Iranian Journal of Analytical Chemistry
Volume 5, Issue 2, September 2018 (17-22)

مجله ایرانی شیمی تجزیه
دوره ۵، شماره ۲، مهر ماه ۱۳۹۷ (۲۲-۱۷)

استفاده از جاذب‌های زیستی مقرون به صرفه، جهت حذف رنگ از پساب‌ها

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تاریخ دریافت: ۱۲ مرداد ۱۳۹۷ تاریخ پذیرش: ۱۶ شهریور ۱۳۹۷

Use of Cost-Effective Untreated Biomasses as Potential Biosorbents for Dye Removal From Wastewater

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Received: 3 August 2017 **Accepted:** 7 September 2018
DOI: 10.30473/ijac.2018.5095

چکیده
در این مقاله دو گیاه بومی به عنوان جاذب‌های زیستی با نام‌های سیمرنیوپتسیس‌اوچری و ایسرنگوندا، به صورت فرآوری نشده، جهت حذف رنگ متیلن‌بلو از پساب‌ها، مورد استفاده قرار گرفته‌اند. در این طرح، بررسی ایزوترم‌های لانگمویر و فرندلیچ، بررسی‌های سینتیک و بررسی پارامترهایی نظیر غلظت بهینه جاذب و زمان بهینه‌ی جذب انجام شده است. اسیدیته‌ی مناسب محیط به هنگام حذف آلاینده برای سیمرنیوپتسیس‌اوچری برابر با ۶ و برای ایسرنگوندا برابر با ۵ گزارش شده است. غلظت بهینه‌ی جاذب زیستی برای سیمرنیوپتسیس‌اوچری برابر با ۰,۳ گرم و برای ایسرنگوندا برابر با ۰,۵ گرم می‌باشد. زمان بهینه‌ی جذب برای برای سیمرنیوپتسیس‌اوچری ۱۰ و برای ایسرنگوندا ۱۵ دقیقه گزارش شده است. زمان بسیار کوتاه و میزان کم جاذب‌های زیستی مورد استفاده، نشان دهنده‌ی کارایی بالای این دو جاذب زیستی در حذف آلاینده رنگ می‌باشد. جذب متیلن‌بلو بر روی هر دو جاذب از الگوی جذب لانگمویر تبعیت می‌کند. بررسی‌های سینتیکی جاذب‌های سیمرنیوپتسیس‌اوچری و ایسرنگوندا به ترتیب از الگوهای شبه درجه‌ی دوم و شبه درجه‌ی اول پیروی می‌کنند.

واژه‌های کلیدی
سیمرنیوپتسیس‌اوچری؛ ایسرنگوندا؛ متیلن‌بلو؛ جاذب زیستی؛ فرآوری نشده.

Abstract
Two locally available, cost-effective, renewable biosorbents including the untreated straw of Smyrniopsis Aucheri and untreated leaf of Acer Negundo were used for the removal of Methylene Blue dye. The influence of initial dye concentration on the dye removal was investigated. Isotherm and kinetics of the biosorption process were studied. The optimum pH was found to be 6 and 5 for Smyrniopsis Aucheri and Acer Negundo, respectively. The optimum biosorbent dosage was found to be 0.3 g for Smyrniopsis Aucheri and 0.5 g for Acer Negundo. The removal of Methylene Blue by Smyrniopsis Aucheri and Acer Negundo occurred during 10 and 15 min, respectively. The quick biosorption using reasonably small amount of such natural and untreated materials is a big advantages of this work for wastewater treatment applications in an environmental friendly way. The Langmuir adsorption isotherm model, was found to be the best applicable one to fit the experimental data. The pseudo-second and pseudo-first order kinetic models were applied well to describe the kinetics of Smyrniopsis Aucheri and Acer Negundo biosorption, respectively.

Keywords
Smyrniopsis Aucheri; Acer Negundo; Methylene Blue; Biosorbent; Untreated.

1. INTRODUCTION

Many hazardous compounds are being entered into the waters worldwide. Among these compounds, dyes (because of their toxicity, stability and making the water opaque) have been of concern. Dyes are extensively used in lots of industries, such as food, leather and textile industry, to color the products [1]. The existence of the dyes in water, even at very low dosage, is extremely undesirable.

Methylene blue (MB) dye (Fig. 1) is widely used by industries [2]. At dosages exceeding 5 mg/Kg, MB may precipitate serious serotonin toxicity, serotonin syndrome. Some of the by far known

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side effects of MB are mild bladder irritation, dizziness, headache, sweating, nausea/vomiting, diarrhea, frequent urination or stomach cramps.

