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Title: pH Adjustable Dye Adsorption and
Recycle by Electrostatic Interaction

2020

Statement of Originality

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Date: September 5, 2020

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Abstract

This study utilizes amino-riched polyethylene polyamine and polydopamine to chemically decorate sponge that can be used to efficiently absorb dyes in mimic dye-polluted water. The sponge surface exhibits positive charge in acidic condition due to the protonation of amino group, which is easy to attract anionic dye with negative charge through electrostatic interaction, but has an exclusion to cationic dye, thus the adsorption efficiency of anionic dye is much greater than cationic dye. In alkaline condition, the sponge surface has no charge, thus the absorbing ability to dyes is very low since only a certain degree of weak adsorption occurs due to the porosity of the sponge and the rough structure after its modification. Accordingly, the mixed anionic and cationic dyes can be effectively separated by pH adjustable process, i.e., adsorption (in acidic condition) and elution (in alkaline condition). The decorated sponge also has excellent renewability after washing in alkaline condition and can be reused for many times, providing it application potential in the actual dye-polluted water treatment, as well as dye separation and recycle.

Key words: amino-riched decoration, dye adsorption, pH adjustable, electrostatic interaction, recycle

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1. Introduction

1.1 The Harm of Dye-polluted Water Discharge

The discharge of dye-polluted water, mainly from the textile printing, leather, food processing, cosmetic industries and so on, is harmful for ecological environment [1-3]. According to the statistics, textile industries consume over 700,000 tons of dyes, which are the one of top three pollutants [4]. When the dye-polluted water flows into the environment, it will consume a great deal of oxygen in the water, also reduce the transparency of the water, which will cause serious harm to the water ecology [5]. The majority of dyes are organic compounds with complex composition and stable molecular structure, which can absorb to substances to impart color even in very little concentration, thus it is extremely difficult to remove from water.

1.2 Current Methods for Dye-polluted Water Treatment

Nowadays, industrial processes for treating dye-polluted water mainly include air floatation, membrane filtration, flocculation, catalytic method, coagulation, chemical oxidation, electrochemical destruction, ion exchange, and aerobic/anaerobic microbial degradation etc., but they all suffer inherent limitations such as high cost, high energy consumption, not effective for all dyes, high sludge production and large area required, thus to some extent block their further development and application [6-9]. Therefore, to quickly and efficiently treat dye-polluted water before discharging has become a very important issue.

In addition, because of the industrial demand for dyes to their products such as dyestuff, textile, paper, printing, carpet, plastic, food and cosmetic, the recycle technology of dyes also needs to be paid attention to. However, due to the high solubility and similar structure of various components, the selective separation of dyes is also difficult to be implemented, and it is difficult for traditional industrial processes to achieve efficient separation and recovery of dyes. Based on the above background, it is necessary to develop a simpler and more efficient way for the treatment of dye-polluted water, and simultaneously selectively separate different types of dye molecules, thereby promoting the development of the field of dye-polluted water treatment.

1.3 Adsorption of dyes

It is noticed that adsorption is superior to other techniques in terms of cost-effective and highly efficient, flexibility and simplicity of design, easy operation and no secondary pollution [10-13]. The commonly used adsorbents include activated carbon, non-conventional low-cost adsorbents such as clay, zeolite, silica beads, and biosorbents, where the porous structures can promote their absorption rate [14-16]. Recently, some novel absorbing materials such as polymer hydrogel, nanomaterials (including carbon nanotubes, nanodiamond, nano titanium dioxide, nano magnesium oxide, and nanochitosan etc.), three-dimensional graphene-based macrostructures, metal-organic frameworks have been emerged and developed [17-20]. However, these materials often face one or more of the following problems, including low adsorption efficiency, high recover difficulty, and poor selectivity.

Adsorption includes chemical sorption and physical sorption, which provides an attractive alternative for treating polluted water, especially if the adsorbent is inexpensive and additional pretreatments are not required before application [4]. Considering the advantages of removing dyes through adsorption, as well as the characteristic of chemical and physical adsorption, we propose ion adsorption based on electrostatic interaction will have great perspective for dye removal [21], since such interaction is weaker than chemical bonds but stronger than physical forces, thus will cause the firm adsorption of dyes and meanwhile easy to regenerate. Moreover, according to the classification of different charged dyes, the selective adsorption and separation are expected.

1.4 Amino-riched Materials

Polyethylene polyamine (PEPA) is a low-cost copolymer rich in amino groups, whose monomers include forms like ethylene diamine, diethylene triamine, triethylene tetramine and tetraethylene pentaamine [22-24]. Therefore, it is a great candidate to prepare a new type of material richen in amino groups on the surface, which will expose positive charge after protonation in acidic condition. Another amino-riched material we choose is dopamine (DA), which could also be connected the substrate with PEPA, thus

can ensure them to react by chemical bond and have good stability [25]. It has been confirmed that DA can form strong interactions through self-polymerization with various substances and coat the polydopamine (PDA) layer in alkaline environment, thus can be applied in surface decoration with strong adhesive force [26]. Moreover, it can also provide the surface with high active reaction sites after modification by simple immersing the substance in DA, making it a simple and effective way to obtain multifunctional coatings [27]. In this case, PEPA is expected to decorated to suitable substrate through the adhesive of PDA in the middle just like a sandwich structure, where both PEPA and PDA can provide amino groups.

