Al-Khwarizmi Engineering Journal, Vol. 17, No. 1, March, (2021) P. P. 43- 50

Al-Khwarizmi Engineering Journal

Adsorption of Indigo Carmen Dye by Using Corn Leaves as Natural Adsorbent Material

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(Received 26 September 2020; accepted 16 November 2020)
https://doi.org/10.22153/kej.2021.11.002

Abstract

In this paper, the ability of using corn leaves as low-cost natural biowaste adsorbent material for the removal of Indigo Carmen (IC) dye was studied. Batch mode system was used to study several parameters such as, contact time (4 days), concentration of dye (10-50) ppm, adsorbent dosage (0.05-0.25) gram, pH (2-12) and temperature (30-60) ºC. The corn leaf was characterized by Fourier-transform infrared spectroscopy device before and after the adsorption process of the IC dye and scanning electron microscope device was used to find the morphology of the adsorbent material. The experimental data was imputing with several isotherms where it fits with Freundlich (R^2 = 0.9937) and followed pseudo second order kinetic. The highest removal percent was equal to 91% of the dye which makes the corn leaves a suitable efficient material for the removal of IC dye from aqueous solutions.

Keywords: *Adsorption, batch, Corn leaf, Indigo Carmen dye, Isotherm, Kinetics.*

1. Introduction

The wastewater that produced from textiles, papers, food, and pharmaceutical industries contains complex organic and aromatic compounds due to the types of dyes used that may be harmful and toxic to humankind and other living creatures. The major problem of the contaminated wastewater is that it contains very low concentrations of the dyes that minimizes the quality of water resource and increase environmental concern, that is why it must be treated before disposal to the assigned places [1]. Many methods are used these days for the treatment of polluted and colored wastewater. One of the common methods that widely used is adsorption due to its ease of operation, high recovery and efficiency [2].

Agriculture bio-waste is used as alternative adsorbent materials for the adsorption of dyes because of its cheapness, high surface area, high removal efficiency, availability, and eco-friendly to the environment which are used for fixing environmental pollution problems. The adsorption of dyes by using biowaste adsorbents had been studied by many researchers such as the adsorption of Methyl orange by corn leaves [3], Aniline blue by rice husk [4] and methyl red by tree park powder [5].

Indigo carmine is a synthetic dye which is used as dermatological agent, biological stain and antibacterial agent. Also it is a carcinogen material, recalcitrant, and very toxic to mammalian cells [6]. Indigo carmen dye structure is shown in Figure 1.

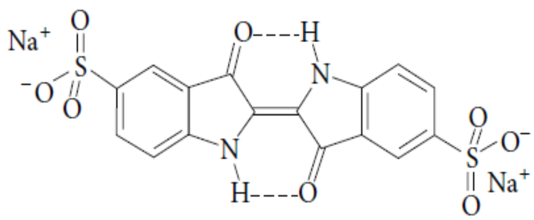

Fig. 1. Structure of Indigo carmen dye.

The aim of this paper is to study the adsorption of Indigo carmen dye by using corn leaves from aqueous solution.

2. Materiais and Methods

A group of runs were conducted at Al-Khwarizmi college of engineering / Baghdad University to study the effect of several parameters on the adsorption process.

A sets of design of experiments were used for batch adsorption studies in which different concentrations of the dye from 10 to 50 ppm were put in 100 ml containers and mixed with various amounts of the adsorbent from 0.05 to 0.25 g/L with constant temperature (30°C) and initial pH (6.2). In the first set of experiments, containers were shaken at 150 rpm with contact time in the range (1-4) days with a step of one day.

The effect of both pH and temperature was investigated using another set experiment. The ranges were (2-12) for pH and (30-60)°C for temperature respectively. Factors studied in the first set were fixed at the optimum values.

The equilibrium concentrations of IC dye were determined by measuring the absorbance using UV-visible spectrophotometer (Shimadzu 1800) device at a wavelength of 610 nm. The plot of absorbance vs. concentrations was observed as linear as shown in Figure 2.

