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Regeneration Research of Porous Magnetic Microspheres during Treatment of Wastewater Containing Cationic Dyes

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The application feasibility of porous magnetic microspheres in the removal of cationic dyes from wastewater was investigated. Various desorption solutions were employed for the recovery of cationic dyes from absorbents and regeneration of porous magnetic microspheres. The results showed that 1 M NaCl or 1 M KCl in water/methanol co-solvent had excellent desorption ability for methyl violet. This fact was further demonstrated in the removal cationic gold yellow from its aqueous solution. Overall, this provided a simple methodology for the treatment of wastewater containing cationic dyes and the regeneration of porous magnetic microspheres.

Keywords desorption solution; magnetic separation; porous microspheres; regeneration

INTRODUCTION

Cationic dyes have wide industrial applications such as dyeing of silk, leather, paper, wool, and cotton (1). However, these organic dyes in discharged wastetwater often create a threat to human health and are an environmental problem. Therefore, up to now, various techniques like chemical oxidation (2), biological treatment (3), coagulation (4,5), and adsorption (6–12) were explored for the removal of cationic dyes. Among them, chemical or physical adsorption is generally recognized as a simple and efficient technique. In this regard, ion exchange membranes (6), activated carbon (7), clay (8,9), zeolite (10), and other natural materials (11,12) have been employed for lowering the concentration of cationic dyes in wastewater. However, there are still some problems in the adsorption of cationic dyes by chemical or physical adsorbents, such as the high cost for regeneration (6), low flow rate (7), and difficult separation of absorbent from wastewater (11). Hence, attempts to explore a novel adsorption medium and treatment process for the removal of cationic dyes from wastewater will be valuable.

Recently, our group has successfully employed porous magnetic microspheres (PMMs) with sulfonic groups for the removal of cationic dyes from wastewater. After adsorption or desorption, the magnetic property of the microspheres made separation quite easy and simple. However, regeneration of PMMs needs to be extracted with ethanol for at least two times; furthermore, the adsorption efficiency of PMMs declined slowly with increasing adsorption/desorption cycles. Therefore, in order to use the adsorbents economically and in a feasible manner, it is necessary to find a suitable desorption solution for the effective recovery of cationic dyes from the adsorbents and regenerating PMMs.

In the present manuscript, we attempt to optimize desorption solution by ethanol/water, methanol/water, aqueous salt solution (NaCl, KCl, $CaCl_2$, and $MgCl_2$), and methanol/water co-solvent with salts.

MATERIALS AND METHOD

Materials

Porous magnetic microspheres were prepared in-house with sulfonated poly(divinylbenzene) microspheres. Methyl violet (MV) and cationic gold yellow were purchased from Zhejiang Wanfeng Chemical Co. Ltd., and used without further purification. KCl, NaCl, $CaCl_2$, $MgCl_2$, methanol, and ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd., and used as received. A 5.2 × 5.2 × 2.8 cm Fe-SrBr magnet was used for the magnetic separation.

Batch Adsorption/Desorption Experiments

Batch adsorption/desorption experiments were performed in a 5.0 mL glass bottle. 0.2 g PMMs and 4.0 mL

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MV solution (1.51×10^{-4} mol/L) were added into that bottle. Then the solution was treated ultrasonically for 2 min. After magnetic separation, the MV solution was removed. Another 4.0 mL desorption solution was introduced into the bottle, and was also sonicated for 2 min. The desorption solution was collected by magnetic separation. The above adsorption/desorption process was repeated with varying the desorption solution. MV concentration in desorption solution was tested by a vis-UV spectrophotometer at 585 nm.

Removal of Cationic Gold Yellow Dye from Its Aqueous Solution

In a 5.0 mL glass bottle, 0.106 g PMMs and 4.0 mL cationic gold yellow (GY) solution (9.69×10^{-5} M) were added. After the solution was treated ultrasonically for 5 min., the solution was collected by magnetic separation (A-GY1) for VIS test at 440 nm. Another 4.0 mL desorption solution (1 M KCl in 40 vol% methanol and 60 vol% water) was added into the bottle, and was also sonicated for 5 min. Then the desorption solution was collected by magnetic separation (D-GY1). The above process was repeated for another seven times to investigate the reusability of PMMs and the desorption ability of the desorbent.

