Adsorption performance of mixed dyes on alkalization loofah fibers

Yongli Wang, Jinyan Liu[1] and Xingxing Li

College of Chemistry and Chemical Engineering , Inner Mongolia University of Science & Technology, Baotou 014010, Inner Mongolia, China.

[1] liujinyan2007@163.com

Abstract: When the polyporous structures of loofah fiber is adequately exposed after alkali treatment,lignin, hemicellulose and pectin are removed. Specific surface area is increased to maximum, which means the efficiency of absorptivity is highest. In this paper, by using alkalization loofah （AL） as adsorbent, the effect of loofah fiber on waste water treatment is studied under the efficiency of loofah fiber which contain acridine yellow, methylene blue, mixed solution of the two dyes. The optimum treatment conditions of loofah fiber were studied from five aspects which include dosage, temperature, mixing time, pH and concentration. The results showed that the optimal conditions are 30°C, pH 8.0, 20mg dosage of loofah fiber in 40ml solution and mixing time 25min. The optimal treatment conditions of mixed dyes were studied from the aspects of mixing time, the dosage of AL and the molar ratio of the two components in the mixed dyes.

1. Introduction

Dye wastewater treatment, which has the characteristics of complex composition and is difficult to be degraded by nature [1].It has good stability and has been a problem of today's environmental management. As a result, it is of great significance to take the treatment of dye wastewater treatment into consideration seriously. Nowadays, the methods of treating dye wastewater can be physical adsorption, chemical method (chemical oxidation method, electrochemical oxidation method) and biological method (biological filtration, biological adsorption, activated sludge, etc.) [2,3] Activated carbon adsorbent is most widely used among many methods of adsorption[4]. However, it is too expensive to use activated carbon in large-scale industrial treatment.

Compared with the traditional physical and chemical methods, bioabsorbents [5] are increasingly favored by researchers and enterprises with the advantages of small energy consumption, recyclable, environmentally friendly and low cost.

The status of research on adsorbent made by modified plant materials: The effect may be poor when many plant materials adsorption are used directly. However, after having done a modified experiment, capacity of most of them is generally greatly improved[6-9]. Loofah has the porous structure of the three-dimensional fiber tube with better mechanical strength, mature loofah have the characteristics of having bigger pores and larger specific surface area. So that it has to play the role of adsorption of dyes or metal ions in the potential of adsorbents [10]. Loofah used as an adsorbent has been reported [11], cellulose mainly contains carbonyl and hydroxyl, lignin contains a variety of functional groups, such as phenols and aliphatic carbonyl, hydroxyl functional groups and methoxy, they combine with the aqueous solution by forming the ion bonding of with the lone pair electrons in

oxygen. Because hydroxyl in the glucopyranyl ring in cellulose, hemicellulose, lignin is active, they can occur a series of chemical reactions, such as etherification, esterification and graft copolymerization [12] modified methods generally through alkalization [13] to increase the specific surface area of the adsorbent, so as to achieve the purpose of enhancing the adsorption force. Its surface area value is of up to 123 m^2/g and it can also be used as natural adsorbents to the organic dye molecules or ionic contaminants. The adsorption process of natural loofah fiber on adsorbate is mostly spontaneous adsorption process. The adsorbability is related to the initial concentration of adsorbate, pH, adsorption time and temperature. The lignin and hemicellulose in the loofah can be removed to some extent by the treatment of loofah, which does not destroy the basic chemical structure of the loofah, and can effectively increase its specific surface area and thermal stability.