This curve will be the standard expression of the dye concentration with respect to the absorbance recorded at 610 nm using UV-Vis spectrophotometer all over the experimental work. The equilibrium concentrations and dye removal efficiency were calculated using the following equations [7]:

$$Q_e = (C_o - C_e) \times \frac{V}{M} \quad \dots (1)$$

$$\%\ removal = \frac{Co-Ce}{Co} \times 100 \quad \dots (2)$$

where C_e and C_o are the equilibrium and initial concentrations of the dye (mg/L), respectively, Q_e is the equilibrium dye concentration per adsorbent amount (mg/g)

V is the volume of dye solution (L)

M is the dosage of adsorbent (g).

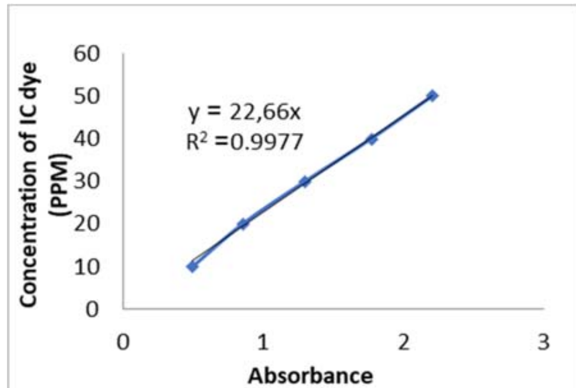

Fig. 2. Calibration curve of IC concentration vs. absorbance.

The corn leaves were collected from College of Agriculture Engineering Sciences, University of Baghdad during the summer season. Washed few times to get rid of dust and other impurities, then, dried in the oven at 50 °C overnight. After that, they crushed and sieved to get a particle size of 125 μm, then, saved in a dried containers for further use.

The dye was prepared by dissolving 1 g in 1 L of distilled water to get the stock solution with concentration of (1000 ppm), then diluted to obtain several concentrations of (10-50) ppm.

3. Resuits and Discussion

Characterization of Corn leaves

Fourier Transform Infrared spectroscopy (FTIR) was used to characterize the corn leaves powder. The spectrum is shown in Figures 3 and 4. By observing Figure 3, it can be seen that the functional OH group absorption at the region of (3200-3500) cm^{-1} stretching vibration in phenolic and aliphatic structures. The band at (2910-2920) cm^{-1} is assigned to C–H stretching vibration in aromatic methoxyl groups. A peak of C=C stretch was observed at (1650-1660) cm^{-1} which refers to alkenyl group, also, C-O single bonds appear at around 1180 cm^{-1} [8][3].

The change in the surface of adsorbent shows that there was an adsorption process happened during the sorption and strong interaction between IC dye and the corn leaves was predominant. The Scanning Electron Microscopic (SEM) showed the morphological picture of the corn leaves particles which is bright on the surface as shown in Figure 5.

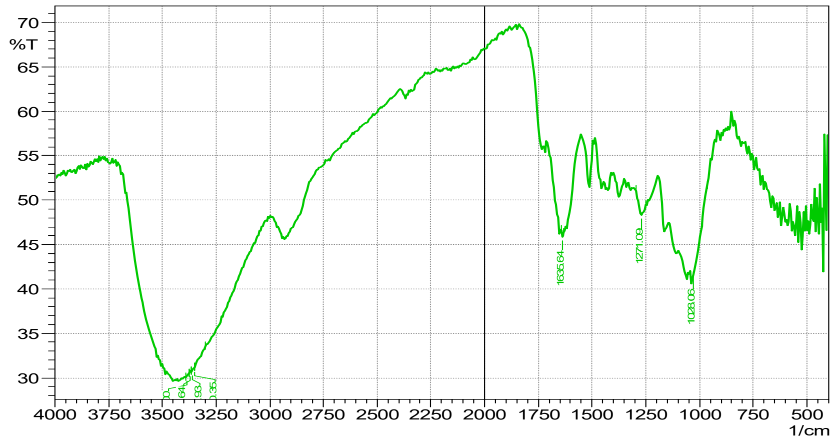

Fig. 3. FTIR spectrum of corn leaves adsorbent before adsorption.

