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Highly Selective Separation of Dyes by Using Compressed CO₂ and Spherical Polyelectrolyte Brushes

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Spherical polyelectrolyte brushes (SPBs), consisting of a poly(styrene) core and poly(acrylic acid) shell densely grafted from the core surface, were synthesized by photoemulsion polymerization. In this paper, a novel method for highly selective separation methylene blue (MB) and other dyes has been proposed which employed spherical polyelectrolyte brushes as adsorbent while compressed CO₂ as antisolvent. Actually in the whole process, neither polymer brush nor CO₂ alone can separate the dyes. The SPBs and adsorbed dyes can be precipitated simultaneously from organic solutions by the easy control of CO₂ pressure. The effects of several parameters such as CO₂ pressures, initial dye concentration and temperature on the removal of MB by PS-PAA have been determined. MB could be adsorbed selectively by PS-PAA with high efficiency from the mixed dyes solution and it indicated that the binding of MB onto PS-PAA was probably dominated by electrostatic interaction. Due to the Donnan effect of polymer brush, the adsorbed dyes can be easily eluted by NaCl aqueous solution through ion exchange to obtain the regeneration of polymer brush. And the recovered PS-PAA still kept high adsorption capacity even after five times of regeneration. It provides a simple and effective way for separation ionic materials which could be applied in environmental engineering.

1 Introduction

Organic dyes have been widely used in many industries including textile, paper, leather, food, and other industries.¹⁻² Their direct discharge can cause serious water pollution, such as reducing light penetration and visibility and increasing the chemical oxygen demand.³⁻⁴ Even worse, because of their potential mutagenic and carcinogenic effects, their release into the environment cause seriously health problems.⁵ Therefore, it is vital importance to the remove dyes from solution.

Various techniques, such as adsorption, biological treatment, ion exchange, chemical oxidation, photodegradation, and membrane separation, have been proposed to treat organic dye wastes.⁶⁻⁷ Adsorption is considered as one of the best technique, due to its high efficiency and low-cost. And a host of adsorbents including activated carbon, zeolite, magnetic nanoparticles, and waste from agriculture have been utilized

to remove dyes from solution.⁸⁻¹⁰ However, these adsorbents usually suffer from the low adsorption rate¹¹ or poor selectivity towards targeted dyes¹². Therefore, it is necessary to develop a novel adsorption material which has highly adsorption capacity and could remove targeted dyes selectively.

Spherical polyelectrolyte brushes (SPBs) are latex particles, consisting a lay of shell which densely grafted on the core, first reported by Guo et al.¹³ Due to the Donnan effect, SPBs could carry large numbers of charges and they have been widely used for immobilize nanoparticles, nano-reactors, proteins adsorption and separation.¹⁴⁻¹⁶ So it could be a good candidate as adsorbent for selective separation of dyes. However, SPBs have not received enough attention as other potential organic dye adsorbents have because it is quite hard to remove the SPBs from solution.

It is known that carbon dioxide, CO₂, can precipitate the solutes in the organic solution¹⁷⁻¹⁸, which is called gas antisolvent effect. And that has been widely used in many processes, such as extraction, fractionation¹⁹, recrystallization of chemicals²⁰ and micronization²¹. Our group previously found that SPBs can be separated from solution perfectly by the easy control of CO₂ pressure and a novel and environmentally harmless method to recover SPBs by using compressed CO₂ as antisolvent have been developed.²² Therefore, in this contribution, it is possible to utilize SPBs as adsorbent and

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Electronic Supplementary Information (ESI) available: (1) synthesis process of PS-PAA, (2) the size and distribution of PS core, PS-PAA and PS-PAA@MB, (3) the volume expansion coefficient of pure ethanol, PS-PAA and PS-PAA @MB solution in CO₂ at different pressures and temperatures, (4) chemical structures of dyes. See DOI: 10.1039/x0xx00000x

compressed CO₂ as antisolvent to separate dye wastes from organic solution.

In this work, an anionic SPBs, polystyrene-poly acrylic acid (PS-PAA) brushes, were synthesized by photoemulsion polymerization. Electrostatic interaction between PS-PAA and cationic dye, methylene blue (MB), was the main promotion of highly selective adsorption process. The common way to recover SPBs is that put the solution into the high speed centrifugal machine for more than 1 hour which is obvious time and energy consuming process.¹⁶ Thanks to compressed CO₂, we can solve this problem easily. However, without SPBs, the compressed CO₂ can't precipitate the dyes in our experimental pressure range, not to mention selectivity. In other words, the mixture of dyes and SPBs can be precipitated from the solution assisted by the compressed CO₂. To the best of our knowledge, it is the first report of removing organic dyes in a highly selective adsorption process employed SPBs and compressed CO₂ and it could be applied in environmental engineering in near future.