1.5 The Purpose of the Research

To deal with the current problem of dye-polluted water discharge, this study proposes to design a material that can achieve efficient and selective adsorption of different dyes through electrostatic interaction, as well as separation and recycle of specific dyes from dye-polluted water. Responding to the different charge of dye molecules in dye-polluted water, materials with different functional groups can be designed, which could achieve adsorption of the corresponding dye molecules. Specifically, if the surface of the material is decorated with amino groups, amide groups etc., it can be used to absorb anionic dyes; if the surface of the material is decorated with carboxyl groups, sulfonic acid groups etc., cationic dyes-absorbing materials can be obtained. As expected, due to the material's excellent adsorption selectivity, separation efficiency, and stability, it can provide a new idea for the quick efficient treatment of dye-polluted water and the recovery of dyes. Meanwhile, due to its excellent performance and convenient usability (it only needs to be immersed in the dye-polluted water or filled in the drain pipe), it will play an important role in practical industrial applications. By using this material to effectively treat dye-polluted water, it can solve the current high cost of dye wastewater treatment and serious dye pollution, as well as improve the current water resources environment and industrial processes, thus provide a wide prospect in the development of dye-polluted water treatment.

2. Experimental Section

2.1 Materials and Instruments

Polyethylene polyamine (PEPA, $C_{12}H_{15}N_7O_{12}$, 30%), dopamine hydrochloride (DA, $C_8H_{12}ClNO_2$, 99%), and trishydroxymethylaminomethane (Tris, $C_4H_{11}NO_3$, 99%) were used as the decoration agents. Methyl blue (MB, $C_{37}H_{27}N_3Na_2O_9S_3$, BS), Orange II (OII, $C_{16}H_{11}N_2NaO_4S$, BS), and Rhodamine B (RhB, $C_{28}H_{31}ClN_2O_3$, BS) were used as dyes. Polyurethane (PU) sponge was used as the substrate. and solution are used to regulate pH property. Accordingly, HCl solution with pH = 1 and NaOH solution with pH = 13 were used to regulate the acidic and alkaline properties of the dye solution.

Analytical balance was used to weigh the mass of solid. The microphotograph of the sponge and pictures of the solution were obtained by camera and scanning electron microscope (SEM). The concentration of the dye solution was tested and analyzed by an ultraviolet-visible (UV-Vis) spectrophotometer (Figure 1).



Figure 1: Ultraviolet-visible spectrophotometer.

2.2 Decoration of Sponge

60 mg DA and 60 mg PEPA weighed by analytical balance were added to 50 mL of deionized water. Then, 3 mL of Tris with a concentration of 1 mol/L was added to the deionized water using as a buffer solution to ensure the alkaline reaction environment, and the mixture was stirred to form a brown solution. Soaked a clean PU sponge (cut into a cube with a side length of about 4 cm) in the mixed solution covered by a sealing film for 48 h at room temperature (Figure 2). Then took out the sponge and rinse it with

deionized water to remove excess particles on the surface, finally obtained the decorated sponge.



Figure 2: PU sponges immersed in the mixture of DA, PEPA and Tris solution.

In order to obtain more samples, we immersed many sponges in the solutions with the same recipe.

2.3 Adsorption and Separation of Dyes

In the adsorption experiment, Methyl blue (MB), Orange II (OII), and were used as representative anionic dyes, while Rhodamine B (RhB) was used as representative cationic dye. Three aqueous solutions with the dye concentration of 10 ppm were prepared to mimic dye-polluted water. The decorated sponge was immersed in each of the solution, and then used a squeeze-relaxation cycle to make the sponge continuously absorb and release solution/water. During the process, we took samples at different stages to measure the UV-Vis spectrum.

In the separation experiment, mixed solutions of different type of dyes with each of the concentration of 10 ppm were used to mimic the mixed dye-polluted water, and the same squeeze-relaxation cycle was used to absorb dyes. Meanwhile, the sponge was washed by alkaline solution to release dye. In detail, after the sponge absorbed dyes from the mixed solution in one beaker, it was then rinsed in the other beaker.

3. Results and Discussion

3.1 Morphology Analysis of the Decorated PU Sponge

The decorated PU sponge was prepared by immersing the clean sponge into a mixed dopamine hydrochloride (DA) and polyethylene polyamine (PEPA) solution, and using Tris as alkaline buffer solution to make DA self-polymerize to PDA. After soaking for 48 h and rinsing with water, the sponge turned from faint yellow to brownish yellow, indicating that PEPA has been successfully coated on the sponge (Figure 3). Thereby, the decorated PU sponge is now ready for use.



Figure 3: Schematic illustration of the decoration of PU sponge:

(a) the original sponge; (b) the decoration reaction; (c) the decorated sponge

Figure 4a and 4b showed the scanning electron microscopy (SEM) images of the original PU sponge observed in different magnification, indicating the sponge to be irregular porous structure, in which it was smooth and clean without other substances. Figure 4c and 4d showed the images of the coated sponge, in which the sponge was still in irregular porous structure (Figure 4c), indicating that the decoration reaction had no impact on the sponge's porous structure, but its surface was not smooth since rough spherical nanoparticles of PEPA and PDA accumulated on the surface (Figure 4d).

