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本科毕业论文

Preparation of MXene cellulose composite films and their adsorption properties for methylene blue

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Preparation of MXene cellulose composite films and their adsorption properties for methylene blue

MXene/纤维素复合薄膜的制备及其对亚甲基蓝吸附性能的研究

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Content

Abstract

MXene is a kind of inorganic 2D dimensional nano materials with novel structure. It is composed of transition metal carbides, nitrides or carbonitrides with several atomic layers. At present, MXene are widely used in the fields of energy, optics, catalysis, adsorption and so on. Because of its high hydrophilicity, large specific surface area, negative surface charge and high ion exchange capacity, it is used as an excellent adsorbent material. MXene materials will remove heavy metal ions and radioactive elements in the environment through electrostatic attraction, coordination chelation and other interactions.

It is expected to become an ideal carrier for adsorbing heavy metal ions and radioactive. In this experiment, the property of adsorption of MXene is used. It is used to modify the surface of a cotton to make a filter cloth. There are also other liquids used in this experiment to modify the surface of the filter cloth which have some useful functional group. While the MXene play the most important role in this experiment. By using immersing method, the product shows it is playing a role in purify methylene blue liquid. Besides, even though there is some other pollutes in wastewater of industry, MXene is a good adsorbent to absorb other heavy metal ions in terms of in this experiment only the adsorption of dyestuff has been tested.

Keywords: MXene adsorbent materials filter cloth cotton methylene blue

摘要

MXene 是一种结构新颖的无机二维纳米材料。它由过渡金属碳化物、氮化物或碳氮化物组成，具有多个原子层。目前，MXene 在能源、光学、催化、吸附等领域有着广泛的应用。由于其高亲水性、大比表面积、负表面电荷和高离子交换容量，被用作优良的吸附材料。MXene 材料将通过静电吸引、配位螯合等相互作用去除环境中的重金属离子和放射性元素。

有望成为吸附重金属离子和放射性物质的理想载体。本实验利用了 MXene 的吸附特性。它用来修饰棉布表面，制成滤布。本实验中还使用了其他液体来修饰滤布的表面，这些液体具有一些有用的官能团。而 MXene 在本实验中起着最重要的作用。通过浸泡法，最终产物表明它对亚甲基蓝溶液的纯化起到了一定的作用。此外，尽管本实验仅对染料的吸附进行了测试，工业废水中存在其他一些污染源，但 MXene 是一种很好的吸附剂，可以吸附其他重金属离子。

关键词：MXene 吸附材料 滤布 棉布 亚甲基蓝

Chapter 1. Introduction

With the development of industrialization, the content of dyestuff and heavy metal ions were raised，such as, methylene blue, Cu^{2+}. If this polluted water discharged into lake and sea, it would cause big detrimental effect to aquatic plants and animals. Besides, deposition of methylene blue can break the balance of soil biodiversity [1-3]. Therefore, separating this dyestuff has become a challenged topic to our society. To separate methylene blue there were several basic chemical and physical methods, such as coagulation, catalysis, ion exchange, membrane filtration, and adsorption [2]. Exceptionally, there are also some new techniques to purify water, such as micro and ultra-filtration, nanofiltration, reverse osmosis and so on. 1. however, even though these techniques are with high efficiency, it is kind of expensive to use these methods. Hence, there is an urgent need for new methods which not only have high efficiency, but also with low price. With the object mentioned above, the corresponding research has been done on this topic.

1.1 Research background

Nowadays, it is our human being's consensus that drinking water is an important and infrequent resources. The lack of drinking water is a big threat for us. Aquaculture farm, chemical plant, mining, and electronic factory are the main sources where polluted water come from. In this polluted water, it commonly contains heavy metals ions and dyestuff which is harmful to human [4-5].

