



Preparation of polyelectrolyte-functionalized mesoporous silicas for the selective adsorption of anionic dye in an aqueous solution

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ABSTRACT

Polyelectrolytes (PDDA, poly (diallyldimethylammonium chloride)) functionalized mesoporous silica adsorbent (PDDA/MS) was prepared and characterized by N_2 adsorption, transmission electron microscopy (TEM) and zeta potential. The PDDA/MS showed ordered pore structure and the surface charge was successfully converted from negative to positive by PDDA functionalization. The adsorption capability of the prepared adsorbents was evaluated using nine different dye solutions with positive, neutral and negative charges. For the comparison purpose, commercial silica (CS, Davisil) and granular activated carbon (GAC), which are conventionally used as adsorbents, were also treated by PDDA impregnation. The batch adsorption experiments showed that the PDDA/MS exhibited the highest selective adsorption capacity of negative acid dye dissolved in an aqueous solution. Taken together, the results of this work indicate that polyelectrolyte functionalization of the inorganic surface could be a simple and suitable method for the surface modified adsorbent and the PDDA/MS suggested in this study could be used for the effective removal of acid dye from aqueous solutions.

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1. Introduction

Textile processes are known to be major producers of wastewater, and wastewater from textile industries is highly colored and contains many toxic and refractory organic compounds [1]. Among these organic compounds, dye can cause severe environmental problems because it colors the water stream even at extremely low concentrations, which in turn inhibits light penetration resulting in destruction of the aquatic ecosystem. In addition, dyes are considerably refractory to conventional biological treatment due to their complex structure and xenobiotic properties [2].

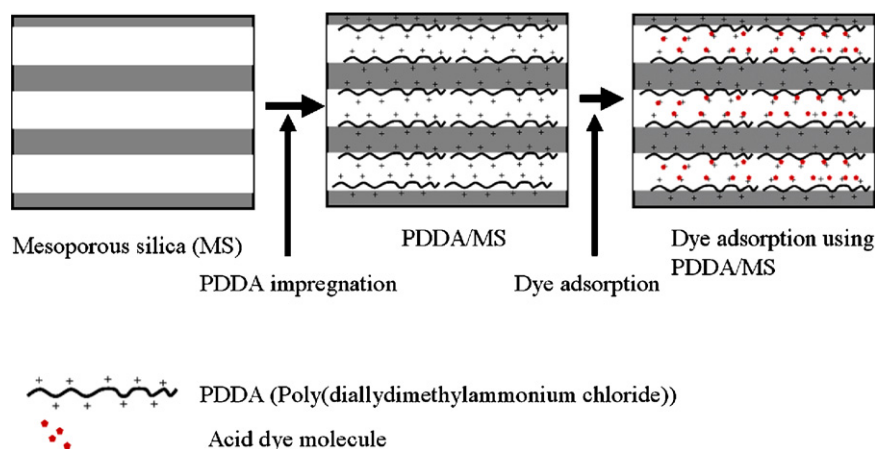
Many techniques for the purification of textile wastewater have been evaluated in fundamental and practical studies. Physico-chemical, catalytic and biological treatment methods are currently employed for the removal of dyes from wastewaters. They include adsorption using organic or inorganic adsorbents, photocatalysis, Fenton oxidation, advanced oxidation processes, and microbiological or enzymatic decomposition [3]. Among the methods, adsorption is considered to be one of the most suitable method for the removal of dyes from wastewaters. Adsorption using activated carbon is a common and popular method, because this method has considerable potential for the purification of wastewater due to its low process costs and relatively efficient dye removal [4–6]. How-

ever, adsorption of dye using activated carbon has some drawbacks such as slow adsorption kinetics and low adsorption capacity of bulky adsorbates due to the microporous nature of activated carbon (blockage of micropores). Therefore, adsorbents should have a high surface area with large pore as well as selective adsorption sites.