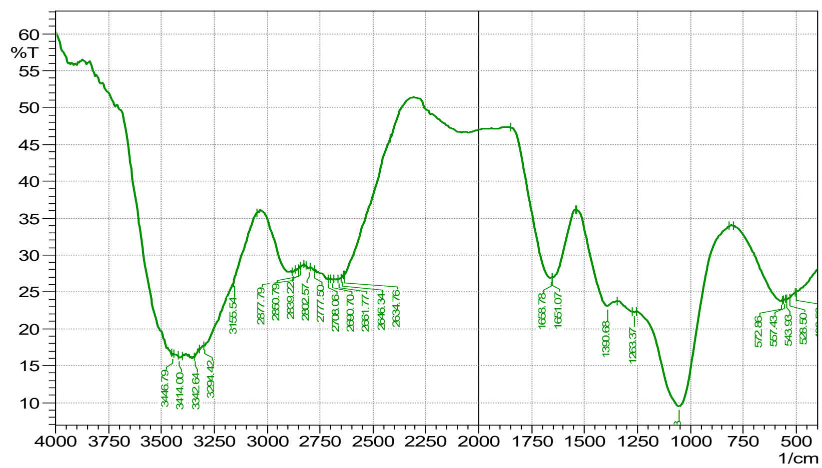

Fig. 4. FTIR spectrum of IC dye with corn leaves after adsorption.

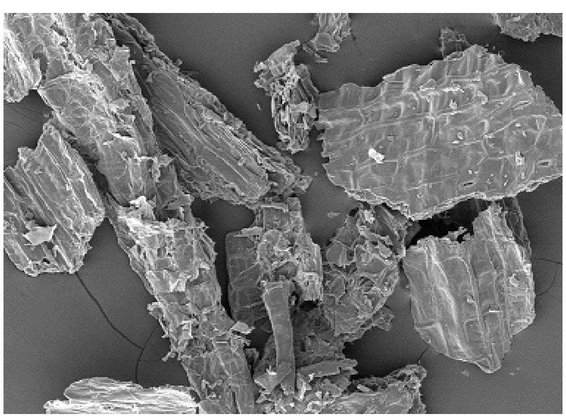

Fig. 5. SEM of corn leaves adsorbent.

Effect of Concentration

The effect of the removal efficiency on the concentration is shown in Figure 6. As the concentration increased from 10 to 50 ppm, the removal efficiency increased at the beginning, then, decreased until it reached the equilibrium point. The adsorption capacity also decreased with increasing the concentration. This can be explained to the lack of the free active sites on the adsorbent surface which is fastly reached to the saturation state. This results is matched with the results of [9] where the removal efficiency also increased then decreased until it reached the equilibrium point (91.2%) for Basic violet dye. The best selected IC dye concentration was equal to 10 ppm.

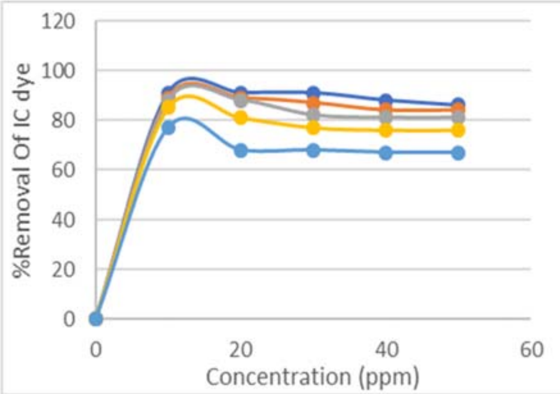

Fig. 6 The effect of initial dye concentration on the removal efficiency of IC dye at 30 ºC and contact time of 4 days.

Effect of Adsorbent Dosage

The effect of the adsorbent dosage on the dye removal percent is shown in Figure 7. As the dosage of corn increased, the removal efficiency increased due to the increase of the surface area of the adsorbent material. The adsorption capacity decreased as the dosage increased as the particles of the adsorbent overlapping, as demonstrated by [10] where the sorption rate of aniline and methyl orange dyes decreases in the higher dosages of aloe vera leaves waste. The best amount of adsorbent dosage was 0.25 gm for achieving the higher removal percentages of dye.