Especially, heavy metal ions can be accumulated in fish, shrimp, and shellfish while these aquatic animals are usually as food to our human beings. High density heavy metals also negative to plants, heavy metal density changes in plant nutrition and antioxidant mechanisms can cause changes in plant quality. Heavy metal elements usually are Cu, Cr, Pb, Hg, As, Cd. What's more, with large amount of dyestuff, it may cause environmental problems like red tide. If these problems aren't be ticked appropriately, it will leave a big safety concern to our living environment

and food safety. Since the property of adsorption of MXene is similar with graphene, there is some work did by others, indicates that graphene aerogel has attracted great attention and been widely used in the field of environmental remediation because of its high specific surface area, high porosity, excellent thermal stability, and mechanical properties. However, there are a series of problems in the preparation of graphene aerogel from graphene oxide. Therefore, using MXene to replace graphene in adsorption area is a good choice to have a try. There is also already some research on the application of MXene indicates that it can be used in sewage disposal area. There is an application that hydrophilic, and oil repellent conductive separation membrane was prepared by using carbon nanotube (CNT) and MXene. The underwater super oil repellency of the membrane was used to weaken the oil adhesion and alleviate the membrane pollution. On this basis, an electrically assisted membrane separation process is designed to enhance the electrostatic repulsion effect and improve the interception and anti-pollution performance of the membrane to emulsified oil and dissolved organic pollutants [6-8].

There is also research about magnetic activated carbon was prepared by hydrothermal synthesis with an adsorption capacity of 106.4 mg / g. Loading Fe_3O_4 did not significantly change the internal structure of activated carbon, but the separability of activated carbon was significantly improved. Magnetic activated carbon precipitates completely under the action of natural gravity for 5 minutes, while solid-liquid separation is realized under the action of magnetic force for 30 seconds. Methylene blue was used as adsorbent to explore the adsorption process of magnetic activated carbon.

Table 1. Fitting parameter table of adsorption kinetics.

吸附剂	Langmuir 模型				Freundlich 模型		
	q_m	K_L	R_L	R^2	n	K_F	R^2
活性炭	90.5	0.614	0.006-0.14	0.996	5.1	39.96	0.881
磁性活性炭	106.4	0.52	0.008-0.16	0.996	6.62	56.54	0.991

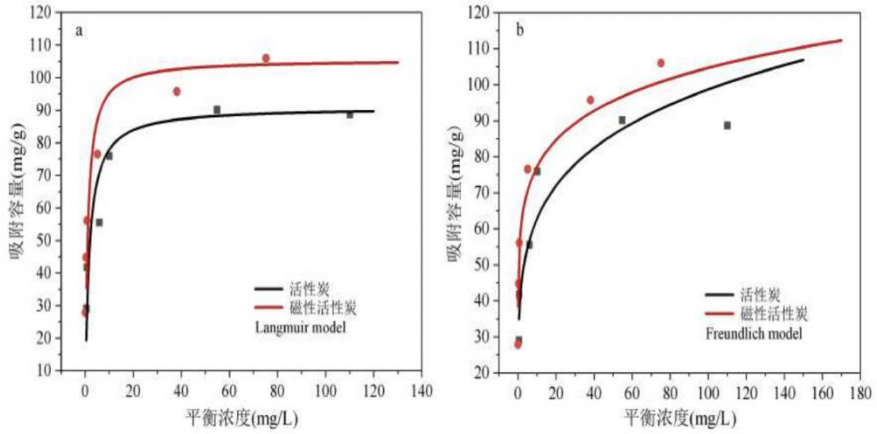

Figure 1. Study on the treatment of methylene blue with magnetic activated carbon [9].

There is research about properties of metal chelating affinity membrane with cotton as carrier, which is carried out by cotton cloth that modified by epoxy activation method to prepare Cu^{2+}- IDA Metal Chelating Affinity membrane. The results show that cotton cloth as membrane carrier has certain research value. Through the comparison of cloth with different cotton content, it is determined that 100% pure cotton cloth is used as the carrier of affinity membrane. It has good storage stability and wide application range of solvent. It can be stored in 20% ethanol, air and deionized water for three months, and the binding amount of copper is basically unchanged. Through repeated experiments, the results show that the membrane has good reusability.

