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Combining ultrasound and stirring for the intensification of methylene blue biosorption from aqueous phase by Jujube stone

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ABSTRACT

This work investigated the potential of Jujube stone (JS) for the sorption of methylene blue (MB) dye from aqueous solution and examined the effects of the simultaneous association of ultrasound and stirring on the sorption process. Batch sorption studies were conducted to determine the effects of solution pH (3–11), initial dye concentration (50–200 mg L^{-1}), sorbent dosage (0.2–0.8 g) and ultrasonic power (0, 30 or 60 W) on the MB uptake at 25°C. The obtained results showed that the biosorption of MB increased with increasing dye concentration and was more favorable at basic pH. Both biosorption capacity and sorption rate were increased when coupling stirring with ultrasonic irradiation. The increase of sorption in the combined method is low for the higher biosorbent dosage, while the improvement is noteworthy for the lower sorbent mass. The biosorption was enhanced both with and without the assistance of ultrasound when the initial dye concentration augmented. The sorption of MB by the JS increased from 35.37 to 58.24 and 71.12 mg g^{-1} when the ultrasonic power increased, respectively, from 0 W (stirring alone) to 30 and 60 W (ultrasound + stirring). The biosorption kinetics were analyzed using pseudo-first-order and pseudo-second-order model equations and the sorption data were very well described by the pseudo-second-order model with high determination coefficients and low average percentage errors for all experimented initial dye concentrations and biosorbent dosages. The biosorption capacities of JS were 82.64 and 104.17 mg g^{-1} for the classical method and the simultaneous association of ultrasound and stirring, respectively. The results revealed that the JS has the potential to be used as a biosorbent for the removal of MB from aqueous solutions and the simultaneous association of ultrasound and stirring leads to an intensification of the process.

Keywords: Sorption; Jujube stone; Cationic dye; Ultrasonic irradiation; Improvement; Coupling ultrasound and stirring

1. Introduction

Dyes are one of the pollutants that had frequently contributed towards environmental pollution. The largest usage of dye came from textile industries [1], while the total usage of dye in the world was identified to be more than 10^7 kg y^{-1} [2]. The presence of low concentration of dyes in the effluent streams is highly visible and undesirable and

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it reduces the light penetration which leads to inhibiting photosynthesis and stringent restrictions on the organic content of industrial effluents [3].

In this study, the dye under consideration is methylene blue (MB), a cationic dye, which is the most commonly used substance for coloring among all other dyes of its category [4]. MB can cause eye burns, and if swallowed, it causes irritation to the gastrointestinal tract with symptoms of nausea, vomiting and diarrhea. It may also cause methemoglobinemia, cyanosis, convulsions and dyspnea if inhaled [5].

There were many types of methods usually used in solving this pollution issue namely flocculation, oxidation processes, ozonation processes, electrochemical techniques as well as adsorption [6–10]. Among these methods, biosorption technique for wastewater treatment has become more popular in recent years owing to economic reasons. Biosorbents are natural materials or mostly agricultural by-products and forest wastes, which have purpose to replace activated carbon. A number of works had focused on biomaterials and bio-composites that are capable of removing various pollutants from aqueous solutions [11–18]. Jujube stone was chosen as biosorbent as it is natural, easily available, and thus a low-cost biomass for the removal of dye from wastewater.

Jujube (*Ziziphus jujuba Mill.*) is a plant of the family Rhamnaceae traditionally cultivated in the Mediterranean region, Southern and Eastern Asia and South China [19]. The jujube trees attract the attention of researchers and food producers because of their drought tolerance and perspective of usage of those in food production [20]. The weight of jujube fruit ranged from 2.52 to 19.37 g in 15 studied varieties of jujube [21]. The weight, length and width of jujube fruit stones varied from 0.18 to 0.88 g, from 18.11 to 40.69 mm and from 16.66 to 35.60 mm, respectively, with high degree of variability of weight but with medium degree of variability for length and width [21].

Ultrasonic technology has been attempted to apply in wastewater treatment [22–24]. The process involves the formation, growth, and subsequent collapse of bubbles which results in the formation of large amplitudes of energy at a particular location [25]. During the process, the energy of ultrasound field is highly centered in the micro-cavitation bubbles, and the physical effects such as high pressure, high temperature, acoustic waves, microjets, microstreaming and microturbulence are generated at the instant that the cavitation bubbles collapse [26].

