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Adsorption of Acid Dyes Using Polyelectrolyte Impregnated Mesoporous Silica

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Abstract−Cationic polyelectrolyte, PDDA (Poly(diallyldimethylammonium chloride)), was impregnated on mesoporous silica SBA-15 (PDDA/SBA-15) and amorphous conventional silica (PDDA/CS) supports. Acid dye adsorption characteristics, such as adsorption kinetics, adsorption isotherms, maximum adsorption capacity, and breakthrough curves of the prepared PDDA/SBA-15 and PDDA/CS adsorbents, were examined by batch and column adsorption techniques where the Acid Violet 17, Acid Red 44, and Acid Blue 45 were used as target adsorbates. PDDA/SBA-15 adsorbent showed fast adsorption kinetics of less than 10 min and much higher adsorption capacities compared to PDDA/CS due to large pore sizes, ordered cylindrical pore structures, and high amount of impregnated PDDA. Results from batch and column experiments showed that practical use of PDDA/SBA-15 adsorbent for effective removal of acid dyes from aqueous solution would be possible. Polyelectrolyte impregnation method was suggested as a simple method for the development of adsorbent with large pore diameters and efficient adsorption characteristics.

Key words: Polyelectrolyte, Mesoporous Silica, Acid Dye, Adsorption Isotherm, Breakthrough Curve

INTRODUCTION

Textile industries, which are well known as massive wastewater producing industries, generally consist of a number of steps such as desizing, scouring, bleaching, mercerizing, dyeing, and washing. Wastewater discharged from textile industries has different characteristics from those of other industries. Dyes discharged through textile wastewater give high colors that inhibit light penetration, and many synthetic dyes do not easily decompose in biological treatments due to their toxic effects on microorganisms [Forgacs et al., 2004]. In fact, activated sludge processes, which are widely adopted for treating organic wastewater, have shown limited color removal on this kind of wastewater. Adsorptions using well-known activated carbons [Rajeshwarisivaraj et al., 2001; Nakagawa et al., 2004], or Fenton oxidation and advanced oxidation processes (AOP) for the complete mineralization or organic contaminants to carbon dioxide and water are used to effectively treat textile wastewater [Andreozzi et al., 1999; Arslan and Balcioğlu, 1999].

Activated carbons with large surface area have shown high adsorption capacities for many adsorbates, but they are mainly composed of micropores of less than 2 nm and thus are not effective for large sized synthetic dyes. Furthermore, it requires relatively high costs for the preparing and using [Forgacs et al., 2004; Rajeshwarisivaraj et al., 2001; Nakagawa et al., 2004]. To overcome these disadvantages, relatively cheap raw materials are used for producing activated carbons [Rajeshwarisivaraj et al., 2001], and the by-products or wastes from other industries are recycled as adsorbents [Garg et al., 2004; Tsai et al., 2004; Acemioğlu, 2004; Gulnaz et al., 2004]. In addition, researches aimed to develop novel adsorbents with large pores have been conducted to develop alternative adsorbents for activated carbons.

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To prepare mesoporous adsorbents having pore diameters of greater than 2 nm, mesoporous silica or alumina adsorbents and also, mesoporous carbons that were synthesized using mesoporous silica as templates, were used for dye adsorption [Jesionowski, 2003; Andrzejewska et al., 2004; Han et al., 2000]. However, recycled adsorbents showed much lower adsorption capacities due to their small surface area and pore diameters as well as their irregular pore structures. Adsorbents prepared by surface modification through silane grafting on mesoporous silicas or mesoporous carbon adsorbents showed relatively large adsorption capacities, but the fact that the preparation methods are too complex and that it is very costly to prepare pose a disadvantage.