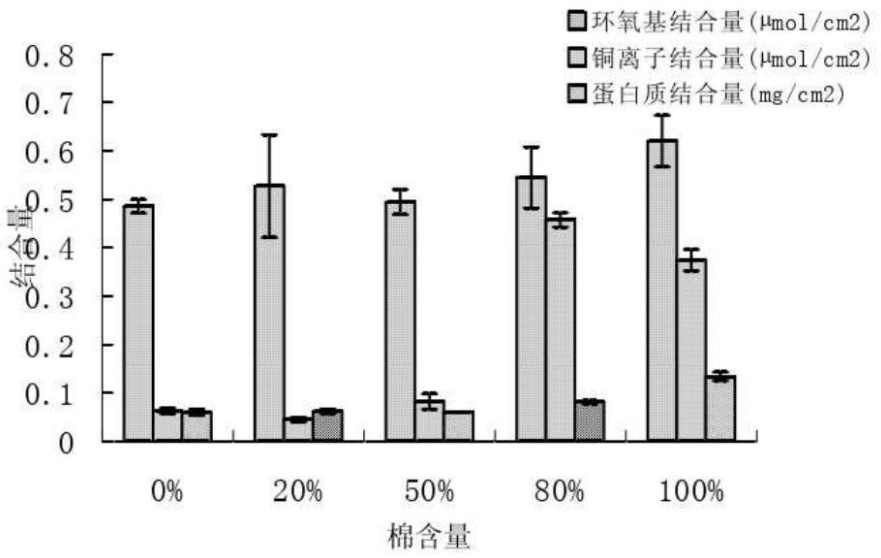

Figure 2. Binding capacity of cotton fabrics with different content [10].

1.2 Common methods to purify water with methylene blue

There are three traditional methods to purify water, electrochemical method including electrolocation, electrocoagulation and electrodialysis. Physiochemical method including chemical precipitation, ion exchange and membrane filtration. Adsorption method including activated carbon, carbon nanotubes and agricultural waste. The conventional filtration process has a certain purification effect on heavy metal pollutants, but when it cannot meet the process parameters required for heavy metal standards, it should reasonably adjust the filter speed, reasonably select the filter material, backwashing intensity, and cycle to reduce this threat [11-13].

1.3 Comparison of wastewater purification methods

All water purification approaches are selective for both high and low heavy metal concentrations in wastewater and all methods have advantages and disadvantages. What's more, adsorption is a cost effective and has more advantages compared with other conventional approaches. The choose of adsorbents depending on the efficiency of removing heavy metals and whether the adsorbents can be reused, whereas with low waste formed in the whole process [14-18]. Although adsorption

method has such a lot of advantages, the speed of it is low. In addition, absorbents also need to have excellent chemical stability and mechanical properties. Moreover, small flux and poor formability are common problems of absorbents. Therefore, to achieve the maximum absorbents benefits, new type absorbents are in urgent needed. To solve problems above, MXene, GLA and APTES are applied on the surface of cotton.

1.4 MXene, GLA and APTES

MXene is a kind of two-dimensional inorganic compounds in material science. These materials consist of transition metal carbides, nitrides or carbonitrides with several atomic layer thicknesses. Unlike the surfaces of other two-dimensional materials, such as graphene and transition carbon dihalide, functional groups can also be chemically modified. Two-dimensional materials, metal organic framework and metal oxide nanoparticles. Because of its high hydrophilicity, large specific surface area, negative surface charge and high ion exchange capacity, it is used as an excellent adsorbent material. Among these adsorption materials, 2D materials have become one of the widely studied adsorbents because of the high surface adjustability and large specific surface area. MXene, described as $M_n+X_nT_m$ (M = transition metal, X = C or N, T = F, OH or O, n = 1, 2, 3), is prepared through selective etching of Al layers from Ti_3AlC_2 (MAX). As for water desalination, the physicochemical properties of MXene, including high redox activity, large specific surface area and high surface hydrophilicity, make it as a promising adsorbent for water pollutants. Besides, MXene has the characteristics of excellent conductivity, rich surface functional groups and easy interface combination with textiles. GLA is usually used in medical science. In the process of human research, scientists found that there is an unsaturated acid in the process of human early growth and development, which plays an important role in the development of infant brain and retina [19-25]. Once the human body lacks this unsaturated fatty acid, it will produce abnormalities and disorders of immune, cardiovascular, cerebrovascular, reproductive, and secretory systems. Moreover, this unsaturated fatty acid cannot be

synthesized or replaced by human beings themselves and can only be taken from food. APTES is easy to hydrolyze and release ethanol to form corresponding silanol condensate.