2. Experimental section

2.1 Materials

Sodium dodecyl sulfate (SDS) and potassium persulfate (KPS) were bought from Aladdin Chemical Company and used without further purification. Methylene blue (MB), methyl red (MR), and sudan III (SD) were bought from J&K Scientific Ltd. The other reagents were all purchased from Sinopharm Chemical Reagent Co., Ltd, unless otherwise specified. Acetone was distilled before use. Styrene and acrylic acid (AA) were distilled under reduced pressure to remove the inhibitor and stored in refrigerator at 4 °C before use. CO₂ (99.9%, purity) was purchased from Shanghai Hukang Industrial Gases Co., Ltd.

2.2 Synthesis of spherical polyelectrolyte brushes

Anionic spherical polyelectrolyte brushes, polystyrene-poly acrylic acid (PS-PAA) brushes, were synthesized by photoemulsion polymerization, which has been described in detail previously¹³. Firstly, polystyrene (PS) particles (~98 nm in diameter) were synthesized by conventional emulsion polymerization using SDS as surfactant and KPS as initiator. Secondly, photoinitiator 2-[p-(2-hydroxy-2-methylpropionophenone)] ethylene glycol methacrylate (HMEM) prepared by Schotten-Baumann reaction was covered on the surface of PS with a very thin layer. Finally, diluted PS core solution (1 wt.-%) was mixed with defined amount of functional monomer acrylic acid (50 mol-% with regard to the amount of styrene) under stirring. Photo-emulsion polymerization was done by use of UV irradiation at room temperature for 120 min. The synthesis process of PS-PAA was shown in Scheme S1. The diameter of the PS core and PS-PAA brush were monitored by dynamic light scattering (DLS) as shown in Fig. S1. It has been demonstrated that PAA chains were graft onto PS core.

2.3 Phase behavior of PS-PAA-MB-ethanol (PS-PAA@MB) system in CO₂

The apparatus for determining the volume expansion coefficient and cloud point pressure was almost the same as that used previously.²³ It mainly consisted of a view cell (volume is 45cm³), a constant-temperature water bath, a high-pressure pump and a pressure gauge. The volume expansion coefficients of PS-PAA solution or PS-PAA@MB solution were obtained by typical experiment as following: a bath of 2mL of PS-PAA ethanol solution and PS-PAA@MB ethanol solution (the mixed concentration of PS-PAA and MB were 200mg/L and 3.75mg/L, respectively) were prepared and charged into the high pressure view cell. The optical cell was heated using a water bath and the temperature was controlled by a temperature controller (Beijing Chichenghuaxing Science and Technology Co., Ltd) with an accuracy of ±0.05 °C. After the desired temperature was reached, the air in the cell was repetitively replaced with CO₂ and then CO₂ was charged into the cell by a high-pressure syringe pump (DB-80). A magnetic stirrer was used to help the mixing of CO₂ and the solution while the pressure remained constant with time which indicating that the equilibrium of the system was reached. The pressure was measured by a pressure transducer (CH6/D-FPTB1, Contronix), which was accurate to ±0.01MPa in the pressure range of 0–25 MPa. The solution became cloudy if the pressure reached a certain value and it keeps cloudy even after 30 mins standing. It was defined as the cloud point pressure (P_c) which means P_c is the pressure at which the aggregation of PS-PAA @dyes beginning to precipitate from the solution. Phase behaviour of (PS-PAA)-MB-ethanol-CO₂ system provides useful information for the later UV experiments.

2.4 High-pressure UV spectrophotometer

A UV-vis spectrophotometer was used to examine the separation efficiency of the dyes. To study the effect of CO₂ and PS-PAA on the removal of MB, the UV high pressure sample cell was flushed with CO₂ to remove the air, and desired amounts of MB or PS-PAA@MB ethanol solution, with a certain concentration (the concentration of PS-PAA and MB were 200mg/L and 3.75mg/L) and stirred for 60 minutes, were injected into the sample cell respectively at 15 °C. CO₂ was recorded every 10 minutes until it has no change occurred, which was an indication that equilibrium had been reached.

In the study of the separation efficiency of the system, PS-PAA@MB was prepared by stirring for 1 h with the solution of PS-PAA and MB which concentration were 200 mg/L and 3.75 mg/L respectively. The following steps were the same as mentioned before except for changing various temperatures and pressures. And the maximum separation pressures (P_{max}) were determined by the study of phase separation high pressure view cell. To study the effect of temperatures on this process, the temperatures were changed from 5 to 55 °C on the adsorption process with the pressures at P_{max}. The other conditions were the same as the separation of dyes from solution which mentioned above.