Characterization

A UV751GW ultraviolet spectrophotometer was used for testing the concentration of methyl violet in desorption solutions, and cationic gold yellow in separated and desorption solutions.

RESULTS AND DISCUSSION

Batch Adsorption/Desorption Performance

In this study, in order to find a suitable desorbent for the recovery of cationic dyes from PMMs, various desorption solutions such as water/ethanol, water/methanol, aqueous salt solution (NaCl, KCl, $CaCl_2$, $MgCl_2$), and water/methanol co-solvent with salts were tested. The water/alcohol volume ratio, and salt concentration of desorption solutions were given in Table 1.

Note that batch adsorption/desorption experiments were performed according to the manner described in Fig. 1. A different desorption solution was added in Fig. 1e for each cycle to investigate the extraction capacity of various desorption solution. Therefore, incomplete desorption in previous cycles must accumulate more MV than that of 4.0 mL original MV solution, which will lead to over 100% desorption percentage in the following cycle. The batch MV desorption percentages were displayed in Fig. 2.

Obviously, use of water/methanol (Fig. 2a) and water/ethanol (Fig. 2b) for MV desorption was not very effective. 1 M aqueous salt solutions (NaCl, KCl, $CaCl_2$, $MgCl_2$) did not exhibit better desorption efficiency (Fig. 2c) than co-solvent. In comparison with $MgCl_2$, the bi-valent cation Ca^{2+} showed a better desorption ability. Therefore, we

TABLE 1
Concentration or volume ratios of alcohol/water for desorbents[a]

Run (M/W)[b]	MW01	MW02	MW03	MW04	MW05
M/W (v/v)	2/8	4/6	6/4	8/2	10/0
Run (E/W)	EW01	EW02	EW03	EW04	EW05
E/W (v/v)[c]	2/8	4/6	6/4	8/2	10/0
Run (NaCl, 1 M)	MW11	MW12	MW13	MW14	
M/W (v/v)	0/10	2/8	4/6	6/4	
Run (KCl, 1 M)	MW21	MW22	MW23[d]		
M/W (v/v)	0/10	2/8	4/6		
Run (M/W = 4/6)	MW31[e]	MW32	MW33	MW34[d]	
KCl Conc.	0.25 M	0.50 M	0.75 M	1.0 M	
Run (KCl, 0.25 M)	MW41	MW42[e]	MW43	MW44	
M/W (v/v)	0/10	4/6	6/4	8/2	
Run ($CaCl_2$, 1 M)	MW51	MW52	MW53	MW54	
M/W (v/v)	0/10	2/8	4/6	6/4	
Run ($MgCl_2$, 1 M)	MW61				
M/W (v/v)	0/10				

[a] The ratios of methanol/water or ethanol/water are volume ratio.
[b] M: methanol, W: water.
[c] E: ethanol.
[d] MW23 and MW34 are the same eluent.
[e] MW31 and MW42 are the same eluent.