2. Materials and methods

2.1. Experimental apparatus and reagents
Instrument: Ultraviolet-visible spectrophotometer(T6 new century,Beijing Purkinje General Instrument Co., Ltd.）, Electronic balance (Sartorious,Germany), Digital acidimeter（PHS-3D,Shanghai Jingke Leici）

Chemicals: Acridine yellow（AR,Sinopharm Chemical Reagent Co., Ltd.）$C_{15}H_{16}ClN_3$,relative molecular weight 438.12,methylene blue（AR,Sinopharm Group Chemical Reagent Co., Ltd.）$C_{16}H_{24}ClN_3O_3S$,relative molecular weight 373.9。loofah, hydrochloric acid, sodium hydroxide are of analytical grade（AR,Sinopharm Group Chemical Reagent Co., Ltd.）(Figure 1).
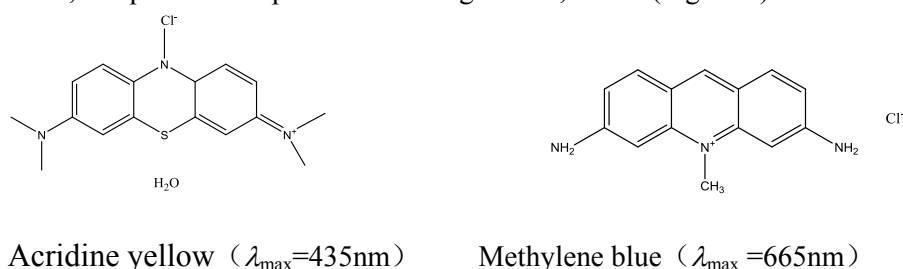

Acridine yellow（λ_{max}=435nm）   Methylene blue（λ_{max}=665nm）

Figure 1. Structural formula of dye molecule

2.2. Experimental Methods

2.2.1. Pretreatment The loofah was dissolved in 500ml 4% NaOH solution, heated to boiling and stirring, reaction 3h, washed with distilled water to neutral, dried 6h (70℃), get alkalization loofah(AL), set in the dryer. After treatment, most of the pectin, hemicellulose and lignin were removed, so that more cellulose leak out, the use of cellulose porous structure, the greater the specific surface area for adsorption.

2.2.2. Dye adsorption Adsorption experiment: The dosage of acridine yellow solution with mass concentration of 1×10^{-5}mol/L is 2000 ml. That was prepared in flask as simulated dye wastewater. 100ml dye solution was added to the conical flask separately, and the alkalized loofah with different mass was added into the each conical flask, then the sample was shaken and standing a certain period of time. After dilution, the absorbance was measured by a spectrophotometer. The concentration of acridine orange in the sample was calculated by the standard curve of absorbance and mass concentration of acridine orange solution which had been drawn. According to the formula, the loofah adsorbability Q_e（mg/g）on acridine orange can be calculated.

$$Q_e = (C_0 / C_e)V / m \qquad\qquad (1)$$

C_0 is the mass concentration (g/L) of the initial sample acridine orange, C_e is the acridine orange mass concentration (g/L) of the equilibrium concentration sample, V is the volume of the aqueous solution (L), m is the loofah quality (g).

2.2.3. The adsorption isotherm equation Added the AL to the mixed dyes solutions, the concentration is from 0.2 to 2.0×10^{-5} mol/L and the molar ratio of the two dyes is 1:1. The concentraion of AL is 500 mg/L. At 303K, the absorption equilibrium was reached after vibration for 1hour. After centrifugation separation, the supernatant was used to measure the absorbance of the two dyes, and the Langmuir and Freundlich isotherm curves were used to simulate.

Langmuir adsorption isothermal equation describes the adsorption of monomolecular layers, such as (2) linear expression:

$$C_e / Q_e = 1/Q_m + C_e /(bQ_m) \tag{2}$$

Q_e is the equilibrium adsorbability of dye(mol/L), C_e is the concentration of dye when the adsorption equilibrium is reached(mol/L), b is the adsorption equilibrium constant(L/mol). With data of temperature and adsorption heat according to experimental, with C_e / Q_e and C_e to make a straight line, through the slope of the straight line and intercept, b and Q_m values can be obtained.

The Freundlich isothermal adsorption equation was expressed with the linear (3) as follows:

$$\ln(Q_e) = \ln(K_f) + \ln(C_e)/n \tag{3}$$

The units of C_e and Q_e are the same, and the values of n and K_f can be obtained by plotting the slope and the intercept of the straight line. K_f is related to the adsorbability, and the greater the value, the better the adsorbent. n reflects the adsorbability of adsorbents, the greater n is ,the better the adsorption performance works.