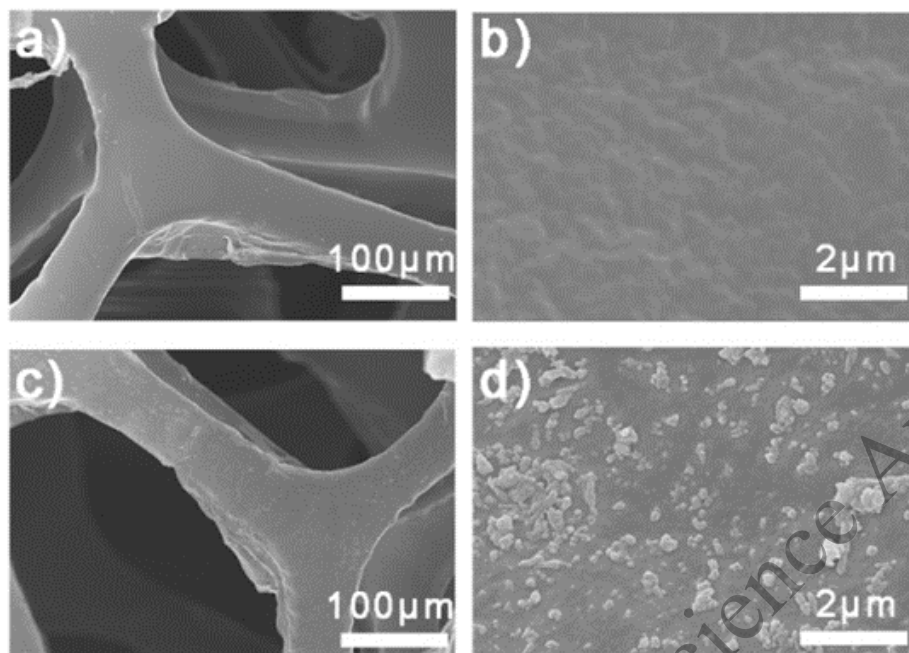
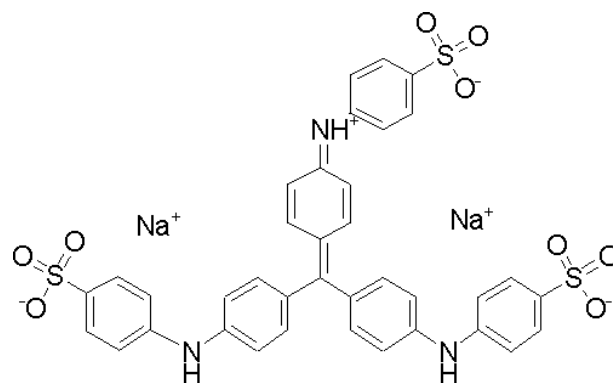


Figure 4: SEM images in different magnification:

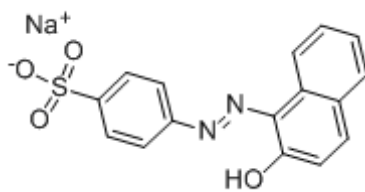
a) and b) are the original PU sponge; c) and d) are the decorated PU sponge.

3.2 Absorbing Ability of the Original PU Sponge

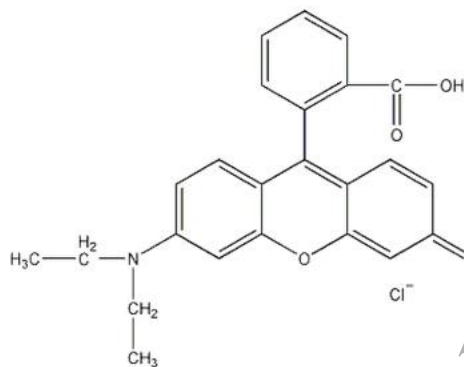
The original PU sponge was immersed into different dye solutions separately to investigate its own absorbing ability. Here, we chose the typical MB and OII as representative anionic dyes, while RhB as representative cationic dye. The molecular structure of them are shown in Figure 5, respectively. To ensure the rational contrast, the concentration of each of the dye preparation solutions is 10 ppm.



(a) MB



(b) OII



(c) RhB

Figure 5: The molecular structure of different types of dye.

The concentration of the dye in each solution is tested by an ultraviolet-visible (UV-Vis) spectrophotometer. Figure 6 showed the UV-Vis spectrum of the adsorption of different dyes by the original PU sponge. A squeeze-relaxation cycle process was used to ensure the sponge continuously absorb and release solution/water, making it sufficiently contact with solution, thus can absorb as much dyes as possible. As seen from Figure 6a-6c, the characteristic peaks of MB at about 630 nm, OII at about 480 nm, and RhB at about 560 nm all decreased in some degree after 10 adsorption cycle times, which indicated that the original sponge itself had a certain absorbing ability for dyes, but due to the different structures of dyes, the absorbing ability was different. From the change of the peak height, it can be calculated that the adsorption efficiency of the original sponge on MB, OII and RhB was about 45%, 10%, and 56%, respectively (Figure 6d). The adsorption ability of the original sponge was due to its porous structure with high specific surface area, but this kind of adsorption was weak interaction, thus

not only the adsorption efficiency was limited, but the adsorption force was not strong enough, and could be easily washed away by water.