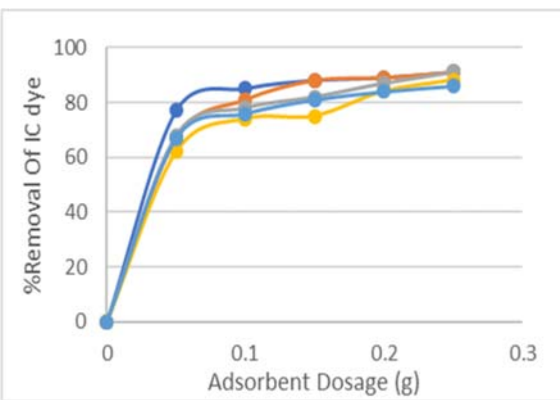

Fig. 7. The effects of dosage on the removal efficiency at 30 ºC , 4 days contact time.

Effect of Contact Time

The removal percentage of the dye was increased as the contact time increased, also the amount of dye adsorbed per unit weight of adsorbent increased. This can be explained by the formation of the driving force between dye solution and the corn leaf adsorbent that leads to high amounts of IC molecules being transferred to the surface of the adsorbent. A similar result was described by [11] where the adsorption increased with the increase of contact time for Congo red dye using Brewers' Spent Grain. The effect of contact time is shown in Figure 8.

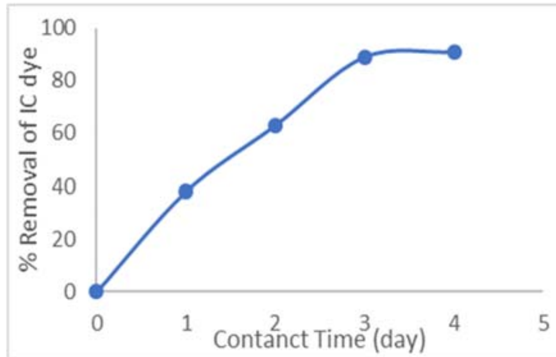

Fig. 8. Contact time effect on the removal of IC dye at 30 ºC, 10 ppm dye concentration and 0.25 gm adsorbent dosage.

Effect of pH

The effect of the pH on the removal efficiency is shown in Figure 9. It is noticed that as the pH increase from 2 to 12, both the removal efficiency and adsorption capacity increased, this may be attributed to the surface functional groups and nature of the dye as evidenced by [12] where the amount of adsorbed crystal violet dye was found to increase with an increase in pH using walnut shell powder.

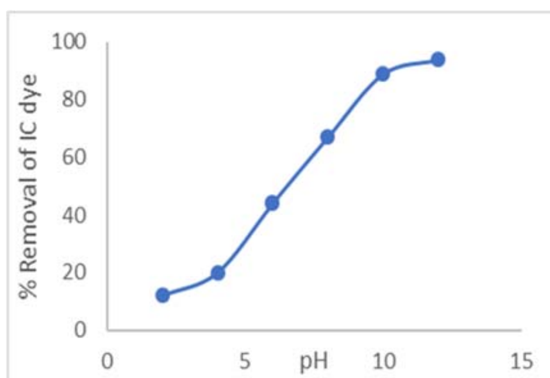

Fig. 9. Effect of pH on the removal of IC dye at 30 ºC, 4 days contact time, 10 ppm dye concentration and 0.25 gm adsorbent dosage.

Effect of Temperature

Figure 10 shows that as the temperature increases from 30 to 60, the removal efficiency and the adsorption capacity both decreased. This can be explained by weak bonds between the IC dye molecules and the active sites of the corn leaves adsorbent at high temperatures. The results are in agreement with [3] where both the removal efficiency and the adsorption capacity of methyl orange dye decreased using corn leaves adsorbent material.

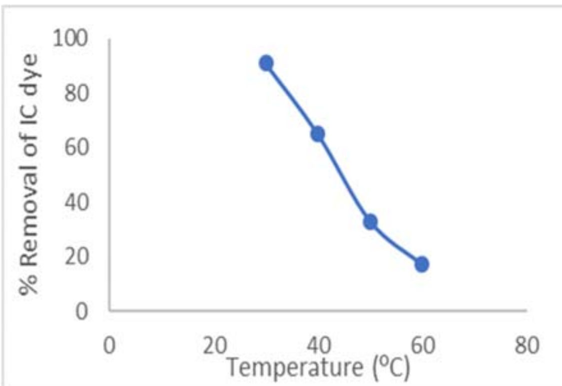

Fig. 10 Effect of temperature on the removal efficiency of IC dye at 30 °C, 4 days contact time, 10 ppm dye concentration and 0.25 gm adsorbent dosage.