2.5 Selectively adsorption and precipitation experiments

The selectivity of absorbed dyes by polymer brush was also investigated. The MB/MR, MB/SD mixed solution were prepared and the initial concentrations of the MB, MR and SD in the mixture solutions were 3.75 mg/L, 3.50mg/L and 2.76mg/L respectively. A certain amount of PS-PAA (200 mg/L) was added in the mixed dyes solutions and stirred at 15 °C for 1 h. Then, a certain amount of them were injected into the UV high pressure sample cell at 15 °C and CO₂ was charged into the cell by a high-pressure syringe pump to reach 4.75MPa. After the equilibrium had been reached, UV spectrum of the solution was recorded every 10 minutes until it has no change occurred, which was an indication that equilibrium had been reached. The colour change of the mixed solution before and after treated by PS-PAA and CO₂ was recorded by digital images.

2.6 Regeneration of the PS-PAA

After MB was separated by PS-PAA and CO₂ as previous mentioned, the PS-PAA@MB sediment was collected and redissolved in water again. And certain amount of NaCl was added into the system slowly and then polymer brush was precipitated gradually from the solution after the concentration of NaCl reached 1M/L. After stirred for 2 h, the PS-PAA solution was stand a while and filtered out and dried in freeze vacuum. The ratio of recovered PS-PAA weight and original one was defined as recovery percent of PS-PAA.

The adsorption capacity of the recovered PS-PAA for MB was then determined again by the study of UV high pressure measurement at 15 °C and 4.75 MPa. Firstly, certain amount of recovered PS-PAA redissolved into ethanol solution to get the concentration about 200 mg/L. And, MB was added into the solution with concentration as 3.75 mg/L. Then the mixed solutions was charged into the high pressure UV cell and please see the experimental details as previous statement of 2.4. The colour change of the regeneration process was recorded by digital images. The regeneration cycle was repeated five times.

2.7 Characterization

The size and distribution of PS-PAA was determined by dynamic light scattering (DLS) (NICOMP 380 ZLS) at a fixed scattering angle of 90°. The results of the size and distribution of PS core, PS-PAA and PS-PAA@MB are shown in Fig. S1. The UV-vis spectra were performed by a UV spectrometer (UV-2550, Shimadzu, Japan, the resolution is 0.5 nm)

3. Results and discussion

3.1 Phase behaviour of the PS-PAA@MB-ethanol system in the presence of CO₂



Fig. 1 Photographs of the PS-PAA@MB-ethanol system with CO₂ at (a) 0 MPa, (b) 3.20 MPa, (c) 4.75 MPa. Condition: PS-PAA concentration: 200mg/L; initial MB concentration: 3.75mg/L; temperature: 15 °C; stirring time: 1 h.

In this work, PS-PAA brushes were selected as the absorbent to precipitate MB in ethanol solution. The PS-PAA brushes were synthesized by photoemulsion polymerization which has been described in the previous paper.¹³ The diameter of the PS core and PS-PAA brush were ~98 nm and ~278 nm respectively, which were monitored by DLS as shown in Fig. S1. Fig. 1 illustrates the phase behaviour of PS-PAA@MB-ethanol system at 15 °C under different CO₂ pressures. In the absence of CO₂, the PS-PAA@MB-ethanol system was transparent and blue, and it was a thermodynamically stable solution which shown in Fig 1a. After a certain amount of CO₂ was charged into the solution, the clear solution became cloudy under stirring and MB which embedded by PS-PAA began to aggregate from the solution, just as shown in Fig. 1b. It's well known that compressed CO₂ is quite soluble in various organic solvents, but many solutes are not soluble in CO₂. Thus the CO₂ in organic solvents can act as a gas antisolvent (GAS) to recover solutes from solution.^{22,24,25} PS-PAA could be removed from the solution started at P_c and the quantity of precipitation increases sharply with the increasing of pressure as shown in Fig 1c. In other words, thanks to compressed CO₂, MB absorbed in PS-PAA and the aggregation of PS-PAA@MB precipitated from ethanol solution together.

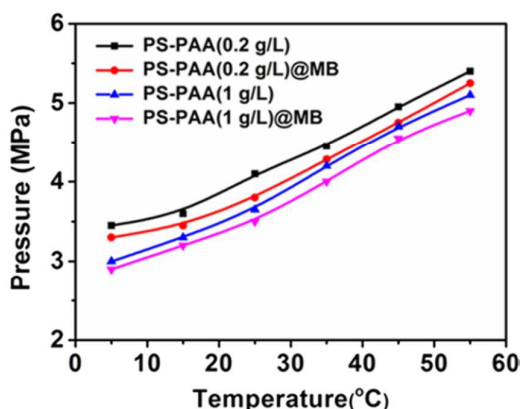


Fig. 2 Cloud pressure of solutions with different concentrations at different temperatures. Condition: PS-PAA concentration were 1000mg/L and 200mg/L; MB concentration: 3.75mg/L; stirring time: 1 h.