Mesoporous materials, such as M41s, HMS-x, SBA-x and CMK-x have well-ordered pore structures with high surface areas [7–9]. Therefore, they have been used for various applications [10–12]. In particular, adsorption properties of mesoporous materials have been studied and shown to be considerable performance [12–16].

In the past decade, many researches have been conducted to synthesize new adsorbents using mesoporous materials, such as mesoporous silica (MS), mesoporous alumina (MA) and mesoporous carbon (MC) [13,17–19]. In addition, various functional groups, which have selective adsorption affinity to targeted adsorbates, have been introduced to mesoporous materials by surface modifications such as silane grafting [12,15,19]. The adsorption properties of surface-functionalized mesoporous adsorbents have been successfully examined and shown to have remarkable adsorption capacity. Consequently, the surface-functionalized adsorbents have selective adsorption affinity to targeted adsorbate molecules. However, the preparation procedures of functionalized adsorbents are much complex, and the costs of functional materials are expensive. Therefore, it is necessary to design a functionalized mesoporous adsorbent for the selective adsorption by a simple and cost-effective process.

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Scheme 1. Preparation and dye adsorption scheme of the PDDA/MS adsorbent.

In this study, ordered MS was prepared and the surface of the MS was modified with polyelectrolyte PDDA (poly(diallyldimethylammonium chloride)). The PDDA functionalized mesoporous silica (PDDA/MS) was characterized by N_2 adsorption, transmission electron microscopy (TEM), and zeta potential, and it was used as an adsorbent for the adsorption of various dyes in aqueous solutions. Compared to the conventional surface modification methods, the method employed in this study are simple and cost-effective for the preparation of positively functionalized adsorbents.

2. Materials and methods

2.1. Reagent

Nine different commercially available dyes classified as negatively, positively and neutrally charged (from Rifa Co., Korea) were used in this study (Table 1). Low molecular weight PDDA MW 100,000–200,000 on average (Aldrich Co.), 20 wt.% in water was used after being diluted with de-ionized water.

2.2. Synthesis of mesoporous silica and polyelectrolyte-functionalized mesoporous silica

MS was synthesized using previously described method [8,15]. Briefly, a Pluronic surfactant P123 (poly(alkylene) oxide tri-block copolymer, EO_{20} – PO_{70} – EO_{20} (BASF Co.)) was used as a template and TEOS (tetraethylorthosilicate, Aldrich Co.) was used as a silica precursor. In a typical synthesis, 5.0 g of P123 was dissolved in an aqueous HCl (Sigma Co.) solution (1.6 M, 188 ml) and 11.4 ml of TEOS was then added. Then, the above mixture was stirred vigorously at 35 °C for 24 h, after which the temperature was increased to 100 °C

for aging and maintained for an additional 24 h with stirring. The resulting precipitates were then filtered off and dried under ambient conditions. The surfactant was removed by calcinations with air at 500 °C for 3 h to obtain MS.

Three different materials (MS, commercial silica (CS) and granular activated carbon (GAC)) were pretreated with 0.1 M HCl solution to remove any contaminants and increase the hydroxyl group content of the supports. The pretreated materials were then dried under ambient conditions, and the PDDA treatment was then carried out using a dilute PDDA solution. Scheme 1 shows the preparation and dye adsorption scheme of the PDDA/MS adsorbent. The detailed procedure is as follows: The MS was suspended (1.0 g in 100 ml solution) in different concentrations of PDDA solutions, ranging from 0.1 to 10.0 wt.%. The mixture was stirred for 3 h and the PDDA impregnated adsorbent (PDDA/MS) was then recovered by filtration. The prepared PDDA/MS was washed with 100 ml de-ionized water. The CS and GAC supports were also impregnated with PDDA using the same procedures, however, only 5.0 wt.% PDDA solution was used for the impregnation of these supports (PDDA/CS and PDDA/GAC). The amount of PDDA was then determined using an elemental analyzer (CHNS-932, RECO Co.) and changes in the pore characteristics were determined by N_2 adsorption using a sorptometer (ASAP 2010, Micromeritics Co.). In addition, the zeta potential changes were measured using a zeta-meter (DELSA 440SX, Coulter Co.).