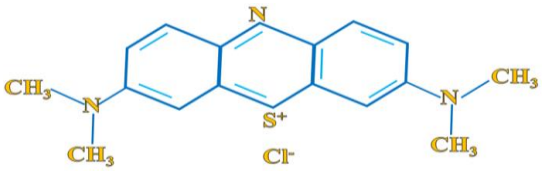

Fig. 1. Chemical structure of MB.

Lots of methods have been investigated and applied for the removal of the hazardous dyes from wastewater [3, 4]. One of the most promising physical methods is activated carbon, which is not eco-friendly and cost-effective [5]. Therefore, the search for effective, environmental friendly and low cost sorbents has been initiated for treating wastewater [6]. Biosorbents are becoming a promising sorbent to substitute the present chemical sorbents of dyes from wastewater [7].

In this paper, two biosorbents including untreated straw of the Smyrniopsis Aucheri (SA) and the leaf of the Acer Negundo (AN) are employed as sorbent of MB from aqueous solution.

Smyrniopsis Aucheri (Apiaceae) is a wild growing perennial plant, robust and massively distributed in Iran, Iraq, Anatoly and S. Transcaucasia regions [8, 9].

Acer Negundo (Boxelder) is one of the most widespread and best known of the maples. Its greatest value may be in shelterbelt and street plantings [10].

SA and AN have been found to be powerful biosorbents because of their wide availability and high efficiency. SA and NA cell walls have many functional groups for binding various pollutants (Fig. 2) [11].

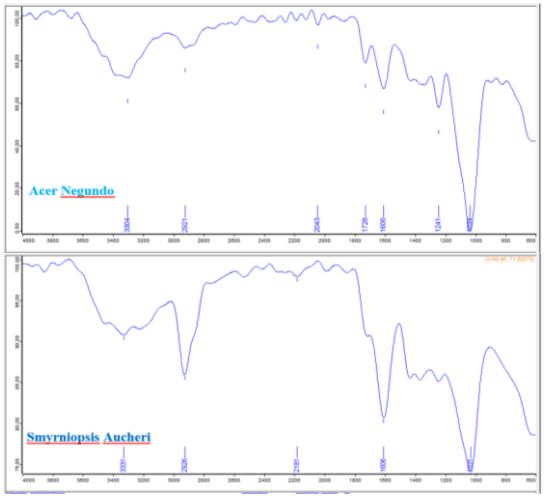

Fig. 2. FTIR spectra of SA and AN biomasses.

2. EXPERIMENTAL

2.1. Materials and instrumentations

All chemicals with the highest purity were purchased from Merck, Darmstadt, Germany. The stock solution of the basic dye of MB was prepared by dissolving it in distilled de-ionized water (pH=6 for SA and pH=5 for AN). The test solutions were prepared by diluting stock solution of MB to the desired concentrations.

The Smyrniopsis Aucheri straw was collected from a mountainous region in Yasouj, Iran. The leaf of the Acer Negundo was collected from a park in Brojerd, Iran. The substrates of SA and AN were dried to a constant dry weight.

The biosorbents substrates were grinded at coarse sizes followed by chopping them. Finely grinded particles were blended in a Waring commercial blender and sieved through a 600 mm sieve from Hebei, China (Mainland), Model Number: YS-C-645.

The pH was measured and adjusted using Metrohm pH/Ion meter model-686. The absorbance spectra of MB were taken in the range of 300 to 800 nm, using V-630 Jasco UV-Vis spectrophotometer.

2.2. Preparation of the dye solution

The effect of MB concentration on the amount of dye removal was studied. A solution with initial concentration of 20 mg/L was prepared, from which 100 mL volumes containing initial concentrations of 1 to 24 mg/L were adjusted. At concentration of 20 mg/L, the time taken to reach equilibrium for SA biosorbent was 10 min compared to the 15 min in the case of AN. For both biosorbents, with increasing time, the concentration of dye remaining in the solution decreased until equilibrium point was reached when no more MB dye can be adsorbed onto the biosorbents.

3. RESULT AND DISCUSSION

3.1. Effect of initial pH

The solution pH at which the sorption occurs may influence the extent of biosorption. The pH influences biosorption by governing the amount of ionization of the basic and acidic materials. In general, initial pH value may increase or decrease the maximum adsorption capacity [12]. It is due to the charge variation at the adsorbent surface with the change in pH.