The ethanol solution can be expanded by the dissolved CO_2 obviously.²⁶ The volume expansion coefficient is a very important parameter for the separation process. In this work, we define the volume expansion coefficient (ΔV) as:

$$\Delta V = (V - V_0) / V_0 \quad (1)$$

in which V_0 is the CO_2 -free solution and V is the CO_2 -charged solution at different pressure. The volume expansion coefficient of pure ethanol, PS-PAA and PS-PAA @MB solution in CO_2 at different pressures and temperatures were shown in Fig. S2. It can be concluded that the PS-PAA and MB have a negligible effect on the ΔV due to the low concentration which agreed with other works.²⁷ However, the volume expansion coefficient data provide useful information for the UV study.

The solution turn to cloudy if the CO_2 pressure reached to P_c , which indicated the dyes absorbed on PS-PAA and the composite was unstable and then began to precipitate. This pressure was defined as the cloud point pressure (P_c). Fig. 2 shows the P_c of PS-PAA and PS-PAA@MB solution with different concentration under the temperatures from 5 to 55 °C. As expected, P_c increases with the increasing of temperature, which main reason was the larger solubility of CO_2 in the solution at lower temperatures.²⁸

Fig.2 indicates that P_c of the system decreases with the increasing of solid content under same temperature which agreed with other researchers' work.²⁹ Compare the different of P_c of PS-PAA and PS-PAA@MB solution, P_c decreased with the addition of MB under same temperature and concentration. For example, at 35 °C, the P_c of PS-PAA and PS-PAA@MB solution (PS-PAA was 1000mg/L) were 4.20MPa and 4.02MPa, respectively. With the addition of MB, a portion of charges on PAA chains was neutralized by cationic dye and that decreased the thickness of electrical double layer on PS-PAA. It was confirmed by the characterization of DLS that addition of MB shrank the PAA chains from ~90 nm to ~77 nm which was shown in Fig. S1. The shrinkage of PAA chains lead to the larger instability of the composite and then lower CO_2 pressure could induce the phase separation later. It was confirmed by the UV study below.

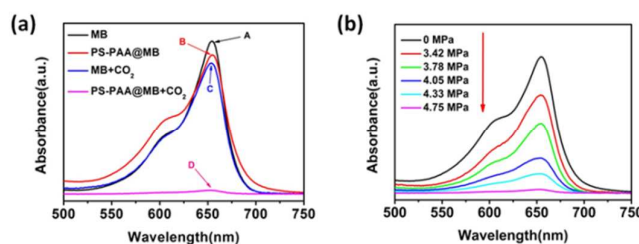


Fig. 3 (a) UV-vis absorption spectra of: A) pure MB in ethanol; B) PS-PAA@MB in ethanol; C) pure MB in ethanol solution under the compressed CO_2 , $P=4.75\text{MPa}$; D) PS-PAA@MB in ethanol under the compressed CO_2 , $P=4.75\text{MPa}$ (b) UV-vis absorption spectra of MB- CO_2 -(PS-PAA)-ethanol quaternary system solution under different CO_2 pressures. Condition: PS-PAA concentration: 200mg/L; initial MB concentration: 3.75mg/L; stirring time: 1h; temperature: 15 °C.

In the concentration range from 10^{-5} to 10^{-3}M , the extent of aggregation of MB is limited to dimerization, which results in absorbances in the visible region at 660 and 610 nm for the respective monomeric and dimeric species³⁰ as A line in Fig.3a shown. In our experimental range, from 500 to 750nm, PS-PAA in ethanol solution doesn't have any absorbance. Adding PS-PAA into the MB solution, the absorbance of 660 nm turned to lower while the 610 nm turned to higher as shown in B line. Due to the Donnan effect, PS-PAA brush can absorb a large number of opposite charge ions, make internal counter ion concentration significantly higher than that of the external environment.³¹ In other words, anionic PS-PAA could absorb a large amount of cationic MB which induced the local concentration of MB around PS-PAA turned to higher than that of the external environment or liquid phase. Furthermore, B line agreed with other's work that with an increasing concentration of MB, the intensity of the dimer band increases at the expense of the monomer band with a clear isobestic point at around 610 nm indicating the presence of an equilibrium between the monomer and the dimer species of MB in the solution.³² C line indicated that MB couldn't be precipitated without adding of PS-PAA even under the 4.75 MPa of CO_2 . D line in Fig. 3a indicates that the MB can be separated from solution because of antisolvent effect of CO_2 which could regulate the solvent properties. In other words, neither PS-PAA nor CO_2 alone can succeed in the sedimentation of dyes and the main motivation of the absorbance process was electrostatic interaction between MB and PS-PAA. The absorbance profiles of MB in the CO_2 -(PS-PAA)-ethanol quaternary system solution with different pressure were illustrated in Figure 3b. From up to down, the absorbance of MB decreased with increasing of pressure which indicates the pressure of CO_2 could be employed as a switch for the precipitation of dyes.