3. Results and discussion

3.1. Adsorption performance of loofah on acridine yellow(Figure 2)

3.1.1. Acridine yellow UV-visible absorption spectrum and the standard curve

3.1.2. The influence of loofah added quantity

As shown in Figure3, when the rotating speed is constant, after stirring for 30 mins, the degradation effect of 40ml 1×10^{-5} mol/L acridine yellow can be calculated.It can be seen from the figure that, with the increase of the amount of adsorbent. When the dosage of 25mg, the adsorbability can be achieved 19mg/g, the maximum adsorbability of 21mg/g when the dosage is 70mg. In order to rational use the adsorbent; the following is selected loofah amount of 20mg in 40ml solution of dye.
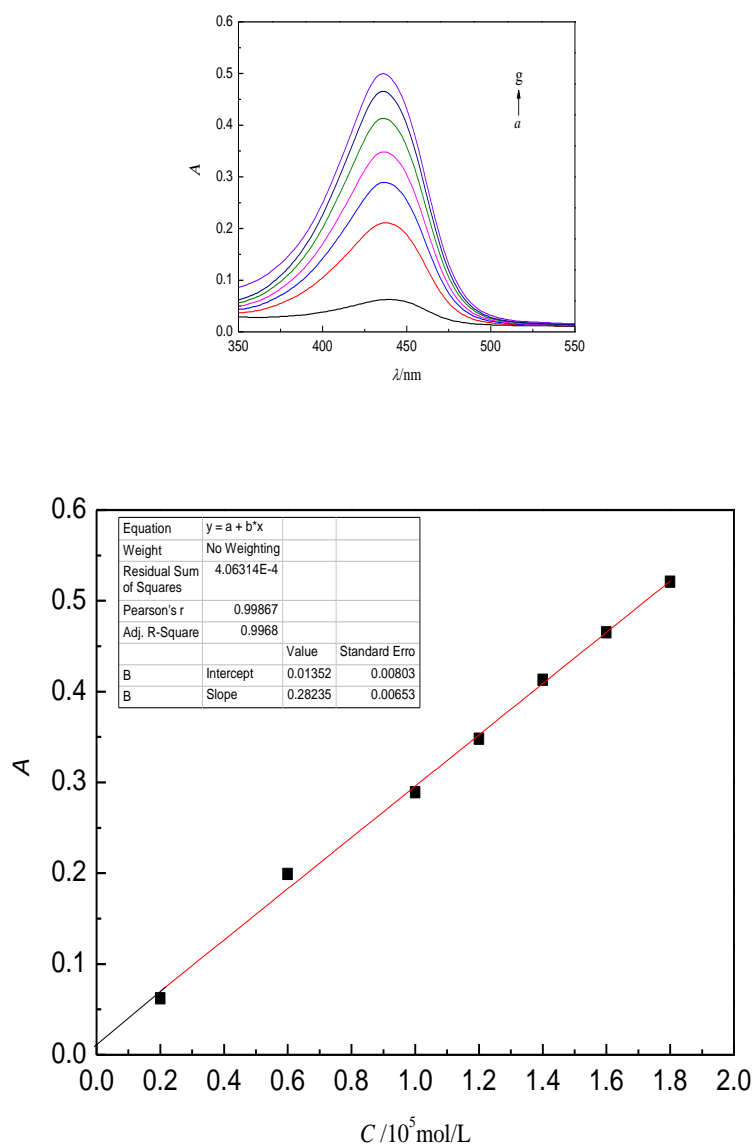
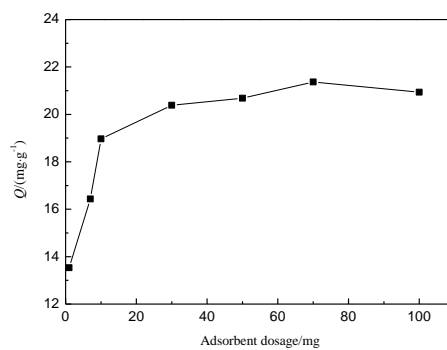| Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	4.06314E-4		
Pearson's r	0.99867		
Adj. R-Square	0.9968		
		Value	Standard Erro
B	Intercept	0.01352	0.00803
B	Slope	0.28235	0.00653

Figure 2. Acridine yellow standard curve.