1.5 Analysis Methods

1.5.1 UV Spectrophotometry

Ultraviolet spectroscopy is an analytical method to determine the absorption spectrum of substances and molecules in the ultraviolet region. Ultraviolet absorption spectrum is formed by the transition of valence electrons from low energy level to high energy level after substances absorb ultraviolet light. Not all organic substances have absorption in the ultraviolet region. Only those compounds with conjugated double bonds (πbonds) are easy to be excited and transition, forming characteristic absorption peaks in the ultraviolet region. In this paper, UV spectrophotometry is the main method to testing the change of density of methylene blue liquid to indicate the purification capacity of modified cotton.

In the UV absorption spectrum, there are four types of electron transitions: σ→σ*, n→σ*, π→π* and n→π*. The energy required for each type of transition decreases in the following order: σ→σ*>n→σ*>π→π*>n→π*σ→σ*. Saturated alkanes have no absorption peak in the ultraviolet region. The circular conjugate system composed of π bond in aromatic hydrocarbons has absorption peak in the range of 200 ~ 300 nm, and the more the number of aromatic core rings, the longer the wavelength of the absorption peak. For example, the absorption peak of bicyclic aromatic hydrocarbons is 230 nm; The aromatic absorption peak above tricyclic is 260 nm; The characteristic absorption peak of pentacyclic aromatic hydrocarbon is 248 nm; Porphyrins have typical absorption bands: the maximum absorption peaks of vanadium porphyrins are 410, 574 and 535 nm, and nickel porphyrins are 395, 554 and 516 nm. Therefore, aromatics and non-hydrocarbon compounds can be detected according to UV absorption spectrum and applied to relevant geological research.

Chapter 2. Experimental Section

2.1 Methods

The materials used in the experiment were MXene, GLA and APTES were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. MXene was made in the experiment laboratory. Where the raw materials are Ti_3AlC_2 and HF liquid. Electrochemical workstation was purchased form Ivium Technologies, Netherlands. Herein, electrochemical workstation worked as the most important instrument in synthesis, analysis, and measurement.

UV spectrophotometer 2800S was purchased from Shanghai Sunny Hengping Scientific Instrument Co., Ltd. In an electrochemical experiment, electrochemical reactions are taken place in a solution in a cell, and the electrical response is measured. All electrochemical measurements were carried out at the room temperature by electrochemical workstation.

2.2 The preparation of MXene

To purify liquid which containing methylene blue. MXene has good purifiaction capacity towards wastewater, especially for wastewater with heavy metal ions and dyestuff. To prepare MXene, there were two methods, one method is using 40% HF reacting with Ti_3AlC_2 in a reaction kettle, because the HF will react with glass, and it is kind of dangerous to tickle this step. First weight 2 g Ti_3AlC_2 and pour it into the reaction kettle, then measuring 40 mL 40% HF with Pipette gun. The 40% HF need to be added in the reaction kettle slowly, or the strong reaction may cause splash of liquid.

At the same time, a magnetic rotor needs to put into the reaction kettle, and the rotation speed is 200 rpm, the reaction last for 24 hours, and in this period, the temperature needs to be controlled in 25℃. After reaction, the top liquid needs to be poured away. The bottom MXene should be taken out into a beaker, and UP water are used to wash the reaction kettle surface for several times and the remained liquid

should be pour into the beaker either, more UP water should be added until the liquid reach 40 mL.

