ADSORPTION OF SUNSET YELLOW FCF ONTO MCM-41

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Abstract: MCM-41, one member of the mesoporous molecular sieves M41S family, possesses a high surface area, high pore volume and a regular hexagonal array of cylindrical pores, which is largery used in selective adsorption, chemical sensors and nanotechnology. Recently, MCM-41 has been used to adsorb dye from aqueous solution. Sunset Yellow FCF is used in food, pharmaceutical and cosmetics industries. Many dyes are toxic and carcinogenic and pose a serious hazard to aquatic living organisms. The adsorption of Sunset Yellow FCF food dye from aqueous solutions by MCM-41 was studied through adsorption isotherms. The effects of adsorbent dosage, contact time and temperature were investigated. Langmuir and Freundlich adsorption models were applied in order to describe the experimental isotherms and isotherm constants.

Keywords: MCM-41, Adsorption, Food Dye, Sunset Yellow CFC, Isotherm, Langmuir, Freundlich.

Introduction

Dye wastewaters are discharged by a wide variety of sources, such as food plants, textiles, printing, dyeing and dyestuff manufacturing. There are more than 100,000 commercially available dyes with over 700,000 tons produced annually. It is estimated that more than 70,000 tons of dye are discharged from textile industries in the world every year. They are the important sources of water pollution due to some dyes and their degradation products may be carcinogens and toxic to mammals (Lee et al. 2007; Erdogan and Oguz Erdogan, 2016). Porous adsorbents are of scientific and technological interest because of their ability to interact with atoms, ions and molecules. Since the discovery of M41S family in 1992, mesoporous materials have attracted intense interest due to their large specific surface areas, well-defined pore structures, inert framework and non toxicity (Boukoussa et al. 2017). MCM-41 molecular sieves have been widely studied because they are promising as adsorbents for removal of environmental pollutants, catalysts and catalyst supports (Sun et al. 2016).

The main objects of this study are: (i) to characterization MCM-41, (ii) to study the feasibility of using the MCM-41 for the removal of sunset yellow dye, (ii) to determine the various parameters affecting sorption, such as contact time, amount of adsorbents and temperature, (iii) to determine the applicability of various isotherm models ((i.e., Langmuir and Freundlich) to find out the best-fit isotherm equation, and (iv) to determine thermodynamic and kinetic parameters and explain the nature of adsorption.

Materials and Methods

Adsorbate

The commercial food dye Sunset Yellow FCF ($C_{16}H_{10}N_2Na_2O_7S_2$, molecular weight 452.37 g/mol, C.I. 15985, λmax=482 nm, chemical structure shown in figure 1) was supplied by Sigma-Aldrich. Distilled water was used to prepare all solutions.

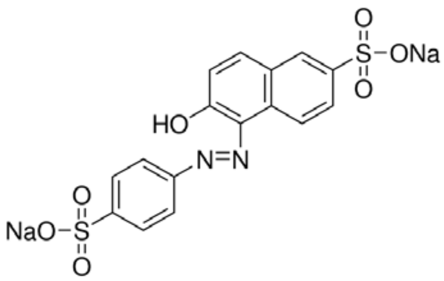

Figure 1. Chemical structure of Sunset Yellow FCF.

Adsorption equilibrium studies

Adsorption of Sunset Yellow on MCM-41 was studied by batch experiments. Equilibrium adsorption studies were conducted in a set of 50 mL capped volumetric flasks containing different amounts of adsorbent weights in the range of 0.1-0.3 g/L, 50 mL initial concentrations of sunset yellow solutions (10 mg/L). Flasks were shaken in a mechanical shaker (GFL 1086) at 100 rpm and different temperature (30, 40 and 50°C). After adsorption, samples were filtered and then the concentrations of sunset yellow in the supernatant solution was analyzed. All concentrations were measured by using UV spectrophotometer (LaboMed Inc.) at 482 nm. The adsorption efficiency E is calculated using Eq. (1):

$$E = \frac{(C_0 - C_e)}{C_0} 100 \quad (1)$$

where C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. The sunset yellow uptake at equilibrium, q_e (mg/g), was calculated using Eq. (2):

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where V (L) is the volume of the solution, and W (g) is the mass of adsorbent used. The equilibrium data were simulated using the Freundlich and Langmuir isotherm models.

Adsorption kinetics

Kinetic adsorption experiments were carried out by adding 0.1 g/L adsorbent to 50 mL of 10 mg/L sunset yellow dye aqueous solutions at 30, 40 and 50°C at optimum pH. The uptake of sunset yellow at time t, q_t (mg/g) was calculated by the following equation:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (3)$$

where C_t (mg/L) is the liquid-phase concentration of dye at time t (min).

