorbent Dosage on adsorption of BG and BY over mesoporous $AlPO_4$

Contact time: 20 min, Concentration: 100 mg/L, Temperature: 30 °C, pH: 10

3.3 Adsorption Isotherms

3.3.1 Langmuir adsorption isotherms

The adsorption isotherm data at different concentrations were measured and presented in Table 2.

The Langmuir equation is represented as,

$$C_e/Q_e = 1/Q_{max}\, K_L + C_e/Q_{max} \text{ ---- Eq. (1)}$$

where,

Q_e is the equilibrium concentration of dye on the adsorbent (mg/g).
C_e is the equilibrium concentration of dye in the solution (mg/L)

Q_{max} is the monolayer capacity of adsorbents (mg/g)

K_L is the Langmuir adsorption constant.

The Langmuir constant K_L is a measure of affinity between adsorbent and adsorbate and $1/K_L$ value gives the half-maximum adsorption. A plot of C_e/Q_e vs. C_e gave a straight line with slope $1/Q_{max}$ and intercepted $1/Q_{max}\, K_L$ (Fig. 7). The R^2 values for the adsorption of BG and BY on mesoporous as well as nanoporous $AlPO_4$ were given in Table 2. The R^2 value was very close to 1, indicating that the adsorption has obeyed the Langmuir adsorption isotherm. The monolayer adsorption capacity of mesoporous, nanoporous $AlPO_4$ for BG was 23.69 mg/g and 8.02 mg/g for BY, clearly indicating that the mesoporous $AlPO_4$ has more affinity with BG molecule than BY.

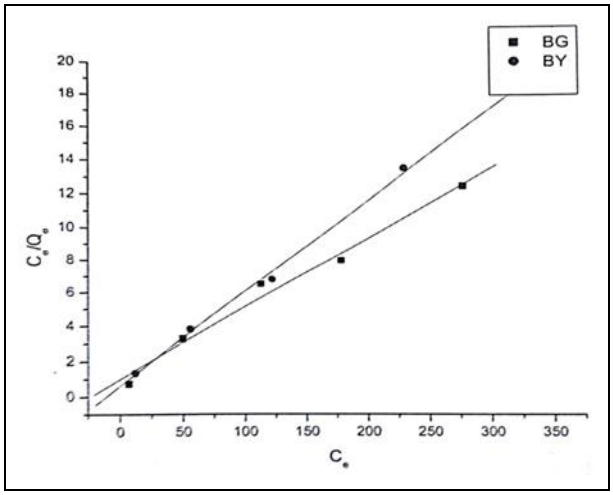


Fig. 7: Langmuir adsorption isotherm plots of BG and BY on mesoporous $AlPO_4$

3.3.2 Freundlich adsorption isotherm

Adsorption experiments were carried out at various concentrations and the adsorption data were used to validate the adsorption isotherms using the Freundlich equation (Table 2). This research was used as a model to better understand the multi-layer adsorption of BG and BY on mesoporous $AlPO_4$.

The Freundlich equation is represented as,

$$\ln Q_e = \ln K_F + (1/n) \ln C_e \text{ ----- Eq. (2)}$$

where,

K_F is the Freundlich constant
Q_e is the equilibrium concentration of dye on the adsorbent (mg/g)
C_e is the equilibrium concentration of dye in the solution (mg/L)
1/n is the number of layers

The plot of ln Q_e vs. ln C_e gave a straight line (Fig. 8) with the intercept K_F and the slope 1/n. The R^2 values for adsorption isotherm of BG and BY were 0.994 and 0.938 respectively (close to 1) on mesoporous, nanoporous $AlPO_4$ molecular sieves, indicating that BG and BY adsorption followed the Freundlich adsorption isotherm.