The influence of pH on the amount of dye adsorbed was investigated by stirring 0.3 g and 0.5g of SA and AN, respectively, in a series of bottles containing 100 mL of MB of initial concentration 50 mg/L at various solution pH ranging from 1.0 to 9.0 for both biosorbents. The pH of MB dye solutions were adjusted using 0.1

M NaOH and/or 0.1 M HCl. Experiments were carried out at room temperature, constant stirring rate for 10 and 15 min for SA and AN, respectively. Concentration of MB before and after biosorption was measured using V-630 Jasco UV-Vis Spectrophotometer, by monitoring the changes in maximum absorbance which occurs at 640 nm for MB.

The percentage of dye removal was increased as the pH increased. It can be due to the electrostatic attraction between the negatively charged SA and AN surfaces and the positively charged MB molecules (Fig. 3). The optimum pH values were found to be 6 and 5 for SA and AN, respectively.

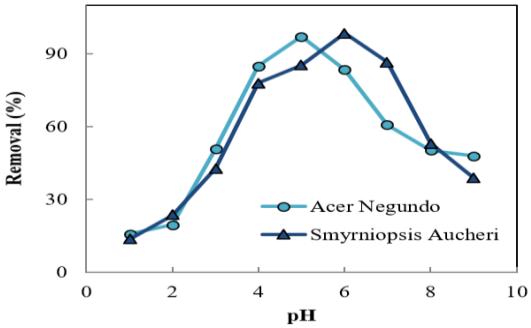

Fig. 3. Effect of pH on the MB removal from the solution by SA and AN at room temperature, contact time of 10 and 15 min for SA and AN, respectively.

3.2. Effect of biosorbent dosage

The influence of biosorbent dosage on the MB removal percentage was studied by contacting initial concentration of MB (50 mg/L) at the pH 6 and 5 where SA (0.1- 0.4 g) and AN (0.1-0.7 g) biosorbents were used, respectively, while stirring for 10 and 15 min. The results were shown in Fig. 4. As seen, the percentage of dye removal increases proportionally with an increase in the amount of SA and AN, until reaching their corresponding optimum values which are 0.3 and 0.5 g. At critical dosage of the biosorbents, the removal percentage almost reaches a constant value.

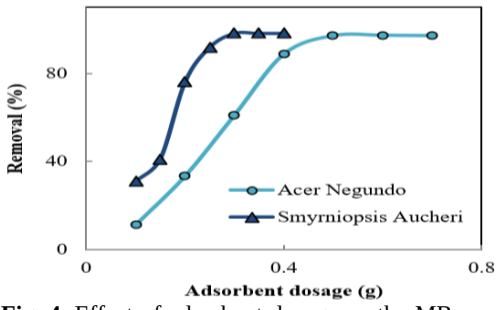

Fig. 4. Effect of adsorbent dosage on the MB removal from the solution by SA and AN at room temperature, pH 6 and 5, contact time of 10 and 15 min for SA and AN, respectively.

3.3. Effect of initial dye concentration

The influence of initial dye concentration on the biosorption efficiency was studied by varying MB initial dye concentration within the range of 1 to 24 mg L^{-1} (the results are shown in Fig. 5). It is obvious that the MB removal percentage was higher at lower initial concentrations of dye and smaller at higher initial concentrations. The outcomes clearly explain that the biosorption of MB, from its aqueous media, onto the SA and AN was dependent on its initial concentration.

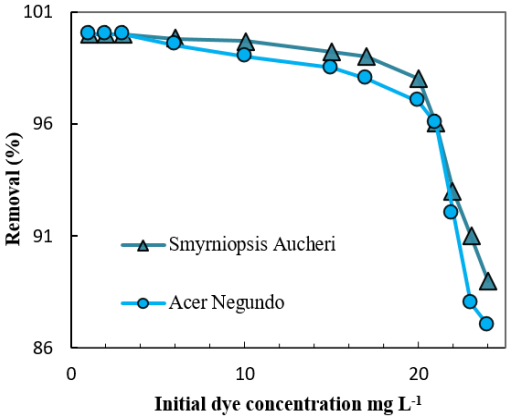

Fig. 5. Effect of initial dye concentration on the MB removal from the solution by SA and AN at room temperature, pH 6 and 5, contact time of 10 and 15 min for SA and AN, respectively.

3.4. Equilibrium sorption studies

Isotherms are essential to study the mechanism of dye adsorption onto the surfaces of the biosorbents [7, 13, 14]. Equilibrium sorption studies were carried out by contacting 0.3 g of SA and 0.5 g of AN with different initial concentrations of MB dye for 10 and 15 min at pH 6 and 5 for SA and AN, respectively, on a stirrer model UKA at room temperature. After stirring, the contents of flasks were decanted and the final concentration of dye was determined at the maximum of absorbance, using V-630 Jasco UV-Vis spectrophotometer.