Adsorption Isotherm

The equilibrium relationship between the adsorbent dose and the dye concentration with respect to time was depicted using Langmuir and Freundlich isotherms. The linear form of Langmuir isotherm can be represented by the following equation [13]:

$$\frac{Ce}{q_e} = \frac{1}{K_I q_m} + \frac{Ce}{q_m} \quad \text{... (3)}$$

where:

q_e (mg/g) the amount of dye adsorbed at equilibrium

q_m (mg/g) the amount of dye adsorbed at saturation

C_e the equilibrium dye concentration (mg/l) and K_l is Langmuir constant.

The linear form of Freundlich equation is expressed as:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad \text{... (4)}$$

Where:

K_f and n are Freundlich constants which give a measure of the adsorption capacity and adsorption intensity, respectively.

(Ce/Qe) vs (Ce) was plotted to find values of the constants (K_I and q_m) and the correlation coefficient (R^2) as shown in Table 1 for Langmuir Isotherm. The results indicate that the adsorption of IC by corn leaves did not match with Langmuir isotherm.

The data in Table 1 indicates that the adsorption of IC by Corn leaf as adsorbent follows Freundlich isotherm.

Table 1,
Adsorption isotherm parameters for IC adsorption on corn leaves at 30°C.

Langmuir	$C_e/q_e = 1/k_L q_m + C_e/q_m$
q_m	-5.8377
K_L	-7.3578
R^2	0.7524
Freundlich	$\ln q_e = \ln K_F + 1/n \ln C_e$
n	-1.7117
K_f	2.2109
R^2	0.9264

Adsorption Kinetics

Pseudo first and second order were used to study the kinetics of IC dye on Corn leaf.

The pseudo first order model is expressed by the equation:

$$\ln(q_e - q_t) = \ln q_e - (k_1)\, t \quad \text{... (5)}$$

Where:

q_e and q_t are the amounts of the adsorbent (mg/g) at equilibrium and at time t (min), respectively.

k_1 is the rate constant of adsorption (min^{-1}).

Pseudo second order equation can be expressed as [14]:

$$\frac{t}{q_t} = \frac{1}{(k_2\, q_e)} + \left(\frac{1}{q_e}\right) t \quad \text{... (6)}$$

Where k_2 (g/mg.min) is the adsorption rate constant of pseudo second order adsorption rate.

Fitting the experimental data into different kinetic models such as Pseudo first and second order was performed to investigate the adsorption rate, model the process and foretell the information of adsorbent/adsorbate interaction [15].

The accordance between the model values and the experimental data was expressed by correlation coefficient (R^2).

Adsorption kinetics was shown in Figure 8 as the change in percentage of dye removal with time. Value of the first order rate constant could be calculated by plotting Lagergren plot of log (qe-qt) with the adsorption time (t) in a linear representation as shown in Figure 11.

Similarly, the pseudo second order constants are calculated by plotting each of (t/q_t) versus adsorption time (t) as shown in Figure 12 with the values of correlation coefficients (R^2).

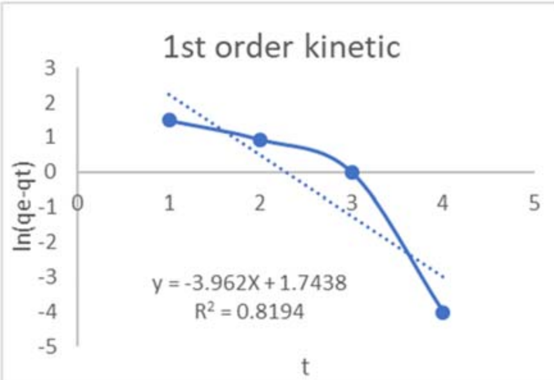

Fig. 11 Pseudo first order plot of IC Adsorption by corn leaves.