3.2 Separation of MB from solution

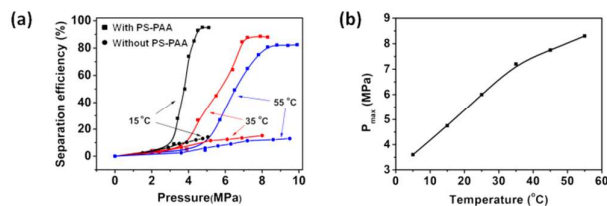


Fig. 4 (a) Separation efficiency of MB from solutions with CO_2 or CO_2 and PS-PAA at different pressures and temperatures. (b) Maximum separation pressures of PS-PAA@MB solution at different temperatures. Condition: PS-PAA concentration: 200mg/L; initial MB concentration: 3.75mg/L; stirring time: 1h.

The mixture of MB and PS-PAA solubilized in ethanol can form a thermodynamically stable solution in the absence of CO_2 . However, they can be precipitated simultaneously by the dissolution of desirable amount of CO_2 in ethanol. The separation efficiency of MB was obtained by the monomer band of MB in 660 nm. Fig. 4a illustrated that the separation efficiency of the PS-PAA@MB solution under different pressures and temperatures with/without PS-PAA. From Fig. 4a, we know that about 95.2% of MB can be separated from organic solution at 15 °C, which indicated PS-PAA could absorb MB firstly and the composite could be separated from the solution by using CO_2 as antisolvent and the maximum separation efficiency could be up to 95.2%. Fig. 4a also shown that separation efficiency of MB would not increase any more with increasing pressure if it reached certain value and which was defined as the maximum separation pressure (P_{max}). For example, 88% of MB can be separated from ethanol at 7.20 MPa and 35 °C. But when the pressure reached 8.23 MPa, separation efficiency did not increase significantly. The P_{max} is higher than P_c and it was determined by the same process. It implied that the adding of PS-PAA is very necessary for precipitation process of dyes although pure compress CO_2 has a little GAS effect on the dyes in our experimental range. Fig.4b indicated that the P_{max} increased with increasing of temperature and the reason is the solubility of CO_2 decreased with increasing of temperature.

3.3 Effects of temperatures

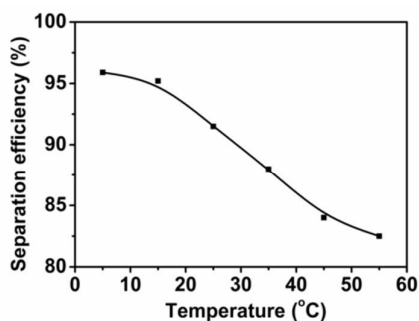


Fig. 5 Dependence of separation efficiency of MB on temperatures. Condition: PS-PAA concentration: 200mg/L; initial MB concentration: 3.75mg/L; stirring time: 1h; pressure: P_{max} respectively.

The maximum separation efficiency of MB under different temperatures, with the concentration of PS-PAA (200 mg/L) and MB (3.75 mg/L) could be a constant even increasing of pressure. How about the situation of temperatures on the separation process? Fig. 5 implied that separation efficiency increases with the decreasing of temperature by the UV spectrum of 660 nm. Take for examples, about 82.5% of MB can be separated from solution at 55 °C. And the separation efficiency increase to 95.9% with the temperature decreasing to 5 °C. Although the molecular chains of PS-PAA don't be sensitive to the temperatures, but there is a fact that the mobility of dye molecules increased with increasing of temperatures.³³ Although there was electrostatic interaction between PS-PAA and cationic dye which banded these together, the mobility of dye increased by rising temperature enough to overcome it and induced the MB molecules escaping from the chains of brush and re-entering into the liquid phase. It is easily to understand that separation efficiency of dyes decreased with increasing of temperature and the unadsorbed MB still stayed in the solution.

3.4 Effects of initial MB concentrations

Fig. 6 displays the effects of different initial MB concentration on the adsorption capacities and separation efficiency. The concentration effect was studied by varying the MB concentrations from 3.75 mg/L to 80 mg/L in the presence of PS-PAA (200mg/L) for 1h at 15 °C and determined by the UV spectrum of 660 nm. It can be easily observed that the adsorption capacity of MB onto PS-PAA increased with the increasing of initial MB concentration while the separation efficiency just the opposite. In other words, initial MB concentration is highly important factor for the adsorption process. In consideration of adsorption capacities and separation efficiency, 50mg/L is chosen as the standard concentration of MB in the following experiments without special indication. As shown in Table 1, the equilibrium adsorption capacity of PS-PAA at concentration of 50 mg/L can reached up to 134.89 mg/g, which is obviously larger than that of most of the adsorbents. It means that's a simple and effective way for separation of dyes.