Figure 3. Different content Loofah on the influence of acridine yellow solution.

3.1.3. The influence of degrading time As shown in Figure 4, the solution of 40ml and 20mg contains acridine yellow, which is 1×10^{-5} mol/L. It can be seen that the degradation effect is the best after 25min treatment, and the amount of adsorption increases with time and increases to 19mg/g. Even if the time extended, the adsorbability is no longer change, so adsorption time should be 25min.
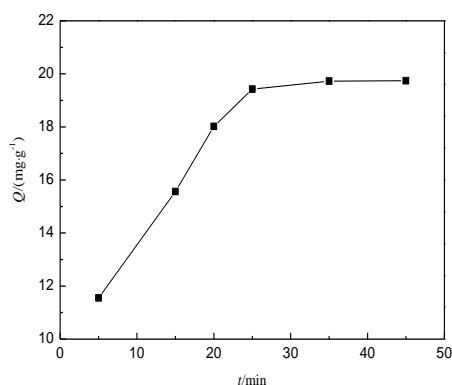

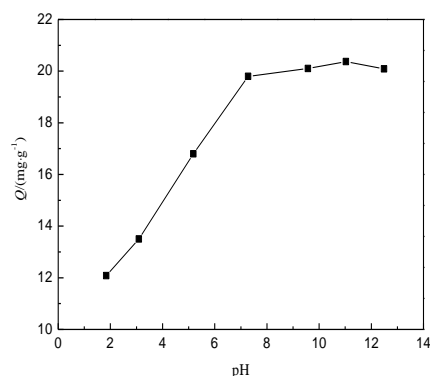**Figure 4.** The influence of adsorption time on adsorption effect.

Figure 5. The influence of pH value on adsorption.

3.1.4. Influence of pH It can be seen in Figure 5, the concentration of acridine yellow solution of 40ml is 1×10^{-5} mol/L. With the increase of pH, when the AL dosage is 20mg and stirring time is 25min, the adsorbability gradually increased. In highly acidic solution, the repulsion of like electric charges is dominated, the -OH on loofah fibers surface is protonated with positive charge. With the pH value increasing, the OH^- adsorption of loofah fiber is negatively charged. According to the principle: the charge are attracted to one another by their opposite charges, adsorption increased. So the pH should be maintained 8.0 in the adsorption process.

3.1.5. The influence of temperature As shown in the Figure 6, when acridine yellow solution of 1×10^{-5} mol/L and 20mg alkalization loofah fibers are mixed in 40ml aqueous solution, With the temperature changing, stirring time is 25min, the adsorbability is 19 mg/g. With the temperature rising, the adsorbability was slightly decreased, so that the temperature was not substantially controlled during the course of the experiment, as a result, the degradation of the dye was carried out at 30 ℃.
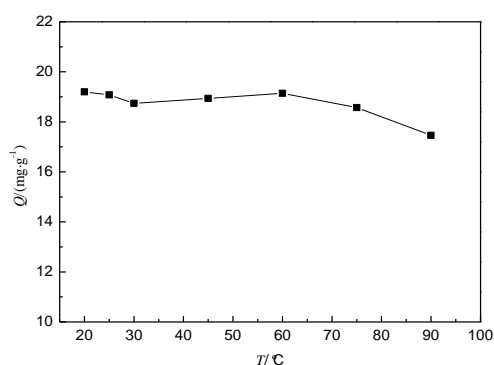

Figure 6. The influence of temperature on the adsorption.
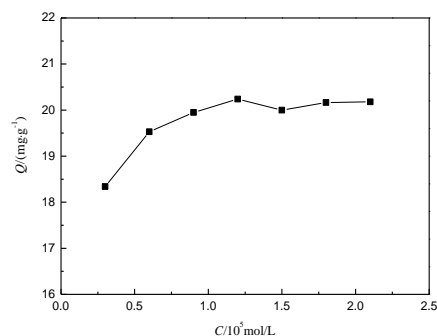

Figure 7. The influence of acridine yellow concentration on adsorbability.