SBA-15, one of the most widely applied mesoporous silicas, is known to have high hydrothermal stability due to their relatively thick wall thickness and many advantageous properties of adsorbents or catalyst supports such as large surface area and low diffusion resistance due to their highly ordered pore structures composed of hexagonal array of cylindrical pores with large diameter. Metal supported catalysts or organic functional group introduced heavy metal ion adsorbents using SBA-15 showed enhanced catalytic activities and adsorption efficiencies [Park et al., 2003; Kang et al., 2002; Kim et al., 2003], respectively. In our group, cationic polyelectrolytes, PDDA(Poly(diallyldimethylammonium chloride)) was impregnated on SBA-15 and thus prepared PDDA/SBA-15 adsorbent was used for the dye adsorption. PDDA/SBA-15 showed high adsorption capacities for acid dyes from aqueous solutions, and the reasons for this enhanced adsorption capacities for acid dyes are thought to be due to the surface modification from anionic to cationic by impregnation of PDDA [Park et al., 2004].

In this work, the acid dye adsorption characteristics of PDDA/SBA-15 were investigated by measuring adsorption rate, adsorption isotherm, maximum adsorption capacity, and breakthrough behavior. The results obtained in this work are essential to ensure the practical use of developed PDDA/SBA-15 adsorbents.

EXPERIMENTAL

PDDA/SBA-15 adsorbents were prepared through impregnation of 2.0 wt% PDDA solution diluted by using 20 wt% PDDA (Aldrich Co.) on SBA-15 support. SBA-15 mesoporous silica support was synthesized by typical template method as reported in the literature [Park et al., 2003; Kang et al., 2002] and used after calcination at 500 °C. The detailed impregnation procedure is described here briefly. SBA-15 support, 1.0 g, was added to diluted PDDA aqueous solution (2.0 wt%) and agitated at 200 rpm using magnetic stirrer for 3 hours. PDDA impregnated SBA-15 was filtered and washed three times with 100 ml of deionized water in order to remove excess PDDA in the pores of the support. In addition, conventional silica support (CS) with irregular pore structures compared to SBA-15 was also used as a support for preparing PDDA/CS adsorbents through the same procedures. Adsorption experiments using both adsorbents were conducted after drying under ambient conditions.

It was well known that the PZC (Point of Zero Charge) of silicas is below pH 2. Thus, SBA-15 and CS supports showed negative zeta potentials in pH range from 3 to 9. However, PDDA/SBA-15 and PDDA/CS adsorbents showed positive zeta potentials after PDDA impregnation in the same pH range according to our previous study [Park et al., 2004].

Acid dye adsorption characteristics of the PDDA/SBA-15 and PDDA/CS adsorbents were investigated using Acid Violet 17, Acid Red 44, and Acid Blue 45 as target adsorbates and molecular structure of these acid dyes are shown in Fig. 1. Dye concentrations in aqueous solution were measured using absorption in the UV/Vis spectrophotometer (HP 8453, Hewlett Packard Co.) at characteristic wavelength. The maximum absorbance (λ_{Max}) of each dye and their basic properties are summarized in Table 1.

Batch adsorption experiments were conducted to measure adsorption rate and adsorption isotherm. Maximum adsorption capacity was calculated from adsorption isotherm data using Langmuir adsorption isotherm equation. Dye solutions of 50 ml with known concentrations were contacted with 0.1 g of adsorbents by stirring. Dye concentrations remaining after 30 min were measured and the amount of adsorbed dyes on each adsorbents was calculated from the difference between initial and final concentrations.

Continuous column experiments were conducted to investigate breakthrough behavior of the PDDA/SBA-15 adsorbents. Quartz column with an inner diameter of 10 mm and length of 50 mm was packed with 0.1 g of adsorbent and dye solution with known concentration was fed through the column at a fixed flow rate using a peristaltic pump (7550-70, Cole Parmer). Dye concentrations at the effluents were measured spectrophotometrically.

These experiments were conducted without pH control. The pHs of three dye solutions are known to be approximately 6 because these solutions are weak acids.