To the best of our knowledge, the utilization of Jujube stones (JS) for the biosorption of contaminants from aqueous media is until now not studied previously. The present work seeks to examine the applicability of a new biosorbent, JS, for the sorption of MB dye from aqueous solution and investigate the simultaneous combination of ultrasound and stirring on the rate and capacity of the sorption process. Batch biosorption experiments were carried out to investigate the influence of various operating parameters such as initial solution pH, biosorbent dose, initial dye concentration, and ultrasonic power on MB dye biosorption in order to clarify the enhancement effect of ultrasound irradiation on the sorption process.

2. Material and methods

2.1. Dye and biosorbent

Jujube fruits (*Ziziphus jujuba Mill.*) were collected from trees growing in Batna, Algeria. The ripened fruits were picked from trees in red maturity stage. Jujube stones were separated from fresh pulp, they were firstly dried, crushed in a ball mill and sieved to obtain a particle size between 0.5 and 1 mm, washed with distilled water until the filtrate appeared colorless, dried in an oven at 50°C for 12 h, then cooled in a desiccator and packaged in sealed bottles.

The cationic dye, MB ($C_{16}H_{18}N_3SCl$), was obtained from Sigma-Aldrich (USA) and used without further purification. 1 g L^{-1} stock solution was prepared by dissolving the required amount of dye in distilled water. The working solutions were obtained by diluting the dye stock solution to the required concentrations. 0.1 M hydrochloric acid (HCl) and 0.1 M sodium hydroxide (NaOH) were used to adjust the pH of the solution. Ionic strength of aqueous solutions was adjusted using Na_2SO_4. All reagents used were of analytical grade and purchased from Sigma-Aldrich.

The dye concentrations were measured by a double beam UV/Vis spectrophotometer (Shimadzu, Model UV 1601, Japan) at 664 nm.

2.2. Procedures and experimental setup

An ultrasonic bath (cleaner model), as shown in Fig. 1, was used for ultrasound-assisted biosorption studies (40 kHz) with ultrasonic powers of 30 or 60 W. Acoustic power dissipated in the medium was measured using standard calorimetric method [27]. The temperature of the suspension was monitored using a thermocouple immersed in the medium. The temperature inside the ultrasonic bath was kept constant by circulating cooling water within a stainless-steel serpentine immersed in the irradiated suspension. For all the experiments, the MB dye solution volume treated was 400 mL and the mixture was stirred with a speed of 300 rpm. The effects of the biosorption conditions such as the initial concentration of the dye (50–200 mg L^{-1}), biosorbent dosage (0.2–0.8 g/400 mL) and ultrasonic power (0, 30 or 60 W) were investigated at room temperature (25°C ± 1°C) and natural solution pH (5.3) to compare between the conventional method (stirring) and the combined method (sonication and stirring). Also, the effects of pH (3–11), temperature (25°C–45°C) and ionic strength (0–500 mg L^{-1} of salt) were studied using a stirring speed of 300 rpm (conventional method). The following equations were used to calculate the biosorption capacity and removal efficiency (%) of MB dye.

$$q = \frac{\left(C_0 - C\right)V}{W} \tag{1}$$

$$\%\text{Removal} = \frac{C_0 - C}{C_0} \times 100 \tag{2}$$

where C_0 and C (mg L^{-1}) are the concentrations of MB dye at initial and any time t, respectively, V (L) is the volume of the dye solution and W (g) is the mass of biosorbent used. The average percentage errors (APE) are calculated as follows:

$$\text{APE}(\%) = \frac{\sum_{1}^{N} \left| \frac{q_{e_{\text{exp}}} - q_{e_{\text{cal}}}}{q_{e_{\text{exp}}}} \right|}{N} \times 100 \quad (3)$$

where the subscripts 'exp' and 'cal' show the experimental and calculated values, respectively, and N is the number of experimental data.

2.3. Determination of active sites

Acidic and basic sites on JS were determined by the acid–base titration method proposed by Boehm [28]. The acidic and basic sites were determined by adding 50 mL of 0.1 N titrating solution and 1 g of JS to a 50 mL volumetric flask. The flask was slowly agitated, partially immersed in a constant temperature water bath set at 25°C, and it was left there for 5 d. Afterward, a sample of 10 mL was titrated with a 0.1 N HCl or NaOH solution.

The total acid sites matching the carboxylic, phenolic, and lactonic sites were neutralized using a 0.1 N NaOH solution while the basic sites were neutralized with a 0.1 N HCl solution. The carboxylic and lactonic sites were titrated with a 0.1 N Na_2CO_3 solution and the carboxylic sites were determined with a 0.1 N $NaHCO_3$ solution, and the phenolic sites were estimated by difference [29].