2.3. Batch adsorption experiments

Batch adsorption experiments were conducted by suspending known amounts of adsorbents (typically 0.1 g) in 50 ml of a dye solution at different known concentrations (ranging from 0.05 to 0.20 mmol/L). The contact time varied from 3 h for PDDA/SBA-15 and PDDA/CS to 24 h for PDDA/GAC. After equilibrium was achieved, the concentration of the dye in the remaining solution was determined by UV–vis spectrophotometry (HP 8453, Hewlett Packard Co.), followed by the calculation of the maximum adsorption capacity. All sorption experiments were carried out at room temperature.

3. Results and discussion

3.1. Stability of the impregnated PDDA molecules on mesoporous silica and amount of loading

In order to control the amount of PDDA loading onto the MS, the stability of the impregnated PDDA on the MS was evaluated by measuring the amount of PDDA loading after each washing step during

Table 1
Characteristics of the nine different dyes used in the adsorption study.

Abb.	Dye chemical name	Charges	λ_{\max} (nm) ^a
A1	Rifazol Yellow GR	Negative	415
A2	Rifazol Red BB 150	Negative	417
A3	Rifaxil Yellow 3RN 150H	Negative	417
C1	Rifa Cationic Pink FG	Positive	525
C2	Rifa Cationic Red 4G	Positive	511
C3	Rifa Cationic G/Yellow GL 200L	Positive	438
N1	Rifalon Black BNF 300 (R)	Neutral	573
N2	Rifalon Red E-FBL 200	Neutral	538
N3	Rifalon Blue 2BLN	Neutral	560

^a Wave number of characteristic peak of each dyes on UV–vis spectroscopy.

Table 2
Changes in pore properties of the supports by PDPA impregnation.

Materials	S_{total}^a (m ² /g)	V_{total}^b (cm ³ /g)	D_{ave}^c (nm)	S_{micro}^d (m ² /g)	$S_{\text{meso-macro}}^e$ (m ² /g)	$S_{\text{micro}}/S_{\text{total}}$	$S_{\text{meso-macro}}/S_{\text{total}}$
MS	738	0.78	4.2	127	611	0.173	0.827
CS	305	1.11	14.5	5	301	<0.02	>0.98
GAC	1101	0.52	1.9	1014	87	0.921	0.079
PDPA/MS	420	0.75	7.1	0	420	0	>0.99
PDPA/CS	270	1.01	15.0	0	270	0	>0.99
PDPA/GAC	920	0.43	1.9	845	75	0.917	0.083

^a BET surface area.

^b Total pore volume.

^c Average pore diameter.

^d Micropore surface area.

^e Mesomacro pore surface area.

the PDPA/MS preparation. The amount of PDPA loading was calculated based on the nitrogen contents using elemental analyses. As shown in Fig. 1, the amount of PDPA loading on the MS increased with increase in the PDPA concentration of the aqueous impregnating solution. When the washing processes were conducted, the amount of PDPA loading was decreased to a certain value. It indicates that some of the PDPA molecules were overloaded both in the pore and on the surface of MS, but they were removed during the washing process. However, PDPA molecules, which strongly interacted with surface of the MS, showed sufficient stability during the washing steps. Binding forces between the supports and the PDPA are thought to be electrostatic interactions. It is well known that the silanol groups of the silica surface can attract the positive charges of the polyelectrolyte molecules [20]. The resulting electrostatic interactions between the silica surface and PDPA molecules could then be well established resulting in alternating layers of oppositely charged molecules by the electrostatic self assembly during the PDPA impregnation.