3.1.6. The effect of acridine yellow solution concentration As shown in Figure 7, when the concentration of acridine yellow is between 0.2 and 2.0×10^{-5} mol/L, the adsorption experiment of the dye under the above-mentioned conditions shows that the concentration of acridine yellow does not substantially affect the adsorption; adsorption amount remained at about 20mg/g. The possible reason is that the adsorption of loofah does not be changed under different concentrations. For any concentrations of solution, the degradation effect is the same.

In summary, the concentration of acridine yellow solution of 40ml is 1.0×10^{-5} mol/L, the dosage of loofah fibers was 20mg, the stirring time was 25min, pH was 8.0, the temperature was maintained at 30℃. The adsorption amount can be up to about 20 mg/g. Under the same conditions, the adsorption amount of the loofah under untreated treatment was merely 13.5mg/g.

The hydrogen bonds between the intramolecular and intermolecular molecules of cellulose make the cellulose aggregate into a multi-layered high-crystallized compound, and the derivatization reaction is difficult to take place. The interaction between cellulose and alkaline solution acts as a function of elimination crystal and improvement of reactivity. After the alkali treatment, the lignin is removed, the surface becomes smooth, and there are many irregularly distributed pores, the fibers are exposed internally. After alkali treatment, the porous structure of the loofah fiber and the surface structure make it a huge adsorption specific surface area, and also make it some special adsorption characteristics.

3.2. Alkalization loofah adsorption of methylene blue solution
According to the above-mentioned method of acridine yellow absorption by the alkalizing loofah, the adsorption of methylene blue on AL is carried out. The optimum adsorption conditions and adsorption capacities are shown in Table 1.

In summary, adsorptions of alkalization loofah on methylene blue and on acridine yellow are similar, so the adsorption characteristics of the mixed two dyes on AL were studied in the following.

Table 1. The optimum adsorption conditions of methylene blue parameters.

Condition	AL added amount (mg)	dye concentration (mol/L)	stirring time (min)	Temperature (℃)	pH	Adsorbance capacity (mg/g)
data	30	3×10^{-5}	30	30	8.0	18.21

3.3. The adsorption characteristics of AL on mixed dyes

3.3.1. The effects of adsorption time Figure 8 was shown the UV-visible absorption spectrum of the mixed dyes solution of the loofah process at three different times. The concentration of methylene blue is 3×10^{-5} mol/L and the concentration of acridine orange is 1×10^{-5} mol/L. It is shown that the maximum absorption wavelength of acridine orange is still 450 nm, the one of methylene blue 650 nm, there is not interference between the two dyes. With the extension of time, the absorbance of the two dyes is reduced, indicating that the two dyes can be adsorbed by AL. Figure 9 shows the relationship between the adsorption amount of the two dyes and time. It is found that the adsorbability increases with the increase of time.

The research about influence on these two mixed dyes adsorbability is studied in the following.
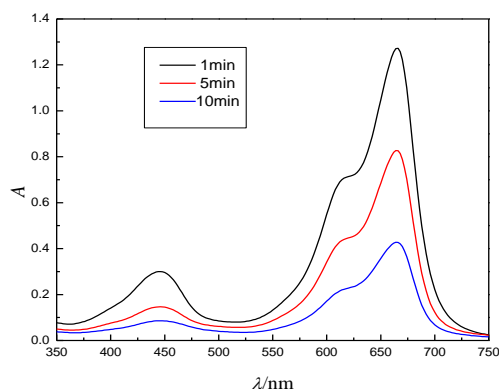
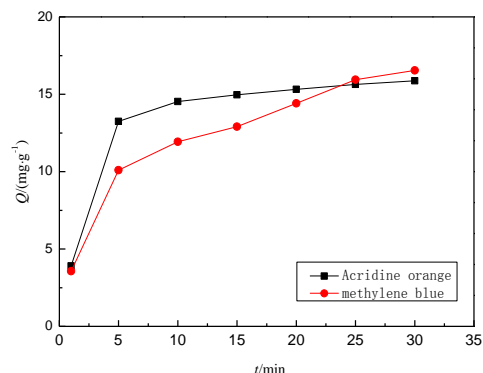**Figure 8.** UV-vis spectra of the two mixed dyes.