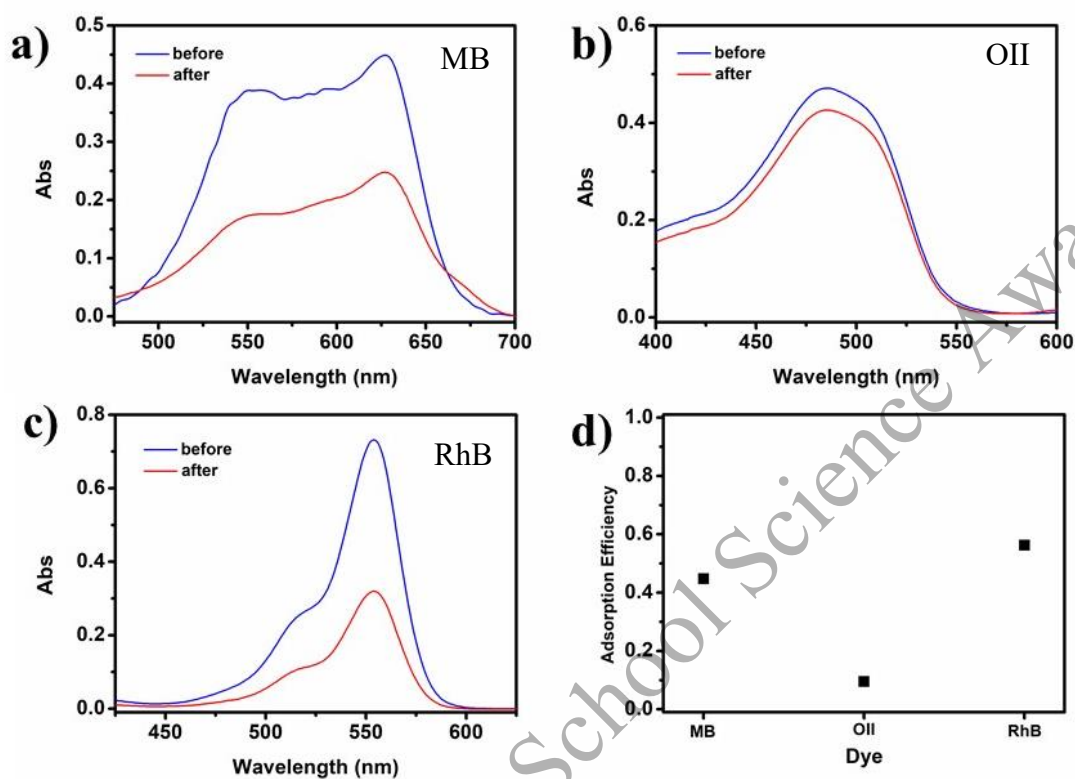


Figure 6: Absorbing ability of the original PU sponge: a-c) UV-Vis spectrum of MB, OII and RhB, respectively; d) the corresponding adsorption efficiency.

3.3 Absorbing Ability of the Decorated Sponge in Acidic/alkaline Conditions

The surface amino groups of the decorated PU sponge can be positively charged through protonation in the acidic solution. Therefore, the acidity/alkalinity of the solution can largely affect the amount of positive charge generated on the surface, thus affecting the absorbing ability of the sponge. Figure 7a showed the absorbing ability of the decorated PU sponge for the anionic dye MB under acidic and alkaline conditions. It can be seen that the characteristic peak of MB at about 630 nm disappeared in acidic condition after 5 adsorption cycles, indicating that MB was almost completely adsorbed by the sponge; while the peak height only slightly reduced in alkaline condition, indicating that the absorbing ability of MB was very low. Figure 7b showed the absorbing ability of the decorated PU sponge for anionic dye OII under acidic and

alkaline conditions. It can be seen that the characteristic peak of OII at about 480 nm was significantly reduced in acidic condition after 5 adsorption cycles, indicating that most of OII was absorbed. Similarly, the sponge had a very weak absorbing ability for OII in alkaline condition. The above results showed that the decorated sponge had a strong absorbing ability for both of the anionic dyes of MB and OII in acidic condition, which was due to the strong protonation of amino groups, resulting in denser positive charge on the surface that can attract anionic dyes through electrostatic interaction. In alkaline condition, the sponge surface has no charge, thus the contribution to dyes absorbing ability was the lower adsorption of the original porous sponge.

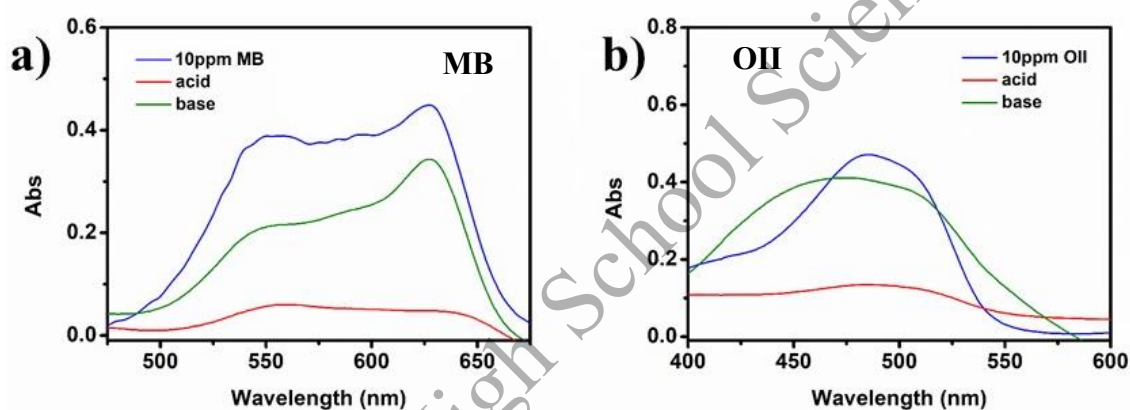


Figure 7: Absorbing ability of the decorated PU sponge for anionic dyes in acidic/alkaline conditions: a) MB; b) OII.

3.4 Adsorption and Separation of Dyes

3.4.1 Absorbing Ability of Different Dyes

Based on above results, it's noticed that the acidic condition was an important factor for dye adsorption by the decorated sponge. Therefore, the absorbing abilities for different dyes in acidic condition were investigated in detail. Figure 8 showed the photos of dye solutions before and after 10 adsorption cycles in acidic condition, which indicated that MB was almost fully absorbed and removed from the dye solution and turned colorless from the original blue (Figure 8a); the OII solution was from orange to light yellow (Figure 8b); and the pink color of the RhB solution has no obvious change

comparing to the original one (Figure 8c). From the color change, it can be deduced that the decorated sponge had strong absorbing abilities for anionic dyes of MB and OII, but it was weak for cationic dye of RhB.