In order to predict adsorption behavior of sunset yellow FCF on MCM-41, pseudo-first-order and pseudo-second-order kinetics equations which are described as Eqs. (4) and (5), respectively, were applied for modeling experimental data

$$log\left(q_e - q_t\right) = log\, q_e - \frac{k_1 t}{2.303} \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where k_1 (1/min) and k_2 (g/mg min) are the adsorption rate constants of the pseudo-first-order and pseudo-second-order, respectively.

Adsorption Thermodynamics

To describe thermodynamics behavior of the adsorption of sunset yellow dye onto MCM-41, thermodynamics parameters including the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated as per the following equations:

$$\Delta G° = -RT lnKc$$

$$lnK_C = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$

where R is the universal gas constant (8.314 J/mol K), T is the temperature (K) and $K_C = C_{ads}/C_e$ is the equilibrium constant of the sunset yellow adsorption equilibrium (which is a ratio of C_{ads}, the sunset yellow concentration in the adsorbent, and C_e, the sunset yellow concentration in the adsorbate.

Results and Discussion

The surface physical properties of MCM-41 were characterized with an automated gas sorption apparatus using N_2 as adsorbate at 77.4 K (Micromeritics TriStar II 3020). Nitrogen adsorption is a standart technique widely used for the determination of porosity of adsorbent. Figure 2 shows the isotherm of the MCM-41. The pore structure of the MCM-41 was calculated by the t-method analysis from the adsorption branch of the nitrogen isotherms (Oguz Erdogan 2016; Erdogan and Oguz Erdogan 2016).

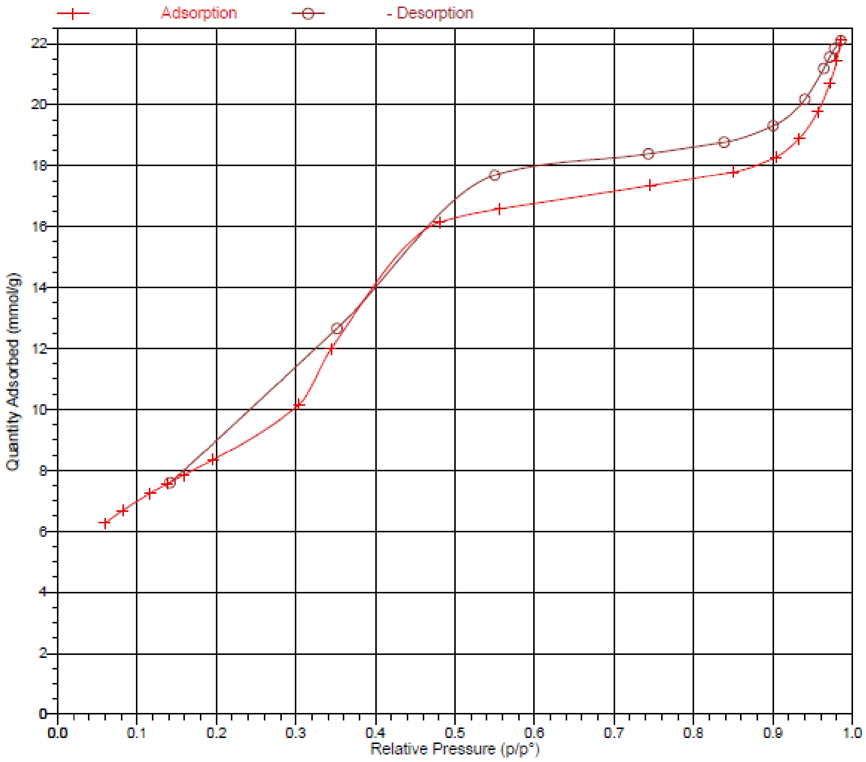

Figure 2. Adsorption-desorption isotherms of the MCM-41.

Table 1 shows the BET and Langmuir surface areas, total pore volume and avarage pore size for the MCM-41. The average pore size of the MCM-41 was 4.32 nm with micropores and mesopores.

Table 1: Textural parameters of the MCM-41.

Properties	MCM-41
Brunauer-Emmett-Teller Surface Area (m^2/g)	689.32
Langmuir Surface Area (m^2/g)	1780
Total Pore Volume (mL/g)	0.598
Average Pore Size (nm)	4.32

Figure 3 showed that the adsorption capacities at equilibrium (q_e) decreased with an increase in adsorbent dose from 0.1 to 0.3 g/L. This is explained as a consequence of partial aggregation, which occurs at high adsorbent amount resulting in decreased active sites. A similar phenomenon was reported by Huang et al., Rubin et al., and Nweke and Okpokwasili.

