

AQUEOUS SOLUTION DYE REMOVAL BY ADSORPTION ONTO SILICEOUS MATERIALS

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Abstract

Methylene blue (MB) was used as probe molecule to investigate the adsorption behaviour of the dye onto two different siliceous materials: SBA-15 (as-synthesized) and silica gel (commercial). The adsorption isotherms on both adsorbents were classified as L3 type according to their shape. At first the MB adsorbed as a monolayer and afterwards, at a higher concentration, the isotherm showed an inflection point at which the shape changes from convex to concave. This can be caused by MB aggregation forming dimers due to the high surface concentration. The Brunauer-Emmett-Teller (BET) and Aranovich-Donohue (AD) equations were selected to fit the experimental data since they describe L3 isotherms. The former is a rational function and the latter is a power function. Both models showed a good fit for silica gel although Aranovich-Donohue equation was slightly better for the entire concentration range. However, for SBA-15 the fit was worse especially the BET equation.

Keywords: Adsorption, isotherm, SBA-15, silica gel.

Introduction

The Directive 2008/1/EC on the prevention and control of pollution put a greater control on industrial activities, so that enterprises should assume important tasks of preventing and reducing pollution. In order to meet the current regulations, technologies that reduce pollution from industrial effluents before discharge based on physical, chemical and biological treatment should be used. Dyes are among the pollutants that are suffering severe restrictions on disposal. This is due to their mutagenic and toxic nature and because they are compounds that, without correct treatment, stabilize and remain in water for many years. Therefore, it is essential to conduct an adequate wastewater treatment for dyes. The method selected will depend primarily on the pollutant concentration and the effluent flow. Certain techniques, such as conventional oxidation are used when the concentration of organic compounds is high, while others like adsorption and advanced oxidation processes are used for low pollutant concentrations. Adsorption stands out in the treatment of wastewater due to its low initial cost, high flexibility, simple design and operation, easy automation, lack of sensitivity to toxic pollutants and the possibility to operate at very low concentrations. However, it presents some negative aspects: it is a non-destructive technique and it has a high operational cost. Therefore, it is applied only with small concentrated pollutants and when the adsorbent has a low cost or can be easily

regenerated. The adsorbent is a crucial parameter and its properties must be considered including: the specific surface area, the pore volume accessible for the adsorbate, the stability, the possibility of regeneration and the cost. Other important factors that influence adsorption are: adsorbate concentration and its affinity for the adsorbent, and the environmental conditions, mainly pH, temperature and ionic strength. Equilibrium isotherms are necessary for the design of adsorption processes. The shape of an isotherm provides significant information about the adsorption process. The affinity parameter calculated from the isotherm equations are related to the nature and strength of the interaction between the adsorbate and the adsorbent. In this work, we have studied the adsorption of dyes on well ordered pore structure materials including a synthesized mesoporous silica SBA-15 and a commercial silica gel. The sorbent materials were tested for the adsorption of dyes from an aqueous solution using a batch technique.

Methods

Synthesis of SBA-15 was carried out according to the method of Zhao (Zhao, 1998) and the silica gel was supplied by Flucka. The adsorption isotherms were performed by means of batch adsorption experiments. The dye solutions with the corresponding adsorbent mass were shaken in a thermoshaker bath with stirring and temperature control. The amount of adsorbed dye was measured from the dye concentrations in the aqueous solution before and after adsorption. These were determined by UV-Vis absorption at 610 nm for MB, using a UV-Vis spectrometer (Lambda 35, Perkin Elmer), according to the Lambert-Beer law ($ABS(\lambda) = \epsilon_{\lambda} \cdot C \cdot l$; $\epsilon_{610} = 34500 \text{ M}^{-1} \cdot \text{cm}^{-1}$).

Results and discussion

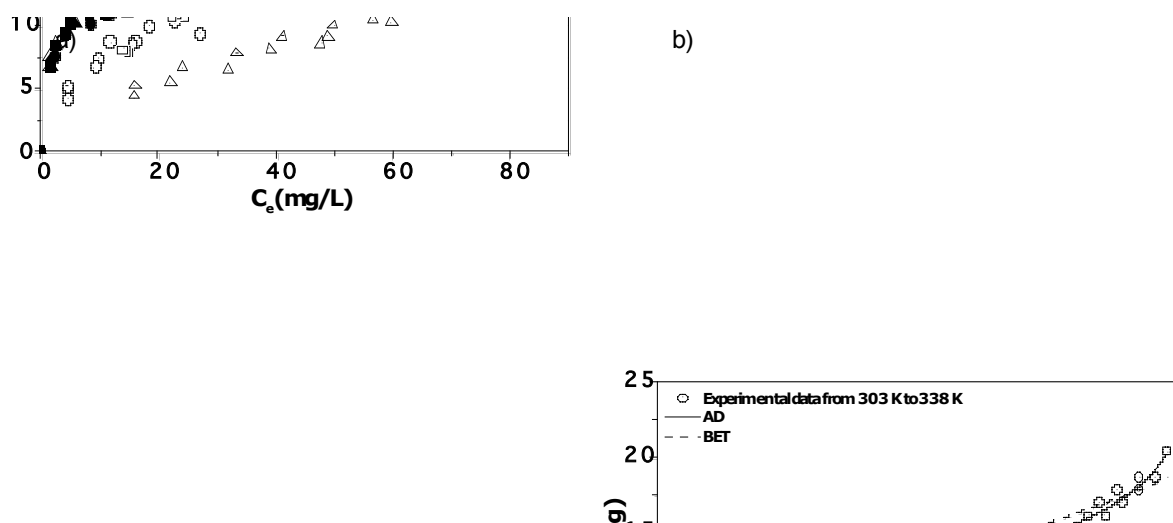


Figure 1. a) MB adsorption isotherms on silica gel and SBA-15: $C_o = 100 \text{ mg/L}$ (ppm); $t_e = 90 \text{ min}$; $pH_{\text{initial}} = 7$. b) Adsorption isotherms fitted to the Brunauer-Emmett-Teller (dashed line) and Aranovich-Donohue (solid line) equations (303-338 K).