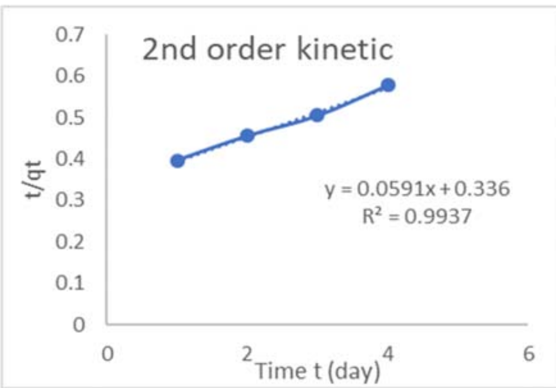

Fig. 12 Pseudo Second order plot of IC Adsorption by corn leaves

Table 2 shows the kinetic models, their constants and the correlation coefficients.

Table 2,
Kinetic parameters values with R^2 for IC adsorption.

Pseudo first order $\ln(q_e\text{-}q_t) = \ln(q_e) - K_1\,t$	
q_e	52.5623
k_1	-1.7438
R^2	0.8194
Pseudo second order: $t/q_t = (1/k.q_e)+(1/q_e)t$	
q_e	16.92
k_2	0.1759
R^2	0.9937

Based on the results, the sorption of IC dye using Corn leaves adsorbent is conformed well by pseudo second order kinetic model.

4. Conclusions

In this study, the feasibility of using corn leaves as efficient, low cost natural adsorbent material for the adsorption of indigo Carmen dye for batch study was investigated. The best conditions were 10 ppm concentration, 0.25 gm adsorbent dosage, pH of 12, temperature of 30°C and contact time of 4 days for 91% removal efficiency. It was found that as the concentration and temperature increased the removal efficiency decreased and as the dosage, contact time and pH increased, the removal efficiency increased. The equilibrium data fits with Freundlich isotherm and the rate of sorption followed Pseudo second order kinetics with a correlation factor of 0.9937. The results proved that the corn leaves as bio waste adsorbent are efficient and economical material for the removal of IC dye from aqueous solutions.

Notation

C_e	Equilibrium concentration of adsorbate, mg/L
C_o	Influent concentration, mg/L
FTIR	Fourier Transform Infrared spectroscopy
k_1	Rate constant of adsorption of pseudo first order, min^{-1}
k_2	Rate constant of adsorption of pseudo second order, g/mg·min
k_f , n	Freundlich constants, dimensionless
k_l	Langmuir constant, L/mg
M	mass of adsorbent, (gm)
PFO	Pseudo First order
PSO	Pseudo second order
q_e	The uptake of adsorbate at equilibrium, mg/g
q_m	Amount of adsorbate required to form a monolayer, mg/g
q_t	Amounts of the adsorbent at time t, mg/g
SEM	Scanning Electron Microscopy
V	Volume of solution, (L)

Acknowledgments

The authors are grateful for the Department of Biochemical Engineering, Al-Khwarizmi College of Engineering, University of Baghdad for the permission to use all the laboratory facilities and the support materials needed in this study.

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امتزاز صبغة كارمن النيلية بأستخدام اوراق الذرة كمادة مازة طبيعية

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الخلاصة

في هذا البحث، تم دراسة قابلية استخدام اوراق الذرة كمادة مازة طبيعيه رخيصه الثمن لأزاله صبغه كارمن النيليه. تم استخدام نظام الدفعات لدراسة عدد من المتغيرات مثل الزمن (٤ ايام)، تركيز الصبغه (١٠-٥٠) جزء من المليون، الكمية (٠,٠٥-٠,٢٥) غرام، الحامضية (٢-١٢) والحرارة (٣٠-٦٠) درجة سيليزية. ورق الذرة تم تشخيص خصائصه بأتسخدام جهاز الFTIR قبل وبعد امتزاز الصبغه وكذلك تم استخدام جهاز الSEM لمعرفه الشكل السطحي للمادة المازة. النتائج التجريبية انسبت لعدة isotherm وانطبقت مع Freundlich ويتبع المعادلة الحركية الكاذبة من الدرجة الثانية اعلى نسبة ازالة كانت ٩١٪ للصبغه مما يجعل اوراق الذرة مادة مناسبة وكفوءة لأزالة صبغه كارمن النيلية من المحاليل المائية.