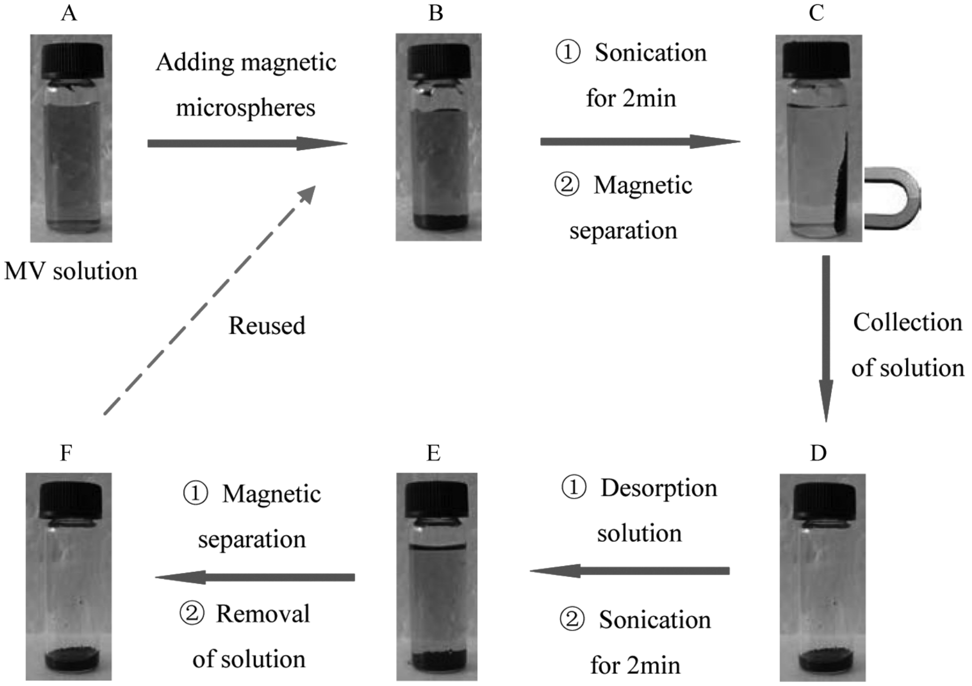

FIG. 1. Schematic illustration of batch adsorption/desorption experiments.

employed 1 M $CaCl_2$ in the water/methanol co-solvent as desorbent for recovery of MV from PMMs (Fig. 2d). Unfortunately, only 60% methanol in co-solvent (MW54) revealed over 80% desorption percentage, which is still insufficient for regeneration of PMMs.

Although the desorption capacity of 1 M $CaCl_2$ aqueous solution was better than that of 1 M NaCl or KCl aqueous solutions (Fig. 2c), under the same conditions, NaCl or KCl in water/methanol co-solvent had higher MV desorption percentages than $CaCl_2$ (Fig. 2e and 2f). For example, 1 M NaCl in 60% methanol (MW14) or 1 M KCl in 40% methanol (MW23) demonstrated their excellent desorption ability, ~140%, and almost complete desorption was achieved under these conditions. This may be related to cation (Ca^{2+}, K^+, Na^+) property such as size and valence, which have a direct effect on the interaction between the cation and the sulfonic group and consequently, on the leaving efficiency of MV. Furthermore, the percentages increased with increasing methanol content in co-solvent (1 M KCl in 60% methanol was not tested due to poor salt solubility). The mechanism of adsorption of cationic dye by PMMs may be based on not only electrostatic attraction, but also hydrophobic interaction, which may be disrupted by organic solvents like methanol (6). As a result a high methanol concentration was favorable of improving MV desorption efficiency from PMMs.

The effect of KCl concentration in 40% methanol on desorption percentages was also investigated (Fig. 2g). Obviously, a decrease of KCl concentration significantly weakened the desorption capacity of desorbents. For instance, the desorption percentage of 0.25 M KCl in 40% methanol was only 40.2% (MW31). However, under this KCl concentration, the desorption ability of desorbents were abruptly increased (MW43 and MW44) after the methanol volume ratio in the co-solvent was increased (Fig. 2h). This fact indicated that desorbents with low salt concentration and high methanol content also had excellent desorption capacity for MV recovery from PMMs.

Generally, acidic or basic NaCl solution was used as the desorption solution for regeneration of ion exchange resins, in which the mechanism of regeneration is ion exchange. However, aqueous salt solution is difficult to regenerate PMMs, indicating that the regeneration mechanism of PMMs is not simple ion exchange. Likewise, it is also hard for methanol (MW05) or ethanol (EW05) to entirely disrupt the electrostatic interaction between cationic dyes and sulfonation groups. However, interestingly, a combination of both inorganic salt and methanol obtained excellent regeneration results. This fact indicates that the PMMs regeneration is a cooperative mechanism of ion exchange and solvent extraction.