Table 1. Typical characteristics of dyes used in this study

Dyes	Molecular formula	M.W. (g/mol)	λ_{Max} (nm)	C.I. number
Acid Violet 17	$C_{41}H_{48}N_3NaO_6S_2$	765.96	545	42650
Acid Red 44	$C_{20}H_{12}N_2Na_2O_7S_2$	502.43	513	16250
Acid Blue 45	$C_{14}H_8N_2Na_2O_{10}S_2$	474.33	595	63010

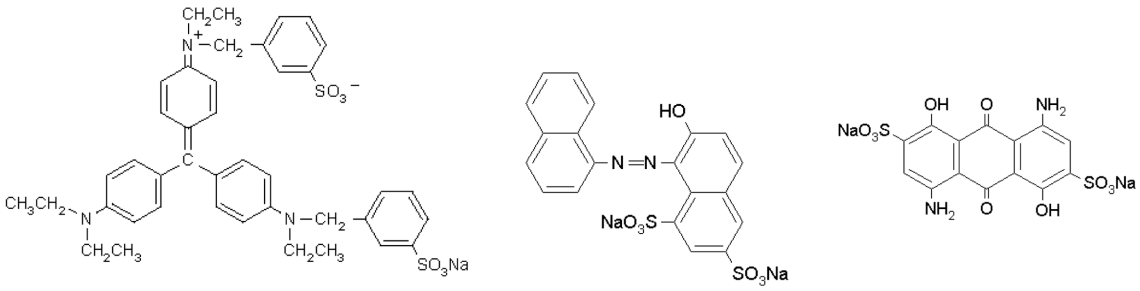
RESULTS AND DISCUSSIONS

1. Dye Characteristics

Three different acid dyes that were used in this study exist as sodium salt but ionize in aqueous solution. Acid Blue 45 has two -SO_3^-, two -OH, and two -NH_2 functional groups and Acid Red 44 has two -SO_3^- and one -OH functional groups. However, Acid Violet 17 has two -SO_3^- functional groups and a nitrogen atom carrying positive charge as shown in Fig. 1. Molecular size of Acid Violet 17 is known as 8 Å(radius)×21 Å(length) and that of Acid Blue 45 is known as 3.8 Å(radius)×13 Å(length) [Han et al., 2000]. Acid Red 44 is assumed to be a little bit larger than Acid Blue 45 considering their molecular structures.

2. Dye Adsorption Kinetics of the PDDA/SBA-15

Activated carbons from wastes or recycled adsorbents require from few hours to days to reach the maximum equilibrium adsorption state [Nakagawa et al., 2004; Tsai et al., 2004]. For example, activated carbons from solid wastes took 15 days for Reactive Black 5 dye equilibrium adsorption [Nakagawa et al., 2004]. However, PDDA/SBA-15 adsorbents showed much faster adsorption kinetics of no longer than 10 min of contact when Acid Red 44 solution was used. PDDA/SBA-15 adsorbent has a large pore diameter with sharp pore size distribution of around 5 nm, and PDDA/CS adsorbent has large pores with rather broad distribution ranging from 5 to 20 nm with a peak at 15 nm [Park et al., 2004]. In general, ad-



(a) Acid Violet 17 (b) Acid Red 44 (c) Acid Blue 45

Fig. 1. Chemical structure of dyes.

sorption mechanism, adsorbate molecules from aqueous phase need to diffuse through pores of adsorbent in order to be adsorbed on adsorption sites. Considering this adsorption mechanism, the relatively low diffusion resistance compared to fully microporous activated carbons is the reason for the fast adsorption kinetics of the PDDA/SBA-15 adsorbents and also for the PDDA/CS adsorbents. Therefore, in this study, the batch adsorption isotherm experiments were completed within 30 min of contact time.