Figure 9. The influence of the utilize time of mixed dyes on adsorbability.
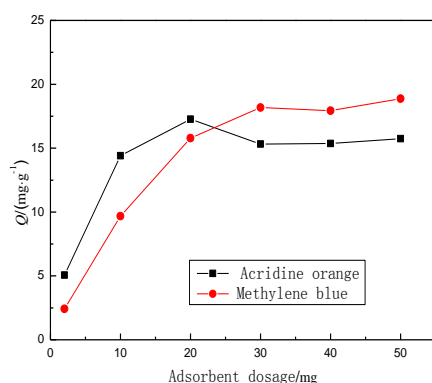

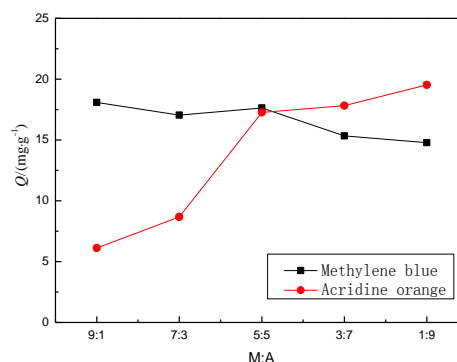**Figure 10.** The influence of the contents of mixed solution on adsorbability.

Figure 11. The influence of the molar ratio of mixed solution on adsorbability.

3.3.2. The influence of quantity alkalization loofah fibers on adsorbability As it shown in Figure 10, the concentration of methylene blue is 3×10^{-5}mol/L and the concentration of acridine orange is 1×10^{-5}mol/L. It can be seen that the adsorbability of the two dyes increases with the increase of the adsorbent. At the beginning, the adsorption amount of acridine yellow is relatively larger than methylene blue. When the adsorbent dosage is 22mg, the adsorption amount of methylene blue would exceed acridine yellow. And both adsorptions are more than 15mg/g.

3.3.3. The influence of two dyes molar ratio As shown in Figure 11, the adsorption effect will be changed when the ratio of the two dyes is different. When the methylene blue is more than acridine orange, the adsorption amount of methylene blue is 18mg/g. The adsorption amount of acridine yellow is increasing with the increasing of molar ratio. At the molar ratio is 1: 9, the adsorbability of acridine yellow was also up to 19 mg/g when molar ratio was changed.

3.3.4. Adsorption isotherm equation The results of simulating various isothermal curves at different temperatures are shown in Table 2 and Table 3.

Table 2. Langmuir isothermal adsorption equation.

	acridine yellow			methylene blue		
T/℃	Q_m(mg/g)	b(L/mg)	R^2	Q_m(mg/g)	b(L/mg)	R^2
30	20.48	0.5584	0.8882	21.59	0.1339	0.8897

Table 3. Freundlich isothermal adsorption equation.

	acridine yellow			methylene blue		
T/℃	1/n	K_f	R^2	1/n	K_f	R^2
30	0.0715	22.53	0.9282	0.0604	32.58	0.8968

In summary, the alkalization loofah has a good adsorption effect on acridine yellow and methylene blue. Adsorption is in mild conditions. The maximum adsorbability can reach more than 15mg/g, consistent with Langmuir and Freundlich isothermal adsorption models. Acridine yellow and methylene blue are similar in structure, with a positive charge.Acridine yellow maximum absorption wavelength is at 435nm, the maximum absorption wavelength of methylene blue is at 665 nm. The UV-visible spectrum between the two does not overlap.There is no interference in the process of alkalizing loofah, which provides a prerequisite for the determination of two dye adsorption.

Acknowledgment

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