In Fig. 1, 10 wt.% PDPA solution induced the largest amount of PDPA loading on MS support. However, the loading amount of PDPA dramatically decreased after washing step. It indicated that excess PDPA was loaded both in the pore and on the surface of MS by physical interaction. When 5 wt.% PDPA solution was impregnated to MS support, ca. 1.5 mmol PDPA/g loading was obtained after three washing steps (Fig. 1). It is similar value when 10 wt.% PDPA solution loaded on MS support. It indicates that the maximum amount of PDPA loading and good stability between PDPA molecules and silica surface were obtained using 5 wt.% PDPA solution for PDPA/MS adsorbent. Based on these results, we pre-

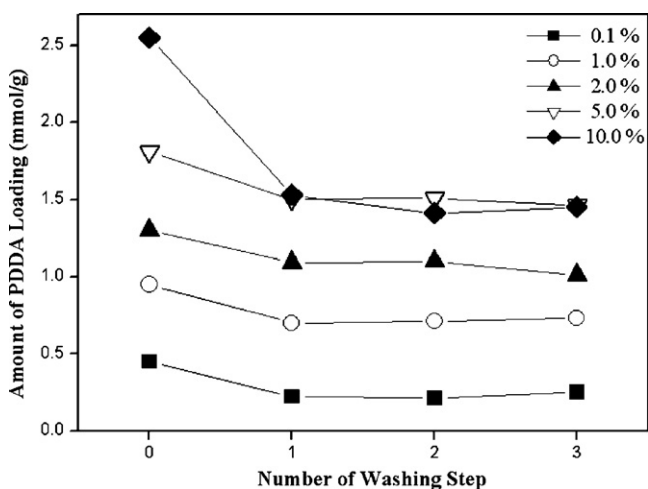


Fig. 1. The amount of PDPA loading on the MS support with different PDPA concentrations in the impregnating solutions and the number of washing steps (Symbols are PDPA concentrations of impregnating solution).

pared the PDPA/MS adsorbent using the 5 wt.% PDPA solution. The prepared PDPA/MS was used for the additional characterization and adsorption experiments. For the purpose of comparison, the PDPA/GAC and PDPA/CS were also prepared using 5 wt.% PDPA solution.

3.2. Pore structures of the PDPA functionalized adsorbents

Fig. 2 shows the N₂ adsorption isotherms of the prepared materials. MS showed typical type IV irreversible box-type isotherms with a H1 hysteresis loop, as defined by IUPAC. It demonstrates the mesoporous characteristics of the prepared materials. However, the GAC showed a sharp uptake of adsorption at a low relative pressure, indicating that it possessed highly microporous characteristics. The CS showed irreversible box-type isotherms with a hysteresis loop at a high relative pressure, indicating the existence of relatively larger pores. The physical properties of the MS, GAC and CS are compared as listed in Table 2. The GAC primarily consisted of micropores with a high S_{micro} value, whereas the MS and CS have high $S_{\text{meso-macro}}$ values. As PDPA was impregnated onto the three samples, the surface area and pore volume decreased, indicating that the PDPA molecules were impregnated in the pore surface of the prepared sample, as shown in Fig. 3.

The pore size distributions of the prepared samples are shown in Fig. 3. GAC and PDPA/GAC are primarily composed of micropores less than 2 nm, whereas CS and PDPA/CS showed larger pore diameters with a broad distribution from 5 to 20 nm (Fig. 3 insert). The MS and PDPA/MS showed narrow pore size distributions centered at ca. 5.4 and 4.8 nm, respectively. In addition, the pore size distribution of the PDPA/MS was slightly decreased, compared to that of