In addition, the MXene liquid should be separate into 8 centrifugal tubes to improve the purification of MXene. Each centrifugal process last 20 mins long. The average separation of MXene liquid is the most important thing in centrifugal process. In the end, the MXene precipitate is collected into a beaker and add UP water until the liquid reach 40 mL. Then, the MXene liquid should be collected into a bottle and having some ultrasonic process. This process last for 20 mins each time, and this process should be ultrasonic for 4 times to have a uniform MXene distribution. Besides, before using MXene liquid on the other steps, using ultrasonic to separate MXene uniformly is a better choice. The chart below shows the technological process.

There is another way of how to prepare MXene which is not used in this experiment. This method is using the reaction of Ti_3AlC_2 and LiF, and then using 9M HCl to react with the product obtained from the last step. This method has similar effect on environment but is more troublesome.

Figure 3. The flow chart of preparation of MXene.

2.3 The preparation of modified cotton

The preparation of modified cotton is using a simple method by immersing the cotton in different beaker separately. In these steps, the MXene prepared below is diluted with the ratio of 2 mL MXene liquid with 33 mL UP water, immerse the cotton in the first MXene beaker for 30 mins, then wring dry the cotton in a petri dish, and immerse the cotton in other four beakers in order are GLA liquid, APTES liquid, MXene liquid and GLA liquid. The ratio of each liquid is marked below.

After the first-round immersing, repeat the above steps but just immerse the cotton for 15 mins in each beaker. After immersing the cotton with all the liquids mentioned above, there are already some functional groups attached on the cotton, where can be reactive with methylene blue. What's more, the surface of the cotton is rougher with such stuff attached on it. In the end, the wet cotton needs to be put in a petri dish and dry in a dryer.

The steps above have been implemented twice, because two cotton has been modified. During the immersing process, a tweezer is used to flip the cotton to make sure that the useful liquids attached on the cotton sufficiently and uniformly.

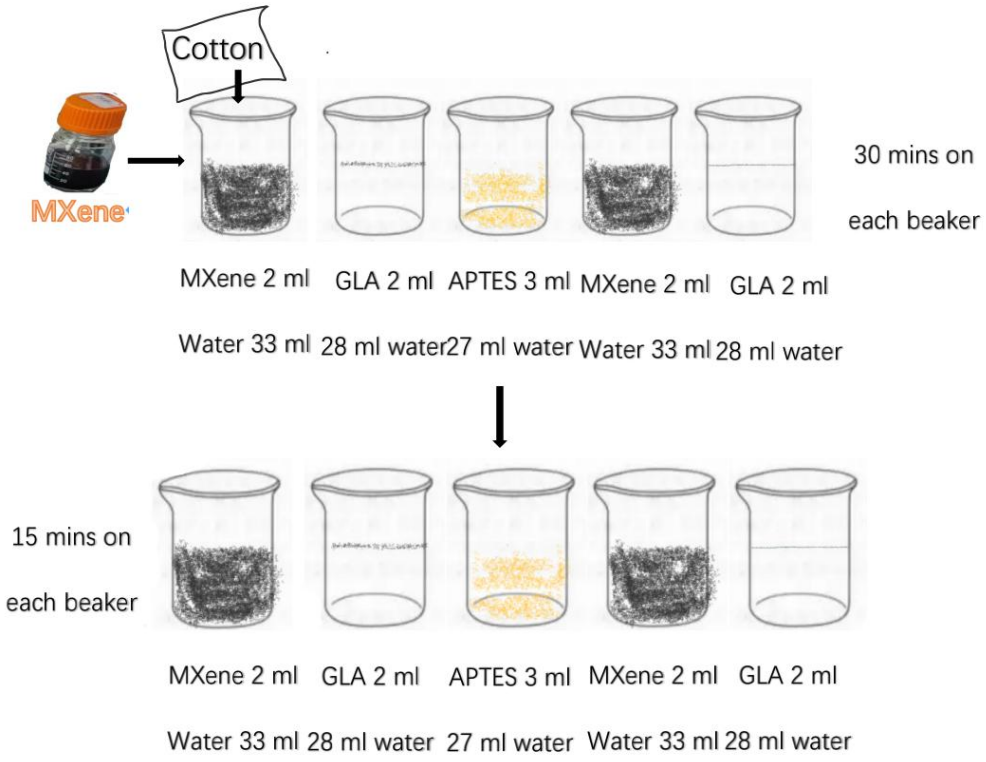

Figure 4. The flow chart of the cotton modification.