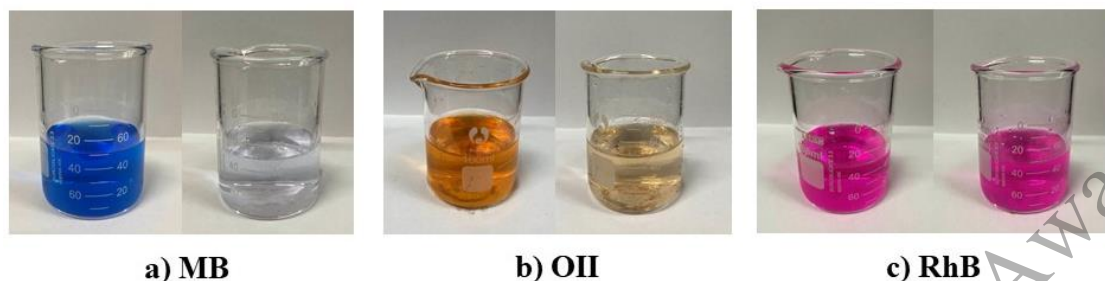


Figure 8: Photos of dye solutions before (left) and after (right) adsorption for 10 cycle times in acidic condition.

Figure 9a showed the UV-Vis spectrum of the adsorption of anionic dye of MB by the decorated sponge in acidic condition. The characteristic peak of MB around 630 nm reduced sharply after only one cycle, indicating the sponge had great absorbing ability to MB. After 10 cycles, the sponge absorbed almost all MB dye, where the characteristic peak could hardly be observed. The ability to absorb the other anionic dye of OII by the decorated sponge in acidic condition was also investigated. Figure 9b suggested that the characteristic peak of OII at about 480 nm only dropped up to 20% after one cycle, while it dropped sharply after 5 cycles and only a little bit characteristic peak could be observed after 10 cycles. To make a comparison, the absorbing ability of cationic dye of RhB by the decorated sponge in acidic conditions was also tested by UV-Vis spectrum. Figure 9c suggested that the height of the characteristic peak of RhB at about 560 nm decreased to a certain extent but the reduction range was not high.

Figure 9d summarized the adsorption efficiency of the decorated sponge to MB, OII, and RhB calculated from the height of the peak in UV-Vis spectrum. As seen, the adsorption efficiency for MB has already been up to 85% after only one cycle, and achieved to 95% after 10 cycles, indicating that the concentration of the dye in the solution was below 0.5 ppm. The adsorption efficiency for OII was only 26% after one cycle, while it had a sudden increase of up to 80% after 5 cycles and achieved 85% after

10 cycles. It can be deduced from these results that the decorated sponge had strong absorbing abilities for anionic dyes of MB and OII, but the adsorption efficiency for MB was greater and the rate was faster. However, the adsorption efficiency for cationic dye of RhB was only 14% after one cycle and about 26% after 10 cycles, even lower than that of the uncoated sponge.

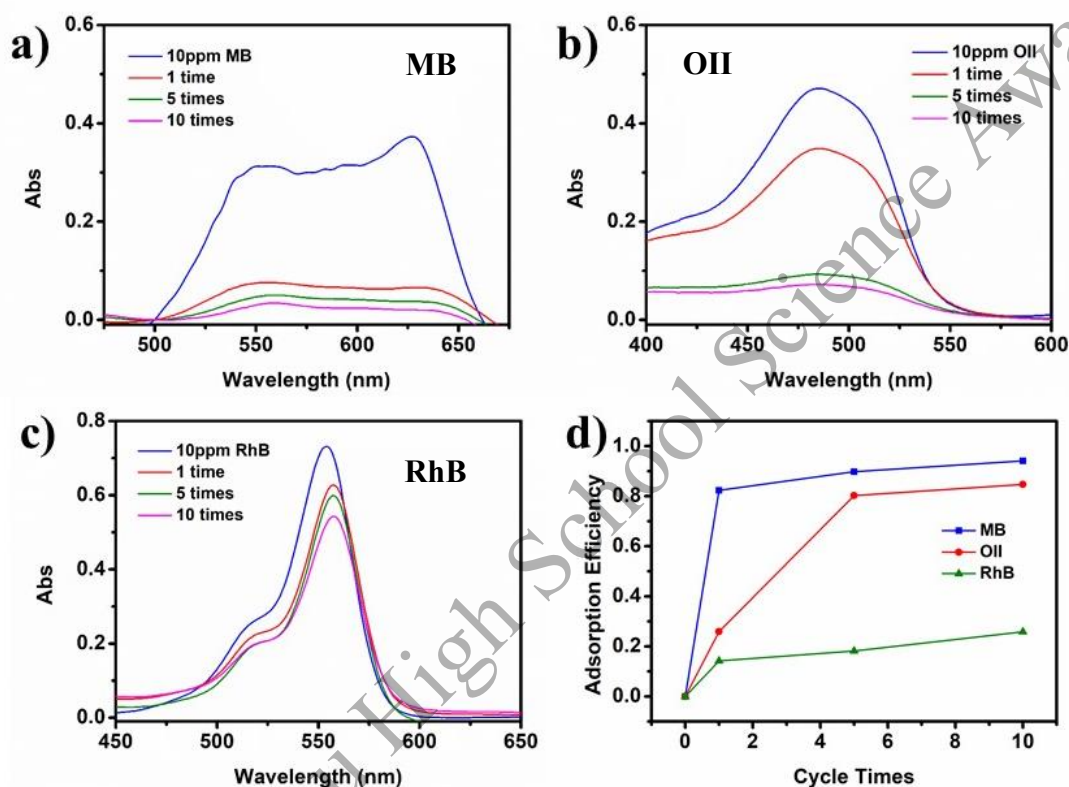


Figure 9: Absorbing ability of the decorated sponge in acidic condition: a-c) UV-Vis spectrum of MB, OII and RhB, respectively; d) the corresponding adsorption efficiency.