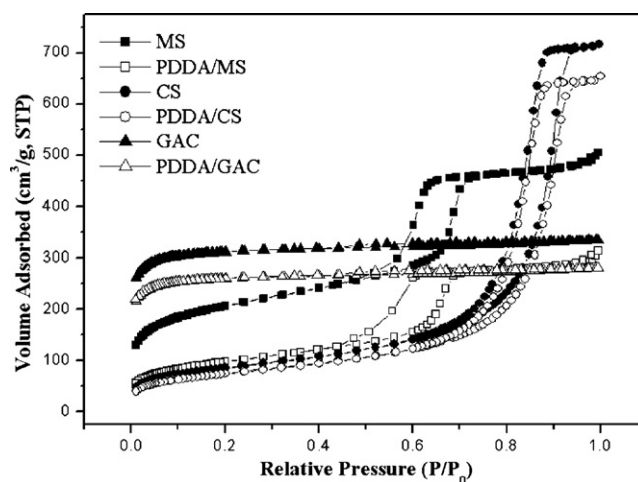


Fig. 2. N₂ adsorption/desorption isotherms of the supports and PDPA impregnated adsorbents.

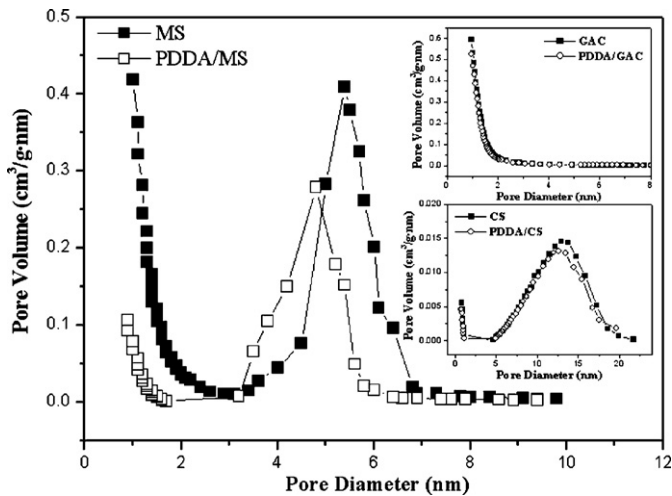


Fig. 3. Pore size distributions of the supports and PDDA impregnated adsorbents.

pure MS. It indicates that PDDA molecules were impregnated into the pores of the MS.

The morphologies of the prepared samples were observed by TEM (Fig. 4). The PDDA/GAC had micropores all over the bulk of carbon surface while the PDDA/CS had relatively large spherical pores. Importantly, the PDDA/MS had the well ordered cylindrical pores with a uniform size. The pore sizes of the prepared samples seen on the TEM images were in good agreement with results of the N₂ adsorption experiment.

3.3. Surface charge conversion by the PDDA functionalization

In order to evaluate the surface charge of the prepared samples, the zeta potentials of the pure MS and PDDA/MS were measured at various pHs. Fig. 5 shows the zeta potential of the CS, PDDA/CS, MS and PDDA/MS in aqueous solutions with different pHs. The CS and MS showed a negative potential which is consistent with the results of previously conducted studies [21]. In addition, the pH value (pH_{IEP}) at the IEP (isoelectric point) of silica materials is known to be around pH 1.5. Therefore, the zeta potential of MS and CS showed negative values under experimental conditions. On the other hand, the PDDA impregnated PDDA/MS and PDDA/CS showed positive zeta potentials under all of the pH conditions due to the presence of amino functional groups of PDDA molecules [22]. Based on these results, it can be concluded that the negative surface of the MS and CS was successfully converted to a positive charge, which indicates that PDDA impregnation could be used as a simple method for the preparation of adsorbents with positive surface charges carrying amino functional groups.