Fig 1a shows the adsorption isotherms of MB onto silica gel and SBA-15 at three temperatures (303K, 313 K and 338 K). The influence of temperature on isotherm shape, as well as adsorption

capacity, was negligible. Adsorption isotherms were classified as L3 (Langmuir type 3) curves according to Giles classification (Giles, 1960). The MB first adsorbed as a monolayer, while at a higher concentration, it showed an inflection point at which the shape changes from convex to concave. This is the typical behaviour when the adsorbate-adsorbent interactions are similar to the interactions between adsorbate molecules. In the first part of the curve, corresponding to the monolayer, it is assumed that all sites are equivalent and there is no adsorption dependence on the adsorbed amount. In the second part, beyond the inflection point ($C_e \approx 60 \text{ mg/L}$), the slope indicates that the presence of adsorbed molecules of MB makes the adsorption of more MB molecules easier. This could be caused by dye aggregation due to the high surface concentration. It is well known that MB easily forms dimers in water even at low concentrations and the dimerization is favoured by high MB concentrations. The formation of MB aggregates on adsorbent surfaces, like montmorillonite, was detected even at low surface coverage. Moreover, the adsorbed dimer-like species occupy the same surface area as the monomer (120 \AA^2) and it is independent of the initial aggregation state of MB in solution. Both adsorbents show similar adsorption capacities, especially at low and moderate temperatures ($q_e \approx 20 \text{ mg/g}$).

To determine the best equation to describe the adsorption experimental data, firstly it must be assigned to one of the classifications and subgroups detailed by Giles. In general, MB adsorption on both adsorbents can be classified as a L3 isotherm. Most of the commonly used isotherm equations are rational functions derived from the theory of adsorption processes. However, equations involving power laws can also describe a wide range of isotherm types. These equations are based on the Langmuir equation with some exponents that are viewed as heterogeneity factors which normally vary between 0 and 1.

The Brunauer-Emmett-Teller (BET) (Eq 1) and Aranovich-Donohue (AD) (Eq 2) equations were selected to fit the experimental data for MB adsorption equilibrium in aqueous solution on silica gel and SBA-15 because they both can describe L3 isotherms. The former is a rational function and the latter is a power function (Eq. 1: $q_e = \left(\frac{k_1 C_e}{1 + k_2 C_e} \right) \left(\frac{1}{1 - k_3 C_e} \right)$; Eq. 2: $q_e = \left(\frac{k_1 C_e}{1 + k_2 C_e} \right) \left(\frac{1}{1 - k_3 C_e} \right)^\alpha$). Table 1 and 2 presents the calculated parameters for both models. In general, for silica gel (Fig 1b) both models showed a good fit although the Aranovich-Donohue equation was slightly better. However, for SBA-15 the fit is worse, especially the BET equation. Therefore, it is possible to fit experimental data keeping the physical meaning of the Langmuir equation. The first term of the Langmuir equation refers to the monolayer adsorption and the second term includes the contribution of the adsorption in the others layers.

Table 1. Equilibrium parameters for the adsorption of MB. Evaluation and comparison of the proposed models: Aranovich–Donohue (AD) and Brunauer–Emmett–Teller (BET).

Silica Gel						SBA-15					
	k_1 $\text{mg}^{-\alpha} \cdot \text{L}^{\alpha}$	k_2 $\text{mg}^{-\alpha} \cdot \text{L}^{\alpha}$	k_3 $\text{mg}^{-1} \cdot \text{L}$	α	R^2		k_1 $\text{mg}^{-\alpha} \cdot \text{L}^{\alpha}$	k_2 $\text{mg}^{-\alpha} \cdot \text{L}^{\alpha}$	k_3 $\text{mg}^{-1} \cdot \text{L}$	α	R^2
303 K						303 K					
BET	16	1.6	0.0057	1	0.980	BET	2.1	0.20	0.0052	1	0.971
AD	12	1.0	0.0124	0.20	0.991	AD	1.7	0.13	0.0131	0.11	0.983
313 K						313 K					
BET	13	1.3	0.0061	1	0.990	BET	4	0.4	0.0075	1	0.969
AD	9	0.8	0.0115	0.26	0.995	AD	1.5	0.12	0.0102	0.4	0.974
338 K						338 K					
BET	10	0.8	0.0041	1	0.994	BET	0.7	0.2	0.0080	1	0.970
AD	9.2	0.73	0.009	0.3	0.995	AD	0.25	0.03	0.0114	0.2	0.974
From 303 K to 338 K (Figure 1b)											
BET	15	1.4	0.0057	1	0.974						
AD	10.7	0.91	0.0120	0.22	0.988						

Conclusions

Adsorption isotherms were classified as L3 type. Initially, the MB adsorbed as a monolayer and afterwards, there was an increase in the adsorption capacity as a result of dye aggregation forming MB dimers. The Brunauer–Emmett–Teller (BET) and Aranovich–Donohue (AD) equations showed a good fit of the experimental data, especially for the silica gel, although the Aranovich–Donohue equation was slightly better. Therefore, it is possible to fit experimental data keeping the physical meaning of the Langmuir equation, with a term that considers the monolayer adsorption and a second term that includes the contribution of the adsorption in the others layers.

References

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