Therefore, the excellent desorption solutions for PMMs were 1 M NaCl in 60% methanol (MW14), 1 M KCl in 40% methanol (MW23) and 0.25 M KCl in 80% methanol (MW44). We think these solutions could be used for the regeneration of PMMs.

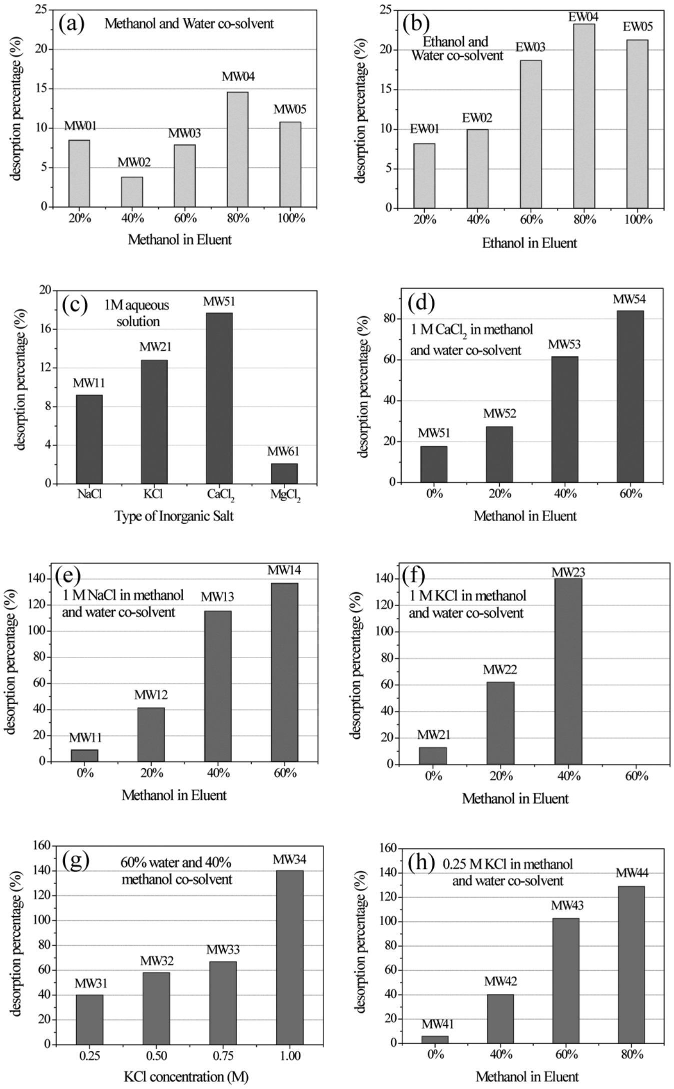

FIG. 2. Desorption efficiency of methyl violet by different desorption solutions. MW23 = MW34, MW31 = MW42.

Reusability of PMMs in Removal of Cationic Gold Yellow

Wastewater containing cationic gold yellow was studied to further demonstrate cationic dye desorption ability of MW23 desorbent (1 M KCl in co-solvent of 40 vol% methanol and 60 vol% water). Here, eight adsorption/desorption cycles were performed to investigate the reusability of PMMs with MW23 as desorption solution. The separated solutions (A-GY1, A-GY2, A-GY3, A-GY4, A-GY5, A-GY6, A-GY7, A-GY8) and the corresponding desorption solutions (D-GY1, D-GY2, D-GY3, D-GY4, D-GY5, D-GY6, D-GY7, D-GY8) were collected, respectively. The adsorption efficiency of PMMs and the desorption efficiency of MW23 desorbent were presented in Fig. 3.