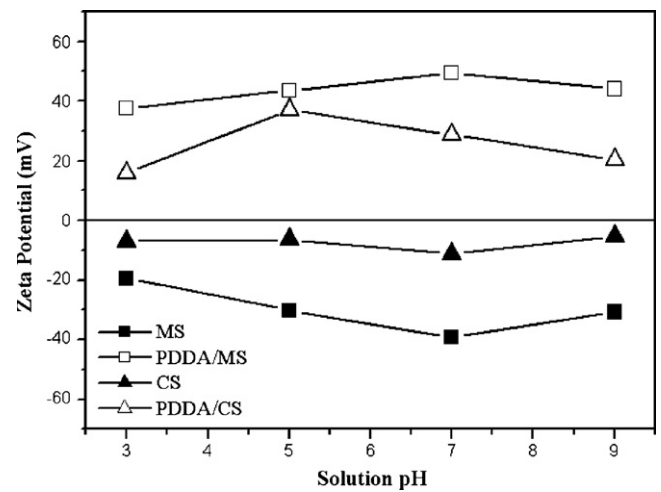


Fig. 5. Zeta potentials of the silica supports and their PDDA impregnated adsorbents.

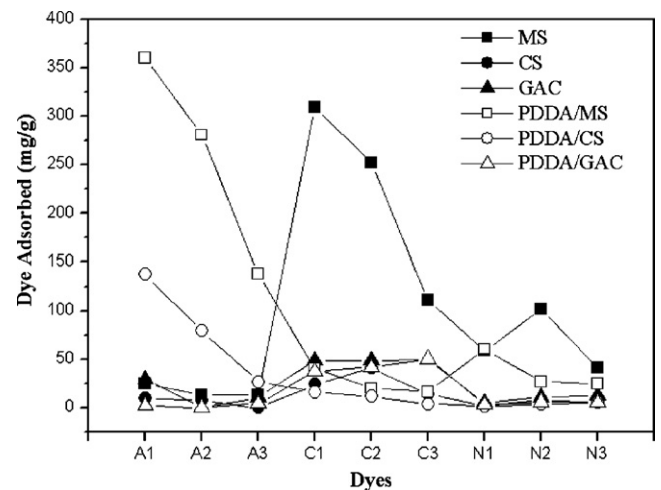


Fig. 6. Adsorption capacities for nine different dyes for the supports and the PDDA impregnated adsorbents.

3.4. Dye adsorption capacities

The batch adsorptions for nine different dyes were examined using the prepared supports and PDDA-functionalized adsorbents (Fig. 6). Among the materials tested, the GAC support showed the lowest adsorption capacities. GAC showed adsorption capacities of approximately 50 mg/g for positive dyes and a maximum adsorption for A1 (29.6 mg/g) among the negative dyes and N3

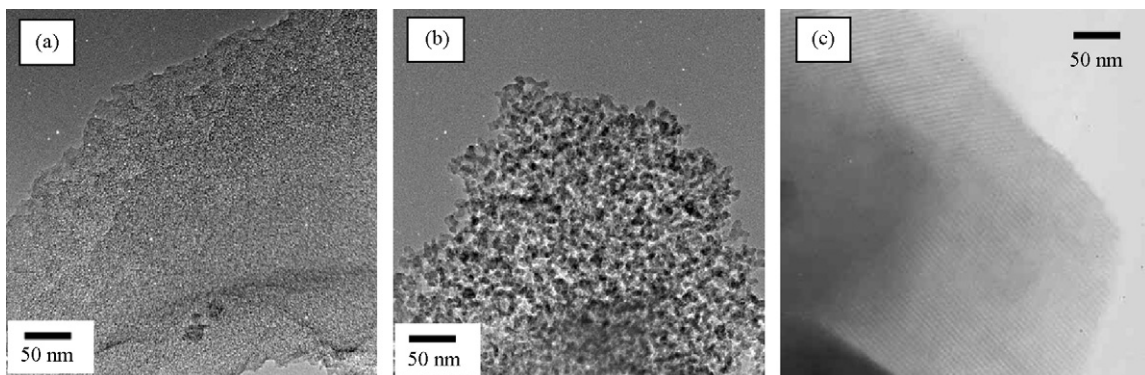


Fig. 4. TEM images of (a) PDDA/GAC, (b) PDDA/CS and (c) PDDA/MS.