3. Results and discussion

3.1. Surface properties of JS

From Table 1, physicochemical characterization of JS shows that the concentrations of acidic surface functions, mainly phenolic and lactonic groups, are more important than basic functions. The capacity of biosorbent for removing MB dye is essentially due to the presence of the acid sites since the dye cations in aqueous solutions can be biosorbed on these sites.

3.2. Influence of pH

The effect of pH on the sorption of MB from aqueous solutions by JS was observed at varying pH from 3 to 11 with 25°C temperature, 0.4 g/400 mL biosorbent concentration, 50 mg L^{-1} initial dye concentration, and 300 rpm stirring speed. It can be seen that the biosorption increases with the increase in initial pH. The result presented in Fig. 2 shows that the sorption is better at basic pH; the higher the pH of the solution, the higher the sorption capacity and the percentage of dye removal. This can be explained by the fact that the pH of the solution governs the electrostatic forces. As the pH of the system decreased, the number of negatively charged sorption sites decreased and the number of positively charged surface sites increased, which did not favor the sorption of positively charged dye cations due to electrostatic repulsion. Also, lower biosorption of MB at very acidic pH value (pH 3) is due to the presence of excess H^+ ions competing with MB cations for the sorption sites of JS. Similar trend was reported for the sorption of MB by *Posidonia oceanic* (L.) fibers [30] and by melon peel [31].

Table 1
Concentration of active sites on JS surface

Acidic sites	
Total (meq g^{-1})	0.875
Phenolic (meq g^{-1})	0.390
Carboxylic (meq g^{-1})	0.150
Lactonic (meq g^{-1})	0.335
Basic sites (meq g^{-1})	0.040

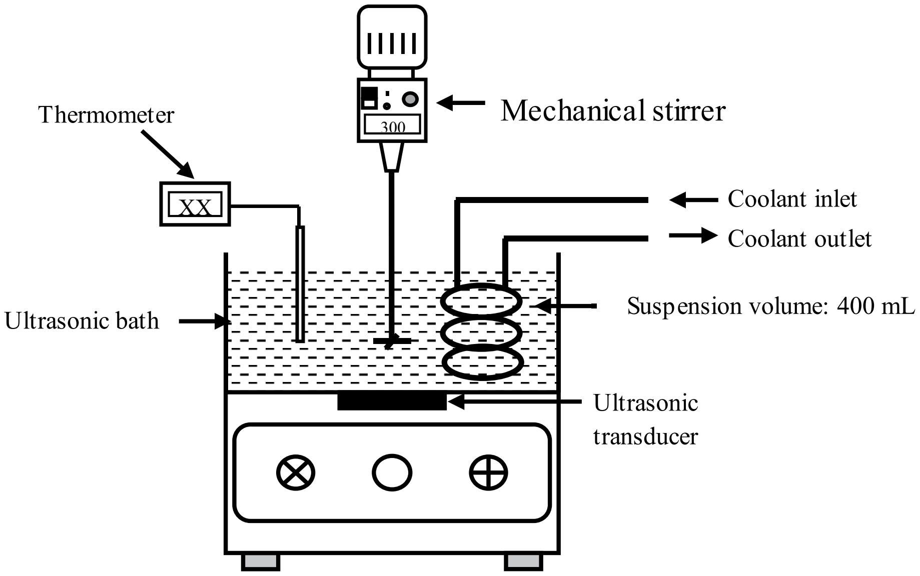


Fig. 1. Experimental setup.

3.3. Effect of temperature

The effect of temperature on the sorption of MB from aqueous solutions by JS was observed at varying temperatures ranging from 25°C to 45°C, natural pH (5.3), 0.4 g/400 mL biosorbent concentration, 50 mg L^{-1} initial dye concentration, and 300 rpm stirring speed. The result presented in Fig. 3 shows that with the increase of temperature of the solution, the sorption is reduced; when the temperature increased from 25°C to 45°C, the sorbed quantity decreased from 31.05 to 20.95 mg g^{-1}. This can be explained by the exothermicity of the sorption process and by the weakening of the bonds between the dye and the active sites of the biosorbent for the highest temperatures. Temperature has a double effect on the sorption mechanism; the increase in temperature improves the diffusivity through the boundary layer thus increasing the frequency of collision between the molecules of the dye and the sorption sites, and on the other hand, the increase in temperature influences favorably or unfavorably the sorption depending on the type of bond between the dye molecules and the sorption sites. For the case of the sorption of MB by JS, the result of the effects of the increase in temperature is against sorption. Similar temperature effect was reported for MB dye sorption onto melon peel [31] and milk thistle seeds [32].