Our previous work indicated that the removal efficiency of cationic dyes declined with increasing the adsorption cycles when anhydrous ethanol was used as desorbent. Here, however, the removal efficiency of cationic gold yellow fluctuated from 90.3% (A-GY4) to 99.9% (A-GY5) rather than progressively falling with more adsorption cycles. Undoubtedly, this was due to excellent desorption ability of MW23. In this connection, the desorption efficiency of MW23 fluctuated from 76% (the 4th cycle) to 137% (the 5th cycle). This fact is easy to understand. Adsorption efficiencies from A-GY1 to A-GY4 exceeded 90%, but the desorption efficiencies from D-GY1, D-GY3, and D-GY4 were about 80%. That is to say, the dyes in PMMs were not completely desorbed in the first four cycles. The dye amount in PMMs had exceeded that of 4.0 mL original solution of cationic gold yellow after the 5th desorption cycle (A-GY5), which resulted in the desorption efficiency of D-GY5 reaching 137% (Fig. 3b). The situation of D-GY8 is similar to that of D-GY5.

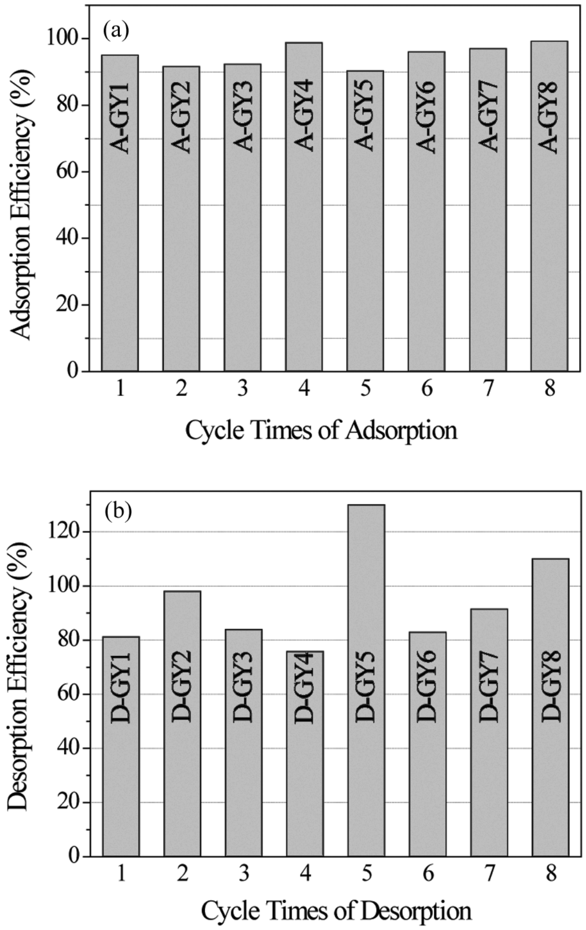

FIG. 3. Adsorption (a) and desorption (b) efficiency of cationic gold yellow for 8 cycles.

Therefore, it seems that several cycles with low desorption efficiency (<100%) was always followed by a cycle with high desorption efficiency (>100%). We think the desorption efficiency was related to high dye content in

PMMs. The former four cycles with low desorption efficiency (78∼98%) accumulated high dye concentration in PMMs, which was favorable for obtaining high desorption efficiency (137%) in the 5th cycle.

CONCLUSION

This study demonstrated that water/methanol, water/ethanol, and aqueous salt solutions were insufficient for the regeneration of PMMs. In the water/methanol co-solvent, addition of NaCl or KCl could significantly improve the desorption ability of desorbents; furthermore, desorption percentages were increased with increasing methanol volume ratio in co-solvent. The optimal desorbent was successfully employed in the recovery of cationic gold yellow dye from PMMs. The removal efficiency of cationic gold yellow fluctuated from 90.3% to 99.9% rather than progressively falling with more adsorption cycles. Overall, this provided a simple methodology for the treatment of wastewater containing cationic dyes and the regeneration of porous magnetic microspheres.

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