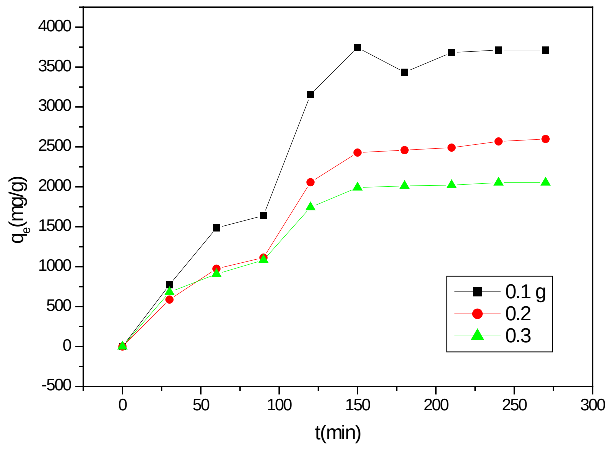

Figure 3. Effects of adsorbent dosage and contact time on the adsorptive uptake of food dye onto the MCM-41 (conditions: C_0=20 mg/L; temperature=40 °C).

The temperature dependence of sunset yellow sorption onto MCM-41 was studied at optimum adsorbent dosage of 0.3 g/L. Figure 4 shows that the food dye adsorption increased with temperature, which may be attributed to the enhanced reaction rate with higher temperature. A possible explanation is that high temperature extends the pore volume and surface area and provides more chances for sunset yellow dye to pass the external boundary layer and penetrate more easily. This corroborates the reports of our previous study (Erdogan and Oguz Erdogan 2016) . Similar behavior has been reported in the literature (Huang et al. 2015; Emami and Azizian 2014).

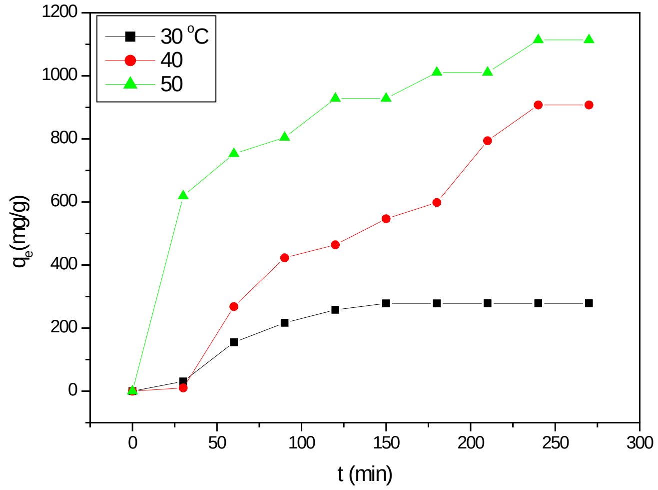

Figure 4. Effect of solution temperature on the adsorption food dye onto the MCM41 (conditions: W=0.03 g/L; C_0=10 mg/L).

Adsorption Isotherms

The equilibrium adsorption isotherms are essential to the practical design and optimization of adsorption process. The adsorption isotherm describes how adsorbates interact with adsorbents. The equilibrium data of food dye adsorption onto MCM-41 was explored using the isotherm model of Langmuir and Freundlich. The parameters obtained of the two isotherm models were calculated and represented in Table 2. The correlation coefficients descended in the order of: Langmuir> Freundlich. The results revealed that the adsorption of food dye on MCM-41 was best described by the Langmuir isotherm, indicating the adsorption was homogeneous and a monolayer was present.

Table 2: Freundlich and Langmuir isotherm constants for the adsorption sunset yellow onto MCM-41 at 40 °C

Isotherms	Parameters		
Freundlich	K_F (mg/g)(L/mg)$^{1/n}$	n	R^2
	3.74E-8	0.158	0.889
Langmuir	Q_0(mg/g)	K_L (L/mg)	R^2
	518.13	0.016	0.999

Langmuir adsorption isotherm constant related to adsorption capacity, Q_0 were found as 518.13 mg/g. To confirm the favorability of the adsorption, the separation factor R_L was calculated by

$$R_L = \frac{1}{1+K_L C_0}$$

where the adsorption process to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). Here, the value of R_L was found to be 0.502, which further confirmed that the Langmuir isotherm was favorable for of food dye on the MCM-41. Similar observation was reported for the adsorption of methylene blue dye onto the safflower seed derived activated carbons (Angın et al. 2014).

Conclusion

MCM-41 was used as the mesoporous adsorbent to remove food dye from aqueous solutions at various temperature. The adsorption capacity of MCM-41 for food dye increased while the temperature of solution was increased. The Freundlich and Langmuir isotherm models were used for the mathematical description of the adsorption of food dye onto MCM-41 at various temperatures and the results suggested that the adsorption equilibrium data fitted well to the Langmuir model. This study has revealed that MCM-41 can be used as a highly efficient adsorbent for sunset yellow food dye removal from aqueous solutions.

Acknowledgements

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