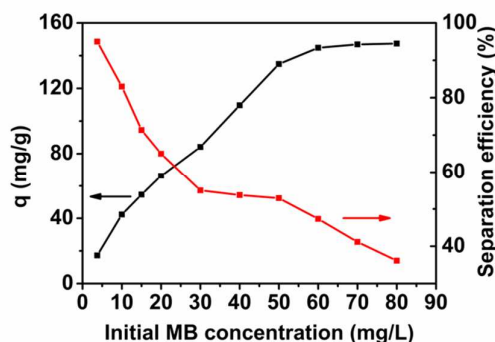


Fig. 6 Effects of initial MB concentration on the adsorption capacity of PS-PAA and the effects of initial MB concentration on the separation efficiency. Condition: PS-PAA concentration: 200mg/L; temperature: 15 °C; pressure: 4.75 ± 0.02 MPa; stirring time: 1 h.

Table 1 The adsorption capacities for MB on different adsorbents in literature

Adsorbents	q (mg/g)	References
Jute fiber carbon	45	[34]
Polydopamine microspheres	90.7	[35]
Poly(cyclotriphosphazene-co-4,4'-sulfonyldiphenol) nanotubes	69.16	[36]
Zeolite	10.86	[9]
Posidonia oceanica (L.) fibres	4.5	[37]
Sewage sludge based granular activated carbon	28	[38]
Spherical polyelectrolyte brushes	134.89	this work

3.5 High selectivity of MB from mixed dyes by PS-PAA

Furthermore, PS-PAA was utilized as adsorbent to selectively separate MB from mixture dyes solution because there has some molecular interaction between them as DLS and UV measurement announced. MB, a cationic dye which has bright blue colour as Fig. 7b1 shown, has two original absorbance in 610 and 660 nm, respectively. MR is an anionic orange dye and has one original absorbance in 495 nm as line 2, Fig. 7a shown. When MB and MR mixed together, there were three absorbent peaks as 495, 610 and 660nm and the solution turn to green colour as Fig. 7b3 shown. After PS-PAA was input as adsorbent to selectively absorb MB and CO₂ was charged into the system as antisolvent to precipitate the polymer@dye aggregation, the mixture solution expanded and the blue precipitation appeared at the bottom of the cell. UV results agreed with the phase behaviour as the absorbance at 610 and 660 nm of MB disappeared and only 495 nm of MR left in the solution as Fig. 7a4 shown. It means that most of the MB in solution was absorbed by PS-PAA due to large numbers of counter ions located on the chain of PS-PAA, and precipitated with PS-PAA under the suitable CO₂ pressure. In other words, PS-PAA selectively separated MB from mixture dyes solution assisted by the compressed CO₂. A neutral dye, sudan II (SD), replaced MR in the experiment and got the same results as shown in the Fig.7c and Fig.7d. All the chemical structures of dyes we used were presented in Fig. S3. On the other hand, the above result further confirmed that the interaction between PS-PAA and MB is dominated by electrostatic interactions.

The possible adsorption mechanism and separation process were schematically illustrated in Scheme 1. In the mixed dyes solution, with the addition of anionic SPBs of PS-PAA, only MB could be captured by PS-PAA due to the Donnan effect and electrostatic interaction. Thanks to the compressed CO₂, which could appropriate regulate the properties of the mixed solvent, the aggregation of PS-PAA@MB could be precipitated under the suitable pressure. Meanwhile, the other anionic dyes (MR) or electrically neutral dyes (SD) still keep in the solution and the highly selective separation of dyes could be figured out perfectly.

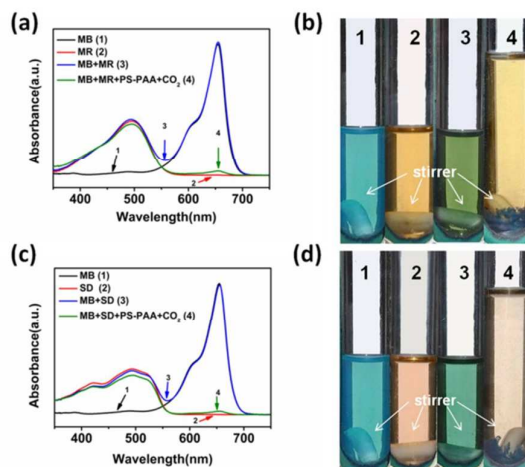
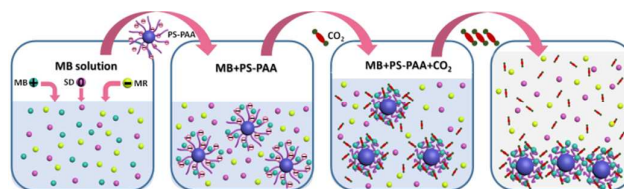