As a result, the amino-riched sponge expressed selective absorbing ability for dyes with different types of charge. To be specific, the adsorption efficiency for anionic dyes was high; while it was low for cationic dye. This was mainly because the positive charged amino group on the sponge surface was easy to attract negative charged anionic dye through electrostatic interaction. However, it had an exclusion for cationic dye, thus only a certain degree of adsorption occurred through weak adsorption due to the sponge had a porous structure and a rough surface after decoration.

3.4.2 Separation of Mixed Anionic and Cationic Dyes by the Decorated Sponge

Based on the selective adsorption ability and adsorption feature of the decorated sponge, the separation and recycle of anionic and cationic dyes can be achieved by adsorption-elution process. The sponge was firstly immersed in the mixed MB and RhB solution, and treated by the same squeeze-relaxation adsorption process. Differently, after the sponge absorbed the dyes in one beaker, it was then rinsed by NaOH solution in the other beaker. Figure 10a showed the UV-Vis spectrum of the original mixed dye solution, where both of the characteristic peaks of around 630 nm and 560 nm attribute to MB and RhB decreased gradually until they almost disappeared after 10 cycles of adsorption-elution process, indicating large amounts of MB and RhB were simultaneously absorbed and removed from the solution. Meanwhile, both of the characteristic peaks of MB and RhB appear in the NaOH solution. Differently, the height of MB was almost the same as that of the original mixed solution, while the height of RhB obviously decreased comparing to the original one (Figure 10b), indicating that MB in the mixed solution had been successfully absorbed by the decorated sponge in acid condition and eluted into the NaOH solution, but most of RhB was still absorbed and retained in the sponge. In this case, the mixed dyes of anionic MB and cationic RhB were effectively separated with the adsorption efficiency of MB higher than 95% and the MB was almost fully eluted.

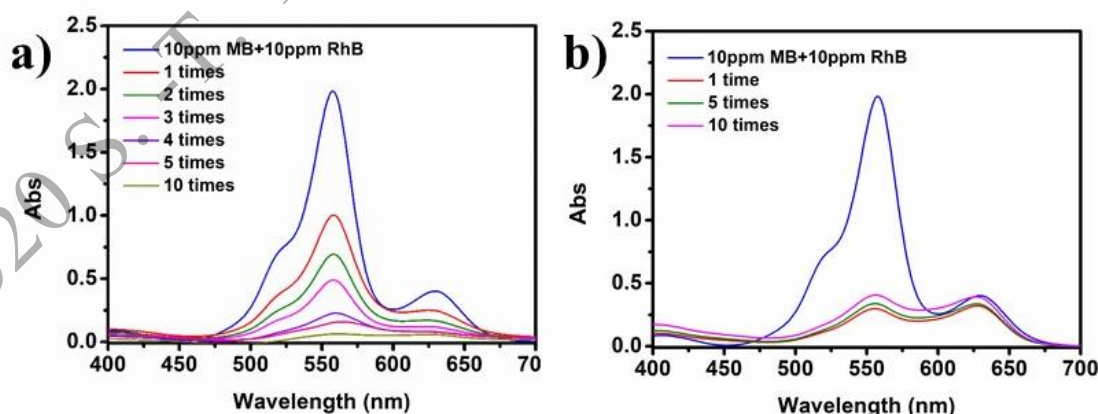


Figure 10: The decorated PU sponge used for adsorption and separation of the mixed dyes of MB and RhB: a) UV-Vis spectrum of the original mixed dye solution after absorbing; b) UV-Vis spectrum of the eluent washing by NaOH solution.

Figure 11 showed the photos that reflected the color of the mixed dye solution and the eluent before and after separation. The left photo in Figure 11a represented the original MB (10 ppm) and RhB (10 ppm) mixed solution, showing purple that is the mixed color of blue MB and pink RhB, while the right photo in Figure 11a was NaOH solution ready for elution. After one cycle adsorption, the mixture turned to light purple (left photo in Figure 11b) and the NaOH solution turned from transparent to blue (right photo in Figure 11b). Furthermore, the mixture turned to be pink (left photo in Figure 11c) and the NaOH solution was dark blue after 5 cycles (right photo in Figure 11c). Finally, the original mixed solution turned to be almost colorless (left photo in Figure 11d), while the NaOH solution appeared the blue color just like that of the pure MB (right photo in Figure 11d). It is obviously that the color in the left beaker, showing the mixed MB and RhB solution, turned from purple, light purple, pink to colorless, indicating the concentration of MB sharply decreased and that of RhB gradually decreased, finally both of them disappeared. As to the right beaker, it showed the washed NaOH solution turned from colorless to more and more blue, indicating the concentration of MB larger and larger.