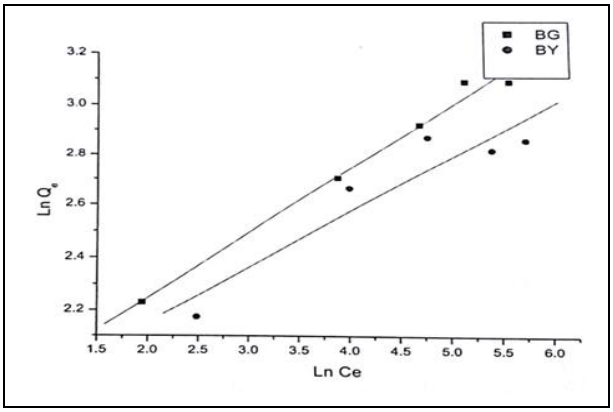


Fig. 8: Freundlich adsorption isotherm plots of BG and BY on mesoporous $AlPO_4$

Table 2. Langmuir and Freundlich adsorption isotherm parameters

Dye	Langmuir adsorption isotherm			Freundlich adsorption isotherm		
	R^2 value	$1/Q_{max}$	K_L	R^2 value	n	K_F
BG	0.992	23.69	0.0420	0.994	3.92	0.5625
BY	0.999	18.02	0.0899	0.938	3.52	0.5499

3.4 Adsorption Kinetics

3.4.1 Pseudo-second order kinetics

The rate constant of adsorption with regular time intervals at room temperature was determined by studying the adsorption kinetics of BG and BY on polythene powder. For computing the rate constant, the experimental values are entered into the pseudo-second order kinetics equation.

The equation is represented as follows,

$$t/Q_t = 1/k\, Q^2_e + 1/Q_e\, t \text{ -----Eq. (3)}$$

where, k is the rate constant

Q_e and Q_t are the amounts of the dye adsorbed per unit mass of the adsorbent at equilibrium and t is the time.

The plot of t/Q_t vs. t gave a straight line. The plot of t/Q_t vs. t (Fig. 9) for BG and BY adsorptions on mesoporous, nanoporous $AlPO_4$ was linear and the linear regression coefficient was close to 1 (Table 3), indicating that the adsorption of BG and BY on mesoporous $AlPO_4$ fitted with the pseudo-second-order kinetics.

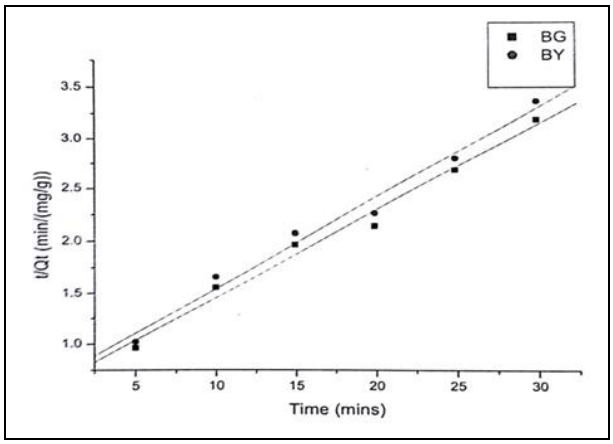


Fig. 9: Kinetic studies for the adsorption of BG and BY on mesoporous $AlPO_4$

Table 3. Pseudo-second-order kinetic parameters

Dyes	R^2 value	Pseudo-second order rate constant (k)	Q_e (mg/g)
BG	0.991	0.0114	11.904
BY	0.990	0.0115	11.386