(13.0 mg/g) among the neutral dyes. After PDDA functionalization (PDDA/GAC), the adsorption capacities for the positive dyes slightly decreased, and those for negative dyes decreased by approximately 50%, which was greater than the decrease observed for the neutral dyes. The CS support showed high adsorption capacities for C2 (40.8 mg/g), C1 (23.9 mg/g) and C3 (14.1 mg/g), but the capacities for the other six dyes were less than 10 mg/g. However, after PDDA functionalization, the adsorption capacities of the PDDA/CS adsorbents increased in cases of negative dyes, with the maximum increase being observed when A1 was used (137.1 mg/g) and values of 79.5 mg/g and 26.8 mg/g being observed when A2 and A3 were evaluated, respectively. Interestingly, the adsorption capacities for positive dyes were decreased after PDDA functionalization and that of neutral dyes remained essentially unchanged. The MS support showed high adsorption capacities for positive dyes of 309 mg/g for C1, 253 mg/g for C2 and 111 mg/g for C3, whereas the adsorption capacities of the MS for negative and neutral dyes were much lower than for positive dyes, with exception of N2, which had an adsorption capacity of 101.5 mg/g. After PDDA functionalization, the PDDA/MS showed superior adsorption capacities when negative dyes were evaluated. The adsorption capacities of PDDA/MS for negative dyes were greatly enhanced by over 10 times with values of 360 mg/g for A1, 281 mg/g for A2 and 138 mg/g for A3. However, the adsorption capacities for positive dyes decreased. Taken together, the above results show that MS has larger adsorption capacities than either CS or GAC due to its relatively large surface area and pore diameters in the mesopore range. After PDDA functionalization, the PDDA/MS also showed superior adsorption capacities for acidic dyes, when compared to the PDDA/CS and PDDA/GAC.

GAC is primarily composed of micropores, which is disadvantageous for the impregnation of PDDA. Pore blocking could occur due to random nature of micropore with high mass diffusion resistance of the dye molecules during the adsorption. CS has an irregular pore structure and broad pore size distribution and CS has a relatively small surface area when compared to MS, which would not be suitable for dye adsorption due to an insufficient amount of adsorption sites. Irregular pore structure is also known to be disadvantageous for adsorption. However, the MS and PDDA/MS have a well-developed pore structure with uniform and relatively large mesopores. In addition, the high surface area is also beneficial for dye molecule adsorption.

3.5. Adsorption isotherms of PDDA/MS on acid dye adsorption

The adsorption isotherms of PDDA/MS on negative acid dyes were measured and the maximum adsorption capacities for each dye were calculated using the Langmuir adsorption model. The Langmuir adsorption isotherm model assumes monolayer adsorption on the surface of the adsorbent that can be summarized by the following equation [23,24]:

$$\frac{C_e}{q_e} = \frac{1}{Q_{\max}b} + \frac{C_e}{Q_{\max}}$$

where C_e is the amount of dye in solution at equilibrium (mg/L) and q_e is the amount of dye adsorbed at equilibrium (mg/g). Q_{\max} is a constant that reflects the maximum adsorption capacity (mg/g) and b is a direct measure of the intensity of the adsorption process that is related to the heat of adsorption (L/mg).

The adsorption isotherms of PDDA/MS on each negative acid dyes and the parameters calculated from the Langmuir equation are shown in Fig. 7 and Table 3. The adsorption isotherms were well fitted by the Langmuir equation, which indicates that the adsorption occurred as a result of an electrostatic attraction mechanism between the acid dye anions and the positively charged surface of the PDDA/MS adsorbent [22]. Adsorption experiments showed