Chapter 3. Results and discussion

3.1 Surface modification of cotton cloth

In the picture below shows clearly that the modification of the attachment on the cotton surface. Where the rougher the surface of filter cloth is, the better efficiency of the filtration. Through the comparison, it indicates that some functional group already attached on the surface of cotton because of the color change. Even though there is some shrinkage of the measure of the area, there is little effect on the filtration steps, when the filter cloth is fix on the armored platform.

Figure 5. (a) The original cotton. (b) The first modified cotton. (c) The second modified cotton.

3.2 Adsorption performance of the cloth

The filtration of methylene blue liquid is implemented in the last step, through the modified cotton, some dyestuff has been absorbed. Therefore, the concentration variation can be tested through UV spectrophotometry. The working theory of UV spectrophotometry can be described as this. Like the visible light absorption spectrum, in the UV absorption spectrum analysis, the relationship between absorbance and substance concentration at the selected wavelength can also be described by the absorption law of light, namely Lambert Beer law:

$A= \lg (I_o /I) = \varepsilon bc$

Where A is the solution absorbance, I_o is the incident light intensity, I is the transmitted light intensity, ε Is the molar absorption coefficient of the solution, B is the thickness of the solution, and C is the concentration of the solution.

The chart below shows the reduction of density of methylene blue liquid. Where the starting concentration is 0.375 mol/L, the concentration of the first filtrated methylene blue liquid is 0.325 mol/L, and the concentration of the second filtrated methylene blue liquid is 0.301 mol/L. The two filtration of methylene blue liquid are implemented separately.

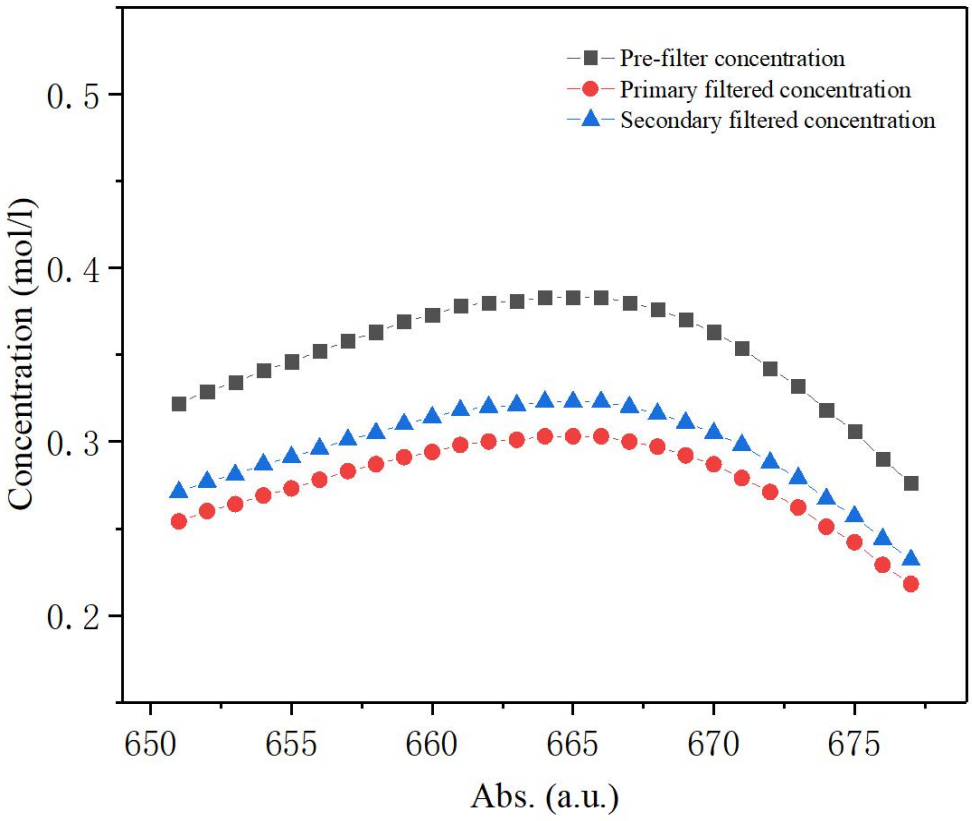

Figure 6. UV spectrophotometry of methylene blue liquid.