Fig. 7 UV-vis absorption spectra (a) and phase behaviour (b) of the MB and MR solution system, original MB in ethanol (1), original MR in ethanol (2), mixture of MB and MR solution (3), mixed solution after treated with PS-PAA and CO₂ at 4.75 MPa; UV-vis absorption spectra (c) and phase behaviour (d) of the MB and SD solution system, original MB in ethanol (1), original SD in ethanol (2), mixture of MB and SD solution (3), mixed solution after treated with PS-PAA and CO₂ at 4.75 MPa; Condition: initial MB, MR and SD concentration are 3.74 mg/L, 2.69 mg/L and 2.76 mg/L, respectively; PS-PAA concentration: 200mg/L, temperature: 15 °C; stirring time: 1h.



Scheme 1 The mechanism of PS-PAA selectively adsorb MB and separation together assisted by compressed CO₂.

3.6 Regeneration of the PS-PAA

It was reported that MB could be absorbed by yellow passion-fruit waste through an electrostatic attraction of negatively charged biosorbent and the complete regeneration of the loaded biosorbent took place using KCl after about 1.0 h of contact time.³⁹ Polymer brush could be used as nano-reactor for negative ions and could be employed for ions exchange process.^{40,41} Thanks to this special properties, we could finish the regeneration process of polymer brush and it was shown in Fig.8. After precipitation of PS-PAA@MB by the compressed CO₂, PS-PAA@MB was removed by the quench process²² which could prevent the loss of aggregation after depressurization and then redissolved in water and got the transparent blue solution as Fig. 8(a1) shown. Then the certain amount of NaCl was added into the PS-PAA@MB aqueous solution to increasing the ionic strength until it decreasing the Debye length enough that electrostatic interaction plays no role anymore. Such a "salted brush" was predicted to resemble the well-studied uncharged systems.⁴² In the process, MB was released from the surface of PS-PAA gradually. With increasing amount of NaCl, MB was escaped from PS-PAA completely and PS-PAA aggregated and precipitated gradually from the solution. In other words, phase separation happened and MB

dissolved in the solution and polymer brush precipitated in the bottom as Fig. 8(a2) shown. After that, PS-PAA was filtered out and dried in vacuum freeze drier and it was the whole regeneration process of polymer brush. The PS-PAA precipitation was obtained and resolved in the ethanol again to get the solution as Fig. 8(a3) shown. Then MB was added and CO₂ was charged into the system to circle again and again. Scheme 2 indicated the regeneration process of polymer brush.

UV-vis spectrophotometer also confirmed that the MB was completely removed from the brush after adding of NaCl as shown in Fig. 8b. It can be seen that absorption spectra of the recovery of MB was almost the same as the initial MB solution. Although the absorbance of 660 nm turned to lower and the 610 nm turned to higher in the absorption spectra of the recovery of MB, it is mainly due to the self-association of MB forming dimers or higher order aggregates in aqueous salt solutions.⁴³ In other words, MB could be removed from the surface of PS-PAA completely assisted by salt solutions and the recovered PS-PAA was very clean as line 3, Fig.8b shown.

In this way, thanks to NaCl, MB could be reloaded from PS-PAA completely and PS-PAA can be regenerated easily with high efficiency. Even after 5 cycles, the recovery percent of polymer brush was 95.1% and the separation efficiency of recovered PS-PAA for MB was above 91.2% as shown in Fig. 8 c. In all, PS-PAA shows a great potential application as a highly-efficiency and selective adsorbent for the removal of organic dyes from organic solution assisted by the compressed CO₂.