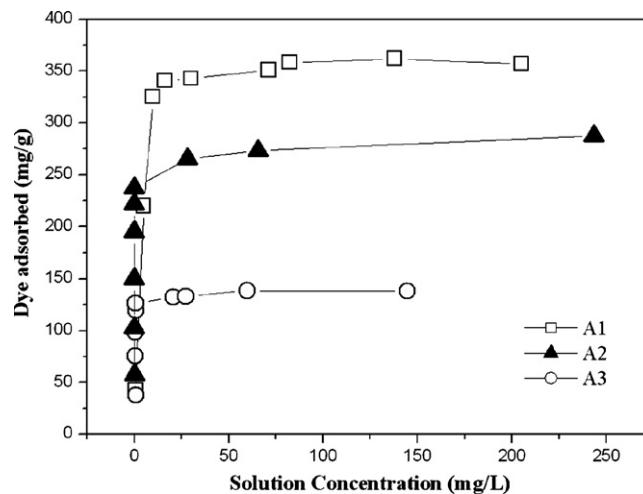


Fig. 7. Adsorption isotherms of PDDA/MS on negative dyes.

that PDDA/MS had the superior adsorption capacity to acid dye compared to others. In addition, PDDA/MS showed the high R^2 values (>0.999) on Langmuir adsorption isotherms to acidic dyes. It indicates that the monolayer adsorption is occurred by electrostatic interaction between PDDA/MS and acidic dye [17,22–24]. However, PDDA/MS has low adsorption capacity to other positively charged and neutrally charged dyes. The adsorption is mainly related to physical interactions between PDDA/MS and positively and neutrally charged dyes. Thus, it is concluded that PDDA/MS have selective adsorption characteristics to acid dye molecules. Practically, PDDA/MS would show selective adsorption behavior in wastewater streams, which contained various dyes.

The experimental results of this study showed that PDDA/MS has a larger adsorption capacity than PDDA/CS or PDDA/GAC, and that this occurred due to its relatively large surface area and pore diameters in the mesopore range. It could be concluded that the pore structures and the superior properties of the MS affect the impregnation of the PDDA which results in high PDDA loading and adsorption performance.

In the practical adsorption process, the relatively large pore, high surface area and selective adsorption sites are more desirable for the adsorption of both bulky and targeted adsorbate molecules. In previous works, novel adsorbents have been synthesized using mesoporous materials and they showed considerable performance in adsorption [25,26]. Especially, functionalized mesoporous adsorbents have showed high performance for selective adsorption to targeted adsorbate, e.g. precious metal or charged molecules [12,13,22].

In this study, PDDA/MS was found to have well-ordered pore structure with large pore diameters and a high surface area. In addition, the surface change of PDDA/MS was converted to a positive charge as a result of PDDA impregnation, which is more favorable for adsorption of negative molecules. Therefore, it can be concluded

Table 3
Langmuir-fit^a parameters and maximum adsorption capacities of PDDA/MS on negative dyes.

Adsorbates	Q_{\max} (mg/g)	b (L/mg)	R^2
A1	364.96	0.392	0.9997
A2	287.36	1.52	0.9998
A3	138.89	2.069	0.9999

^a $\frac{C_e}{q_e} = \frac{1}{Q_{\max}b} + \frac{C_e}{Q_{\max}}$, where C_e is the amount of dye in solution at equilibrium (mg/L) and q_e is the amount of dye adsorbed at equilibrium (mg/g). Q_{\max} is a constant that reflects the maximum adsorption capacity (mg/g) and b is a direct measure of the intensity of the adsorption process.

that PDDA/MS is one of the most suitable adsorbents for the selective acid dye adsorption.

4. Conclusions

Functionalized PDDA/MS was prepared by a simple impregnation of polyelectrolyte on MS, followed by a washing step. The surface charges of the MS were easily converted from a negative to a positive by a simple method. The prepared PDDA/MS showed a well-ordered pore structure with a high surface area. In addition, the PDDA impregnated silica adsorbent could adsorb negatively charged dye because of the electrostatic attractions between the acid dye molecules and the positively charged surface of the adsorbent. Furthermore, the superior pore properties, high surface area and positively converted surface of the PDDA/MS resulted in the highest capacity for selective acid dye adsorption among the adsorbents evaluated in this study.

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