To find the best fitting isotherm, the equilibrium data of this study were examined with two most general isotherm models including Langmuir and Freundlich.

The Freundlich isotherm expresses a specific sorption system while the adsorption occurs on a heterogeneous surface with interaction between the adsorbents. The Freundlich isotherm model can be defined in the following linear form:

$$\log(q_e) = \log(K_F) + \frac{1}{n}\log(C_e) \qquad (1)$$

The values of K_F and $\frac{1}{n}$ are calculated from the intercept and slope of linear plot of $\log(q_e)$versus $\log(C_e)$, respectively.

The Langmuir model indicates that the adsorption is monolayer and that the sorbent surface is made of sites which have the same energy level, thus the sorption energy is constant. This effect shows that the mechanism of sorption of MB onto biosorbents is a physical process.

The linear form of the Langmuir isotherm follows as:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \quad (2)$$

The values of Q_m and K_L are obtained respectively from the slope and intercept of the plot of Langmuir equation. The correlation coefficients for Langmuir isotherm are also obtained and shown in Fig. 6 and Table 1.

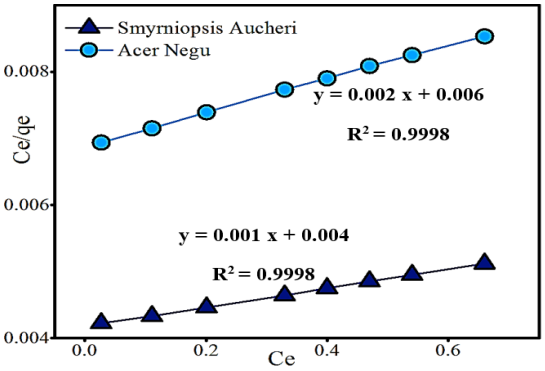

Fig. 6. Langmuir isotherm for MB biosorption by SA and AN at room temperature, pH 6 and 5, contact time of 10 and 15 min for SA and AN, respectively.

Table 1. The parameters corresponding to the Langmuir and Freundlich models.

Isotherm equation	Biosorbent	Parameters	Value
Langmuir	Acer Negundo	Q_m (mg/g)	500
		K_a (L mg^{-1})	3.321
		R^2	0.997
	Smyrnium Aucheri	Q_m (mg/g)	1000
		K_a (L mg^{-1})	2.50
		R^2	0.995
Freundlich	Acer Negundo	1/n	0.107
		K_F (L/mg)	0.693
		R^2	0.714
	Smyrnium Aucheri	Q_m (mg/g)	0.127
		K_a (L mg^{-1})	0.461
		R^2	0.825

The values of the correlation coefficients for Langmuir model are quite higher than those for Freundlich isotherms. The results show that the Langmuir isotherm fits well to the experimental data [14-16].

3.5. Kinetics study

The kinetics of MB dye biosorption by SA and AN was studied by contacting the MB of initial concentration of 50 mg/L with 0.3 g and 0.5 g of SA and AN, respectively, for various time intervals (Fig. 7).

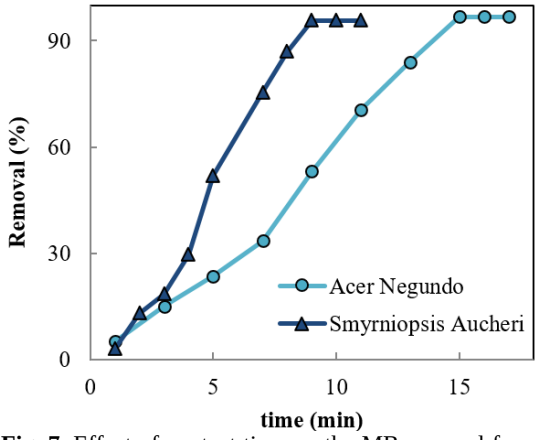

Fig. 7. Effect of contact time on the MB removal from the solution by SA and AN at room temperature, pH 6 and 5, contact time of 10 and 15 min for SA and AN, respectively.

Kinetics study characterizes the dye adsorption rate, which in turn governs the habitation time of any adsorption reaction. It is one of the most significant characteristics to study the efficiency of an adsorption process. In order to study the dye sorption kinetics of SA and AN biosorbents, two generally used kinetic models have been used to test the experimental data [17- 19]. The Lagergren pseudo-first-order model can be defined as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

which reduces to the following linear equation:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (4)$$

From the slope and intercept of the plot of the $\log(q_e - q_t)$ versus t, k_1 and q_e can be determined, respectively where k_1 is the rate constant (L/min), and q_e and q_t (mg/g) are the biosorption capacity, respectively, at equilibrium and at time t [20, 21].