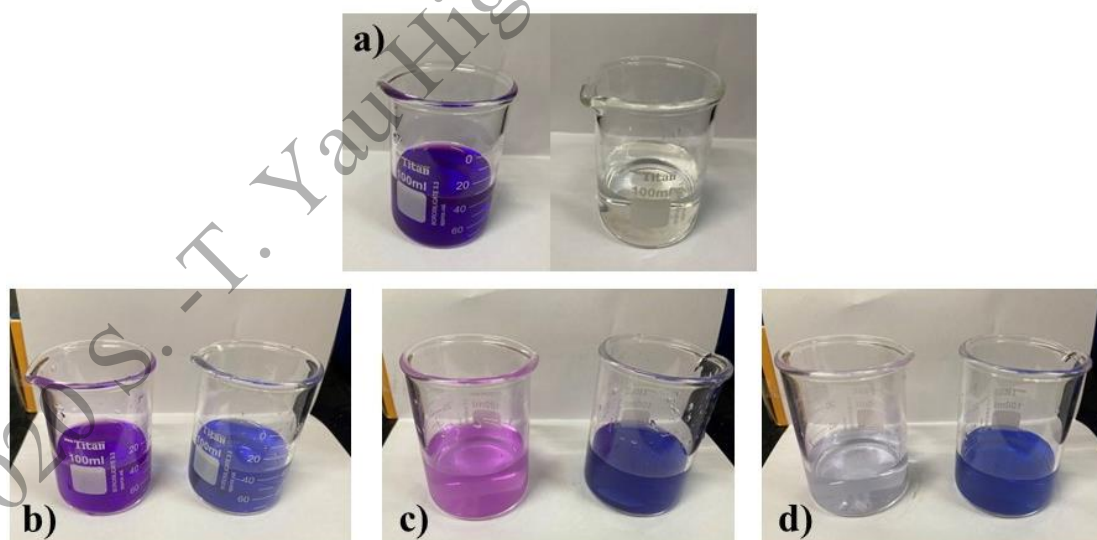


Figure 11: Photos of dye solutions before and after separation of MB and RhB mixed solution. In each image, the left one is the mixed solution, as well as the right one is the eluent of NaOH solution. (a) the original solution; (b) after 1 cycle; (c) after 5 cycles; (d) after 10 cycles.

3.5 Renewability and Reusability of the Decorated Sponge

In order to prove the practical application prospect of the decorated sponge, its performance and morphology after many times of use were characterized. It has been proven that amino-decorated sponges can efficiently attract anionic dyes by generating sufficient positive charges through protonation in acidic condition, while in alkaline conditions, they cannot adsorb dyes because there's no charges on the surface. Therefore, we can use alkaline NaOH solution to wash the sponge after the full adsorption of the dye in acidic condition, thus the desorption of the dye occurred and guaranteed the sponge to be renewed and recycled (Figure 12a). Figure 12b showed the process of MB adsorption in acidic condition and desorption after immersion in alkaline NaOH solution. It can be seen that the dye of MB was completely absorbed by the sponge in the acid condition through electrostatic interaction, and the solution became clear. Immersed the sponge again in the NaOH solution, the dye was washed and desorbed into the alkaline solution, thus solution became blue and the sponge was restored to its original state without dye adsorbed and can be reused for many times.

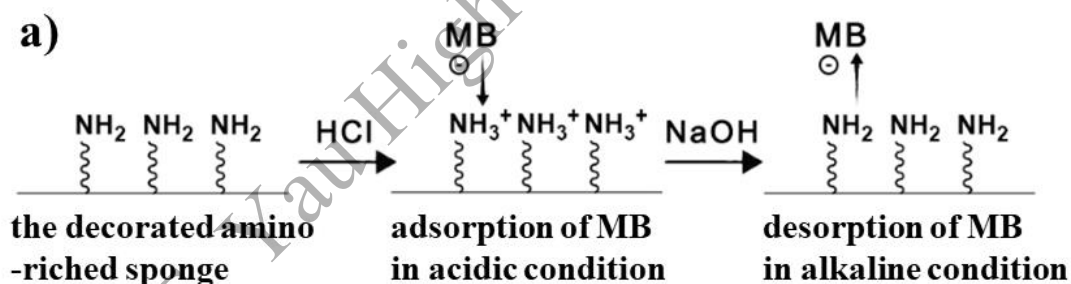


Figure 12: The adsorption and desorption for the decorated sponge of MB in acidic/alkaline conditions: (a) surface chemical structures; (b) color changes.

Figure 13a was the UV-Vis spectrum of the sponge used in 4 consecutive MB removals (here it was defined that the process of almost removing all MB in acidic condition was one use). As seen, after 4 consecutive uses, the sponge still maintained excellent absorbing ability with adsorption efficiency above 90% (Figure 13b). The photos of the sponge (inset of Figure 13b) indicated that it appeared blue after absorbing MB, whereas recovered brown after washing by NaOH solution. In addition, the SEM images can also indicate that the structure of the sponge had almost not been affected after 4 consecutive uses (Figure 13c). Observing at a greater magnification (Figure 13d), the spherical nanoparticles obviously decreased comparing to the original decorated sponge because of the continuous washing, but the surface still maintained a relatively rough structure. All these results indicated that this decorated sponge has excellent reusability, and has potential application in actual dye-polluted water treatment, as well as dye separation and recycle.