3. Dye Adsorption Isotherms and Maximum Adsorption Capacities

Adsorption isotherms of PDDA/SBA-15 and PDDA/CS adsorbents were measured by batch adsorption technique and maximum adsorption capacities for each dye were calculated by using the Langmuir model. The Langmuir adsorption isotherm model assumes monolayer adsorption on surface of the adsorbents and isotherm equation can be linearized as follows.

$$C_e/q_e=1/(Q_{Max}b)+C_e/Q_{Max} \quad (1)$$

In Eq. (1), C_e is the amount of dye in aqueous phase at equilibrium (mg/L) and q_e is the amount of dye adsorbed at equilibrium (mg/g). Q_{Max} is a constant reflecting the maximum adsorption capacity (mg/g) and b is a direct measure for the intensity of the adsorption process or related to the heat of adsorption (L/mg) [Tsai et al., 2004]. The lower value of b means the stronger adsorption between adsorption sites and adsorbates.

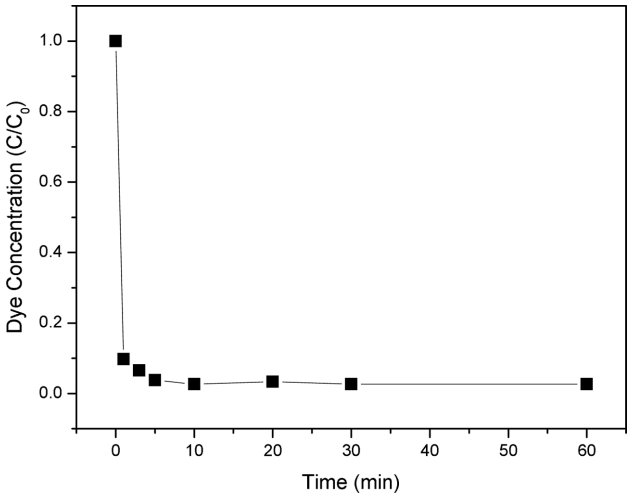


Fig. 2. Acid Red 44 dye adsorption kinetics of the PDDA/SBA-15.

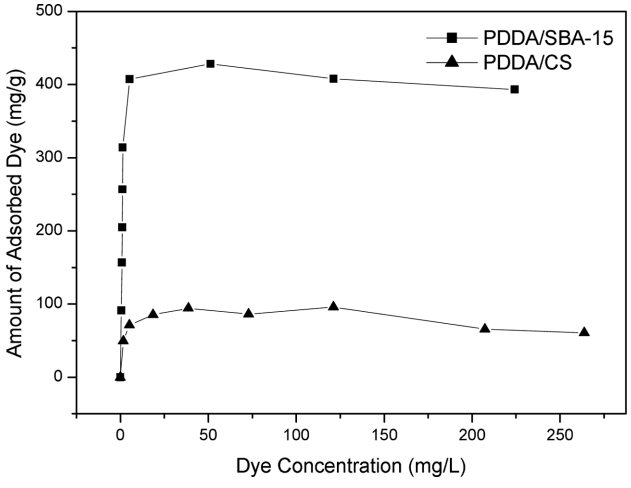


Fig. 3. Adsorption isotherms of Acid Violet 17 on the PDDA/SBA-15 and PDDA/CS.

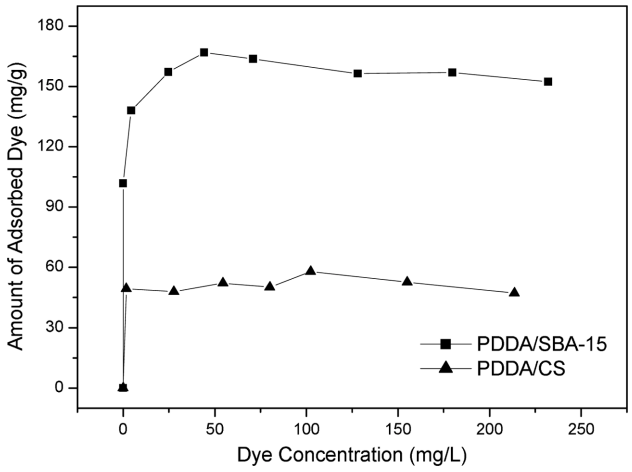


Fig. 4. Adsorption isotherms of Acid Red 44 on the PDDA/SBA-15 and PDDA/CS.