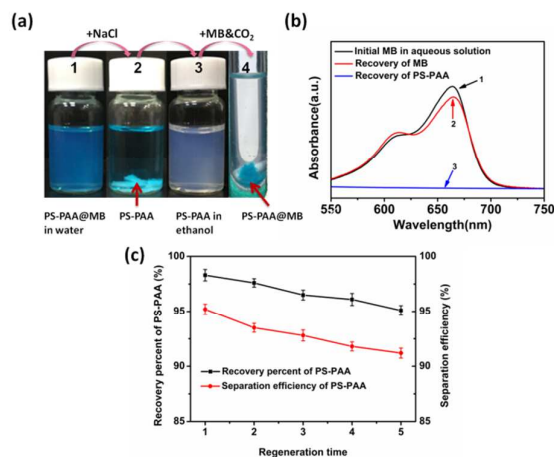
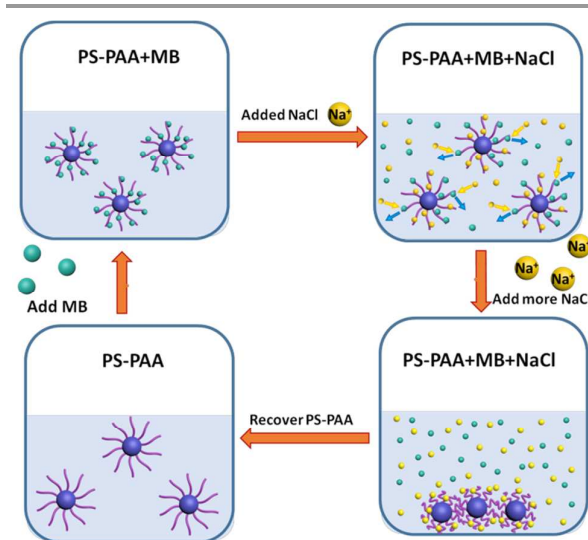


Fig. 8 (a) Digital images of the regeneration process of PS-PAA; (b) UV-vis absorption spectra of initial MB, the recovery of MB and PS-PAA in aqueous solution; (c) recovery percent of PS-PAA and separation efficiency of the regenerated PS-PAA.



Scheme. 2 Regeneration process of PS-PAA.

4 Conclusions

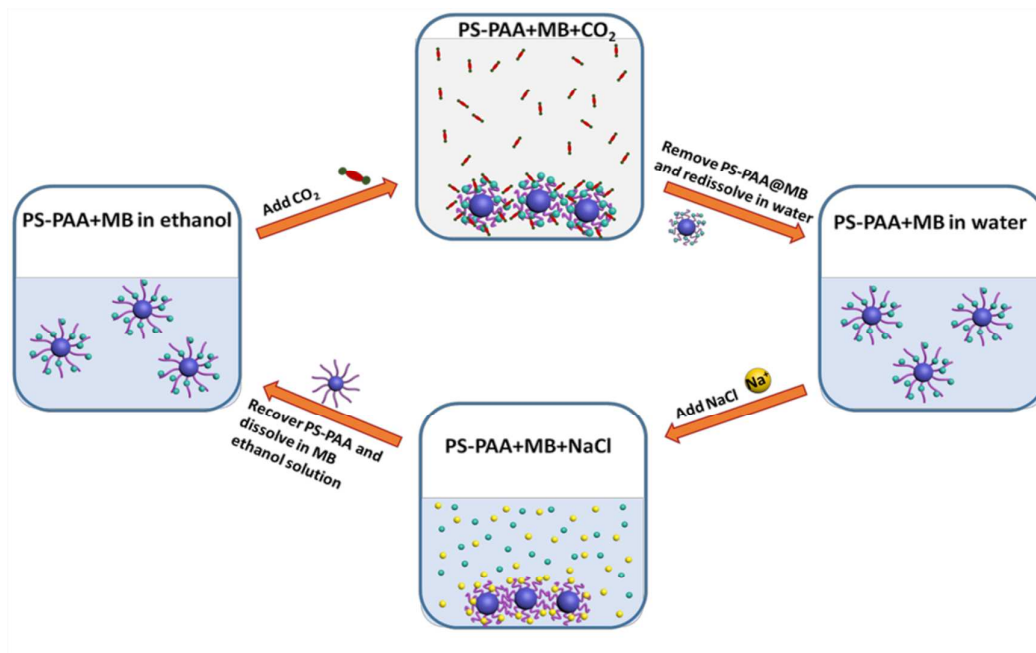
In this paper, anionic PS-PAA have been successfully prepared by photoemulsion polymerization and worked as a high-efficiency adsorbent for the separation of dyes from organic solution with the help of CO₂. The adsorption capacity at equilibrium could reach to 134.89 mg/g which is much higher than most of the conventional adsorbents. The result also showed that the adsorption behaviour of MB onto PS-PAA was highly dependent on CO₂ pressure, temperature and initial concentration. The separation efficiency increased with decreasing temperature and increasing CO₂ pressure. The motivation of selective adsorption of organic dyes on PS-PAA is the Donnan effect and electrostatic interaction between PS-PAA and MB. Furthermore, the absorbed dyes could be eluted by salt solutions, and the regenerated PS-PAA still kept the high adsorption capacity for dyes even after five times. Due to these characteristic, PS-PAA shows a great potential application as a highly-efficiency and selective adsorbent for the removal of organic dyes from organic solution.

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The mechanism of separation dyes and regeneration of polymer brush process. Firstly, PS-PAA selectively adsorbed MB and the aggregation precipitated from solution assisted by the compressed CO₂. Then, thanks to NaCl solution, PS-PAA could be regenerated and it keep good performance on adsorbability even after five times circle .