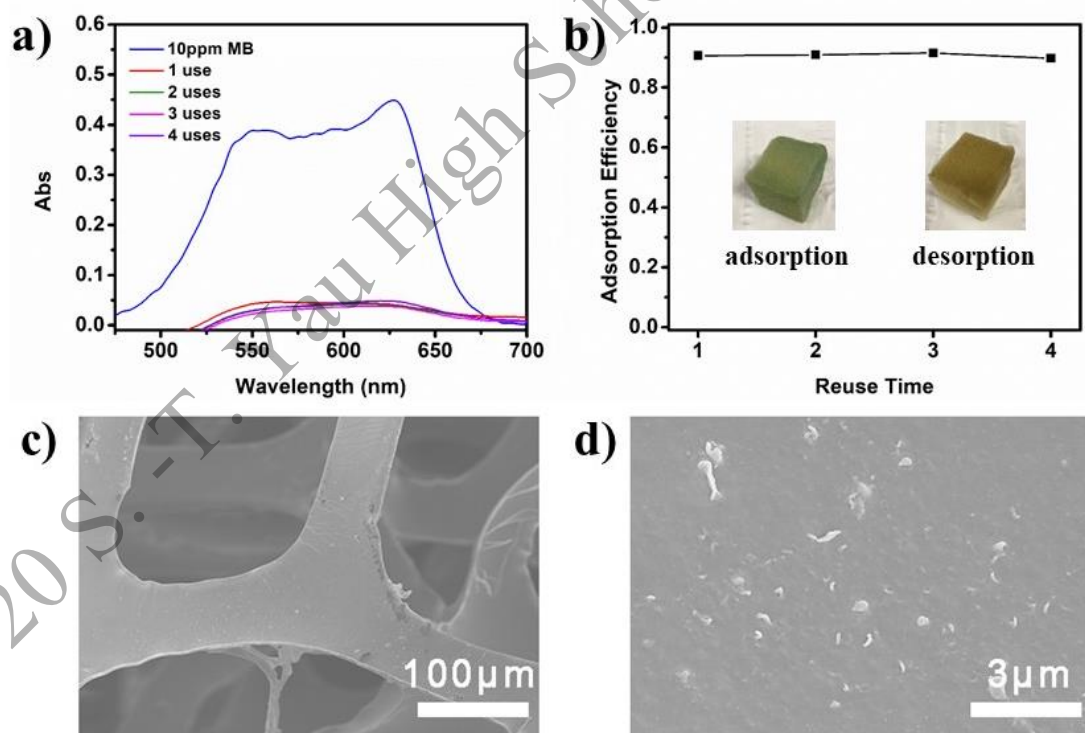


Figure 13: Renewability and reusability test of the decorated sponge: a) UV-Vis spectrum of repeated adsorption of MB; b) adsorption efficiency of repeated adsorption of MB; c) and d) SEM images after consecutive uses for 4 times.

4. Conclusions and Prospect

4.1 Conclusions

The amino-riched sponge designed and prepared in this study is able to efficiently absorb dyes, and is expected to be put into practice in the treatment of industrial dye-polluted water. At the same time, since such sponge exhibits different adsorption ways and mechanisms for different types of dye, which can be separated and recycled. The main conclusions are as follows.

- (1) PU sponge has been successfully chemical decorated by polydopamine and polyethylene polyamine, which provided the sponge surface a rough structure and abundant amino groups that can form positive charges after protonation in acidic condition.
- (2) The amino-riched sponge expresses selective absorbing ability for dyes with different types of charge, *i.e.*, the adsorption efficiency for anionic dye is high, but it is low for cationic dye. This is mainly because the positive charged amino group on the sponge surface is easy to attract negative charged anionic dye through electrostatic interaction, thus integrating the dyes tightly. However, it has an exclusion on cationic dye, thus only a certain degree of adsorption occurs through weak adsorption owing to the porosity of sponge and a rough surface after decoration.
- (3) Based on the selective adsorption ability and adsorption feature of the decorated sponge, the separation and recycle of the mixed anionic and cationic dyes can be achieved by the process of adsorption in acidic condition and elution in alkaline condition, with the separation efficiency higher than 95%.
- (4) The decorated sponge has excellent renewability and reusability after washing by alkaline NaOH solution. At the same time, the structure of the sponge had little affect after consecutive uses, which has potential application in actual dye-polluted water treatment, as well as dye separation and recycle.

4.2 Prospect

This study provides an effective idea for the quick efficient treatment of dye-polluted water and the recovery of dyes through electrostatic interaction. The amino-riched absorbing sponge is of excellent adsorption selectivity, separation efficiency, and stability. As expected, it will play an important role in practical industrial applications only needs to be immersed in the dye-polluted water or filled in the drain pipe.

There's still further research could be conducted.

- (1) Use amino-rich sponge to adsorb more kinds of anionic and cationic dyes, and try to adsorb other harmful anions and cations in aqueous solution, and study their adsorption selectivity and adsorption efficiency, so that the sponge can adsorb dyes or other harmful ions with different charges universally.
- (2) Decorate the sponge surface with negatively charged materials (such as those containing carboxyl groups), and investigate its absorbing ability of different anionic and cationic dyes. Used in combination with amino-rich coated sponge to achieve better adsorption selectivity, greater adsorption efficiency and separation efficiency.
- (3) Because it is manual operation during the adsorption process, there is a certain error every time. It can be considered to be made into an automatic device to facilitate better cycle adsorption and conveniently used in practical applications.
- (4) Use the decorated sponge to absorb and separate the printing and dyeing wastewater discharged from the actual industry, and test its adsorption efficiency, maximum adsorption capacity, etc.

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6. Acknowledgements

I wish to express my sincere gratitude to my instructor Prof. Yong Zhao for his guidance during this research work. Prof. Zhao always encourage me to think and solve problems independently, and give advice when I encounter difficulties. Special thanks to the doctoral student for telling me safety rules and operational details in the lab, as well as the data processing method. Thanks to the technician for SEM testing. Thanks to teachers Xiulin Fang and Jing Ma in Jinpeng Science and Technology Association in my school for their support and encouragement.

2020 S.-T. Yau High School Science Award