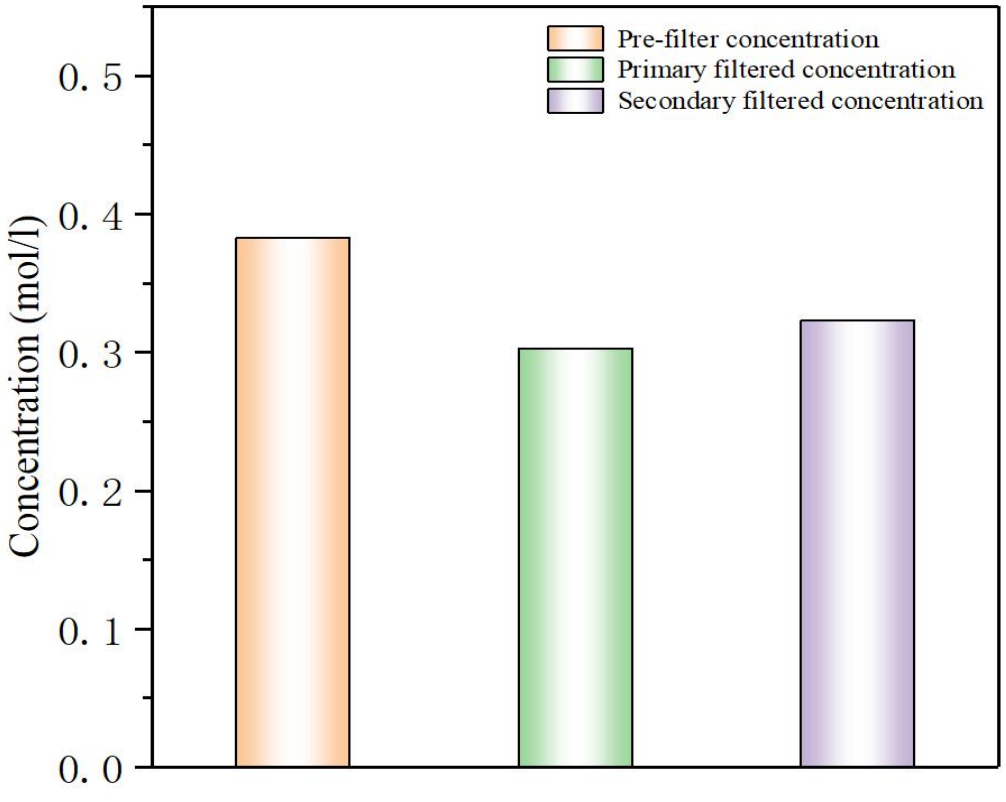

Figure 7. Comparison of concentration of methylene blue liquid.

Conclusion

In this thesis, the detrimental effect of wastewater is discussed in terms of the heavy metal ions and dyestuff contained in wastewater. Therefore, according to the techniques achieved by others before, a high efficiency and low-cost technology or purification filter cloth made by cotton was tested in this experiment. Where the cotton modified by some liquids with functional groups such as MXene. The advantages of this new materials were tested which shows a good performance with the decrease of concentration of methylene blue liquids in this experiment. Last but not at the least, even though this experiment is designed easy, it is obviously to see that the changes on the surface of the cotton, where is rougher, this is already reached a satisfied suppose on the begin of the experiment, and the concentration variation is not having any expectation at the begin of the experiment since no one has done this before. This experiment offers a possible way to filter wastewater by using MXene liquids. The concentration of MXene liquids and the carrier of it is still can be researched. In this experiment cotton is a good carrier with suitable flux and low cost, which is also easy to be attached with functional groups. There is some difference between the first filtrated liquids and the second one, that might because some little variation of MXene liquids concentration of cotton adsorbed.

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