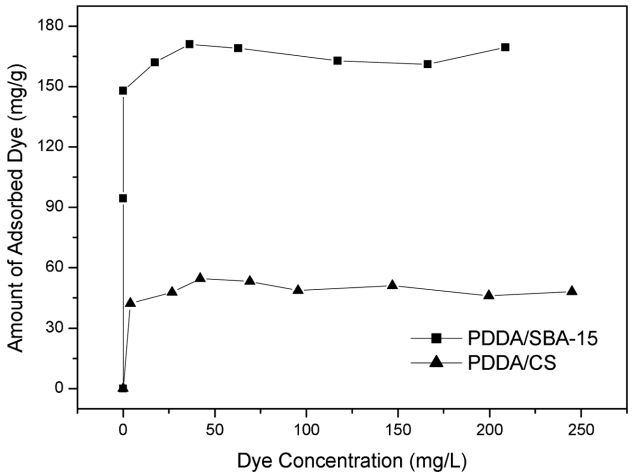


Fig. 5. Adsorption isotherms of Acid Blue 45 on the PDDA/SBA-15 and PDDA/CS.

Experimental results obtained for adsorption isotherms of the PDDA/SBA-15 and PDDA/CS for Acid Violet 17 are shown in Fig. 3, for Acid Red 44 in Fig. 4 and for Acid Blue 45 in Fig. 5, respectively. Parameters calculated from the Langmuir equation are also summarized in Table 2. Acid dye adsorptions on PDDA/SBA-15 adsorbents were well fitted (R^2 values were over 0.998) by Langmuir model and these results can be seen to coincide well with the results reported in the literature on electrostatic attraction mechanism for the adsorption of acid dye anions on cationic adsorbent surfaces [Al-Ghouti et al., 2003]. In contrast, the same acid dye adsorptions on PDDA/CS produced a slightly lower R^2 values of which might be explained by the difference in the pore structure. Pore structure of the CS support is characterized as irregular and broad pore size distribution. Contractions or expansions of pore diameters or

Table 2. Langmuir-fit parameters and maximum adsorption capacities

Adsorbents	Dyes	Q_{Max} (mg/g)	b (1/mg)	R^2
PDDA/SBA-15	Acid Violet 17	398.4	6.46	0.99927
	Acid Red 44	153.6	−0.64	0.99929
	Acid Blue 45	166.1	5.375	0.99863
PDDA/CS	Acid Violet 17	62.3	−0.09	0.97605
	Acid Red 44	48.6	−0.26	0.98884
	Acid Blue 45	47.3	−0.30	0.99652

pore blockings are seen to randomly occur throughout the entire supports and these characteristics of the CS support add complexity to the PDDA layer on the surface as well as the adsorbed acid dye layers. However, smooth PDDA layer and monolayer adsorption of acid dye can be favored in the ordered pore surfaces of the SBA-15 support.

PDDA/SBA-15 adsorbent showed much higher adsorption capacities for all of the tested three acid dyes compared to PDDA/CS, and the differences were 6.4 times for Acid Violet 17, 3.2 times for Acid Red 44 and 3.5 times for Acid Blue 45. However, the surface area for PDDA/SBA-15 was only 1.3 times larger than that of PDDA/CS (349 m^2/g for PDDA/SBA-15 compared to 270 m^2/g for PDDA/CS) and the pore diameters of the PDDA/CS were larger than PDDA/SBA-15 (15.0 nm for PDDA/CS compared to 6.4 nm for PDDA/SBA-15 based on average values using BET equation). Considering these results, it was assumed that the large difference in adsorption capacities might have been caused by some other reasons and not simply by the surface area or pore diameter of the adsorbents.