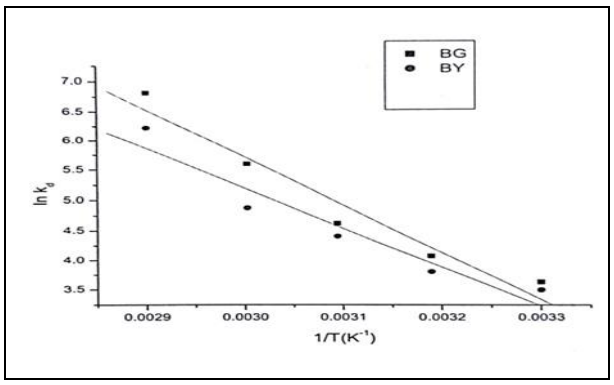


Fig. 10: Adsorption Thermodynamic plots of BG and BY on mesoporous $AlPO_4$

Table 4. Thermodynamic parameters for adsorption of BG and BY

S. No.	Thermodynamic parameters	BG	BY
1.	ΔH° (K/J mol)	67.53	66.21
2.	ΔS° (K/J mol)	0.249	0.211
3.	ΔG° (K/J mol)		
	T = 303 K	-8.0238	-7.723
	T = 313 K	-10.407	-9.833
	T = 323 K	-13.26	-11.743
	T = 333 K	-16.520	-14.053
	T = 343 K	-17.877	-16.163
4.	R^2	0.988	0.990

3.5. Adsorption Thermodynamics

The thermodynamics parameters, namely free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) have an important role in determining spontaneity and heat change for the adsorption process. The thermodynamic parameters were calculated using the following relations:

$$K_D = Q_e / C_e$$
$$\Delta G° = - RT \ln K_D$$
$$\ln K_D = (\Delta S / R) – (\Delta H / R) (1/T)$$

from the above equations,

$$\Delta G = \Delta H – T\Delta S$$

where, K_D is the distribution coefficient of the adsorbate, q_e and C_e are the equilibrium dye concentrations on mesoporous $AlPO_4$ (mg/g) and in the solution (mg/L), respectively, R is the universal gas constant and T is the temperature (K). The enthalpy and entropy can be calculated from the Van't Hoff plot, shown in Fig. 10, for BG and BY adsorptions. The thermodynamic data were given in Table 4. ΔG° values at the temperature of 303, 313, 323, 333 and 343 K were negative, indicating that the process was a feasible adsorption process and spontaneous. The enthalpy (ΔH°) values were greater than 40 K/J mol for both dyes (67.53 K/J mol for BG and 66.21 K/J mol for BY), indicating that the adsorption of BG and BY over mesoporous $AlPO_4$ was chemisorption and that BG was highly adsorbed than BY. The positive values of enthalpy indicated that the adsorption process was endothermic. Moreover, the positive values of ΔS° indicated that the degrees of freedom increased at the solid–liquid interface during the adsorption.

4. DESORPTION

To understand the nature of adsorption of both dyes over mesoporous as well as nanoporous $AlPO_4$ molecular sieves, a desorption study was carried out in water, methanol and propanol, at 30 ºC. 1 g of the dye adsorbed BG and BY mesoporous $AlPO_4$ were taken in a 50 ml reagent bottle separately and agitated for 1 h at 150 rpm. The solution was centrifuged and the percentage of BG and BY present in the solution was found out spectrophotometrically. BG and BY were recovered 99% and 99.5%, respectively, from the mesoporous $AlPO_4$. The percentages of BG and BY dye desorption was very poor in water due to the dyes' chemisorption on $AlPO_4$. After desorption of dyes, the mesoporous aluminophosphate was calcined at 400 ºC for 4 h for regeneration, which can be reused for further dye removal applications.

5. CONCLUSION

Mesoporous aluminophosphate molecular sieves were synthesized successfully. The prepared mesoporous $AlPO_4$ was characterized by FT-IR. It was applied for the removal of Brilliant Green and Brilliant Yellow from the aqueous solution. The adsorption of BG and BY over mesoporous $AlPO_4$ were of the type of chemisorption. By comparing the two dyes, it has been found that BG was highly adsorbed than BY.

The Langmuir and Freundlich isotherms have proved that the adsorption is multi-layer. The adsorption kinetics indicated that the process followed pseudo-second order. The thermodynamic studies have shown that the adsorption process was spontaneous and endothermic. The mesoporous aluminophosphate was regenerated by desorption of dyes with ethanol, followed by calcination of adsorbent for the purpose of reuse. The recovery study has proved that the $AlPO_4$ is reusable. The

study concluded that mesoporous $AlPO_4$ was suitable for the removal of hazardous cationic dye, BG and anionic dye, BY from the dye effluents.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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