The biosorption kinetic may be described by the pseudo-second order model [8], which is given by the equation bellow:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

Integrating the above equation in the interval 0 to t for t and 0 to q_t for q_t gives:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \quad (6)$$

As shown in Fig. 8, the pseudo-first order kinetic model applies well to describe the kinetics of the biosorption process for the SA, while for AN the pseudo-second order model applies (R^2> 0.994) (Table 2).

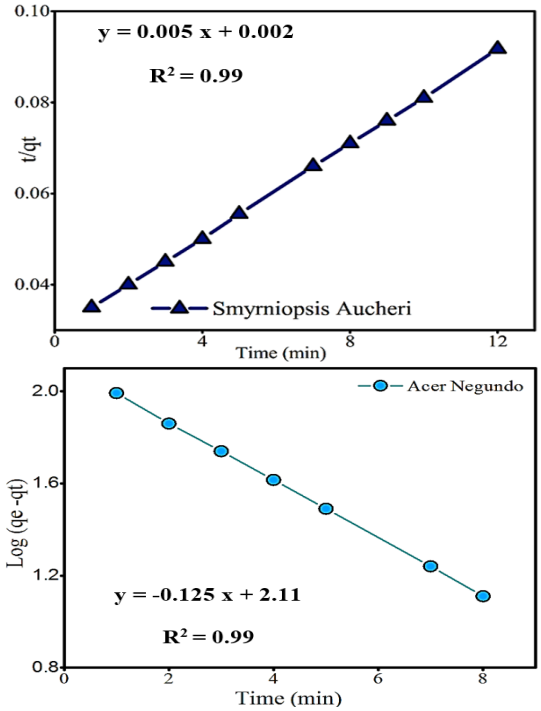

Fig. 8. Kinetics of MB biosorption by SA and AN at room temperature, pH 6 and 5, contact time of 10 and 15 min for SA and AN, respectively.

Table 2. The parameters corresponding to the first and second order kinetic models.

Smyrnium Aucheri		
First-order kinetic model		
K_1	q_e	R^2
0.0126	0.537	0.741
Second-order kinetic model		
K_2	q_e	R^2
0.913	0.974	0.995

Acer Negundo		
First-order kinetic model		
K_1	qe	R^2
0.148	0.987	0.996
Second-order kinetic model		
K_2	qe	R^2
0.0064	0.333	0.648

3. 6. This work compared with literature

The biosorbents used in this work were found to be much more efficient than the other biosorbents reported in literature [22, 23] (See Table 3).

4. CONCLUSION

SA and AN were found to be powerful biosorbents for removing basic dyes from wastewater. Both SA and AN had great capacities to remove dye from wastewater in quite short time using low dosage of sorbents. For SA, the optimum condition of 0.3 g, 10 min and 6 was found for biosorbent dosage, contact time and pH, respectively, while it was 0.5 g, 15 min and 5 for AN. The biosorbents used in this work were found to be much more efficient than the other biosorbents reported in literature. The most significant advantages of these two biosorbents are their wide availability and high efficiency in addition to their cost-effectiveness and eco-friendly nature. Comparing these two biosorbents, shows that the SA is more efficient than the AN in terms of the dye removal percentage and the speed of process

These make the SA and AN applicable for the technology of removing dyes from wastewater. Besides, the considerably short time and very low adsorbent dosage used for the applied biosorption process are the significant evolution for dye removal.

ACKNOWLEDGMENTS

The authors would like to thank Yazd University Research Council, IUT Research Council, Dr. Bohumil Volesky of department of Chemical Engineering, McGill University and Excellence in Sensors for financial support of this research.

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Table 3 The comparison of different biomass adsorbent, in terms of their operating conditions.

Biomass	Pollutant	Amount of biosorbent	pH	Contact time (min)	Reference
Nostoclinckia HA46 (cyanobacterium)	Reactive Red 198	-	2	120	22
Untreated coffee residues	toluidine blue (TB)	2 (g/L)	3	1440	23
	crystal violet (CV)	2 (g/L)	6	1440	
Straw of the Smyrniopsis Aucheri	Methylene Blue	0.3 (g)	6	10	This work
Leaf of the Acer Negundo	Methylene Blue	0.5 (g)	5	15	This work

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