Elemental analysis results showed nitrogen contents of the PDDA/SBA-15 and PDDA/CS as 2.843 wt% and 2.096 wt%, respectively, which means that 1.4 times more PDDA molecules were impregnated on SBA-15 mesoporous silica support. Thus, putting all the results obtained together, we can deduce that the sufficiently large pore diameters for the impregnation and adsorption, regularly shaped cylindrical pores with sharp pore size distributions, and larger number of adsorption sites (impregnated PDDA molecules) are responsible for the much higher adsorption capacities of the PDDA/SBA-15 adsorbents.

4. Column Breakthrough Behavior

Adsorbents are capable of effectively removing dyes in a continuous column operation, thereby resulting in more practical wastewater treatments. Column adsorption experiments were conducted by using an adsorption column packed with PDDA/SBA-15 adsorbents, and dye concentration changes in the effluents with bed volume are shown in Fig. 6. For the column adsorption experiments, 200 ppm Acid Violet 17 solution was fed at 5 ml/min and 100 ppm Acid Blue 45 solution at 4 ml/min. It was found that the PDDA/SBA-15 could suppress dye concentrations in the effluents below 10% of initial dye concentrations (breakthrough point) up to 161 bed volumes for 200 ppm Acid Violet 17 and 217 bed volumes for 100 ppm Acid Blue 45. Adsorption columns were saturated rapidly after breakthrough points for both experiments. These results confirm the effectiveness of the PDDA/SBA-15 in continuous column operations and that acid dyes from aqueous solutions were effectively removed by the PDDA/SBA-15 adsorbent developed in this study.

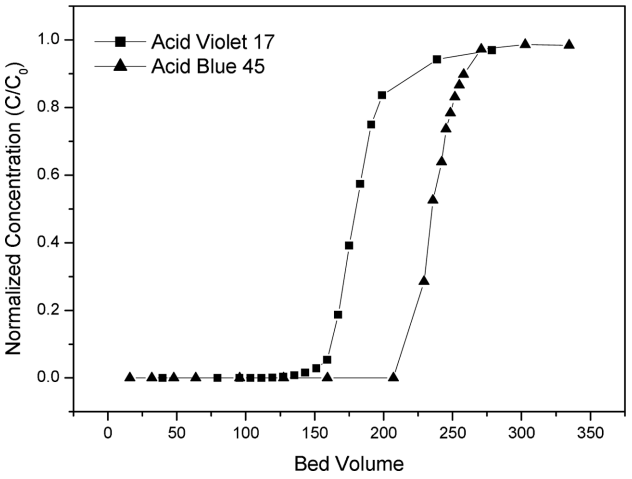


Fig. 6. Column breakthrough behavior of the PDDA/SBA-15 adsorbent for dyes (Acid Violet 17 and Acid Blue 45).

CONCLUSIONS

The cationic polyelectrolyte, PDDA, was impregnated on mesoporous silica SBA-15 (PDDA/SBA-15) and conventional silica (PDDA/CS) for the adsorption of acid dyes from aqueous solution in this study. Batch and column adsorption experiments were conducted, and based on the results obtained from these experiments, we were able to make the following conclusions.

1. PDDA/SBA-15 adsorbent showed high adsorption capacities for acid dyes compared to PDDA/CS due to their superior pore characteristics such as pore diameters that are large enough for impregnation and adsorption, regularly shaped cylindrical pores with sharp pore size distribution, and large surface area. In addition, a larger amount of PDDA was impregnated on SBA-15 due to the above pore structural properties.

2. Adsorption mechanism between acid dye adsorbates and positively charged adsorption sites on the surface of PDDA/SBA-15 adsorbents was thought to be an electrostatic attractive interaction, and this relatively strong interaction made it possible for faster adsorption kinetics within 10 min of contact time for the equilibrium adsorption.

3. PDDA/SBA-15 could effectively remove acid dyes from aqueous solution in a continuous column operation, which is an essential requirement in practical wastewater treatments.

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