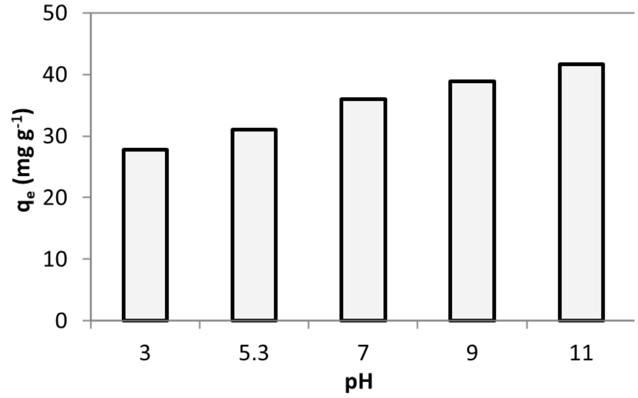


Fig. 2. Effect of pH on the biosorption capacity of methylene blue (biosorbent dosage = 0.4 g/400 mL; dye concentration = 50 mg L^{-1}; temperature = 25°C; stirring speed = 300 rpm).

3.4. Effect of ionic strength

The existence of salts in textile effluents is common and causes changes of solution and sorbent surface chemistry [33,34]. Experimental parameters were chosen as follows: temperature 25°C, agitation speed 300 rpm, pH 5.3, sorbent dosage 0.4 g/400 mL, initial dye concentration 50 mg L^{-1}. Experimental results for ionic strength effect are given in Fig. 4. When the ionic strength was increased from 0 to 500 mg L^{-1} of Na_2SO_4 concentration, the sorption capacity decreased from 31.05 to 10.49 mg g^{-1}. This trend showed that the removal efficiency decreased with the rise of Na_2SO_4 amount in synthetic wastewater dye solution. At high ionic strength, sorption sites are surrounded by counter ions which partially lose their charge, and this weakens the binding force by electrostatic interaction [35]. Similar results have been obtained for the sorption of cationic dyestuff [36].

3.5. Effect of biosorbent dosage

The effect of biosorbent dosage on the sorption of MB from aqueous solutions by JS was studied at varying sorbent doses ranging from 0.2 to 0.8 g/400 mL with 25°C temperature, natural pH (5.3), 50 mg L^{-1} initial dye concentration and 300 rpm stirring speed. The results of the experiments are shown in Fig. 5. With an increase in the sorbent dose from 0.2 to 0.8 g/400 mL, the percentage of MB removal increased from 35.37% to 88.76%, as the number of possible sorbing sites would be increased. It can be concluded that an increase in the biosorbent concentration leads to an increase of the surface area of JS, but the amount of MB sorbed

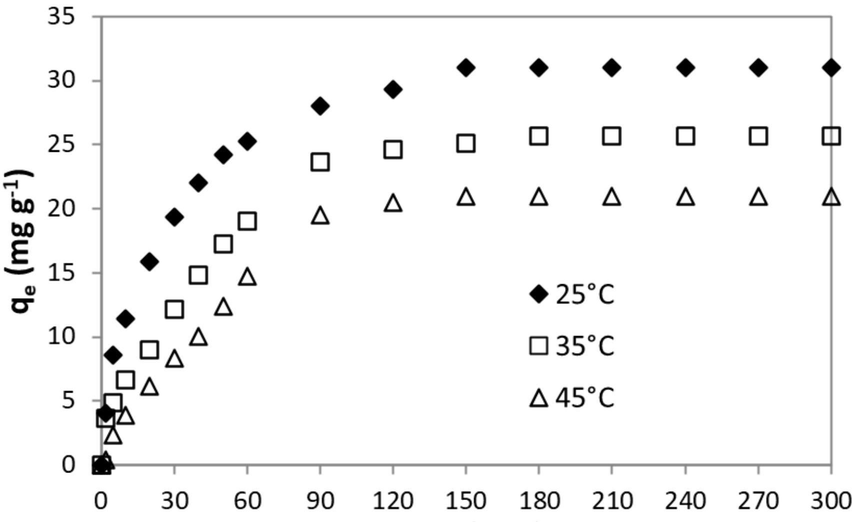


Fig. 3. Effect of temperature on the biosorption capacity of methylene blue (biosorbent dosage = 0.4 g/400 mL; dye concentration = 50 mg L^{-1}; pH 5.3; stirring speed = 300 rpm).

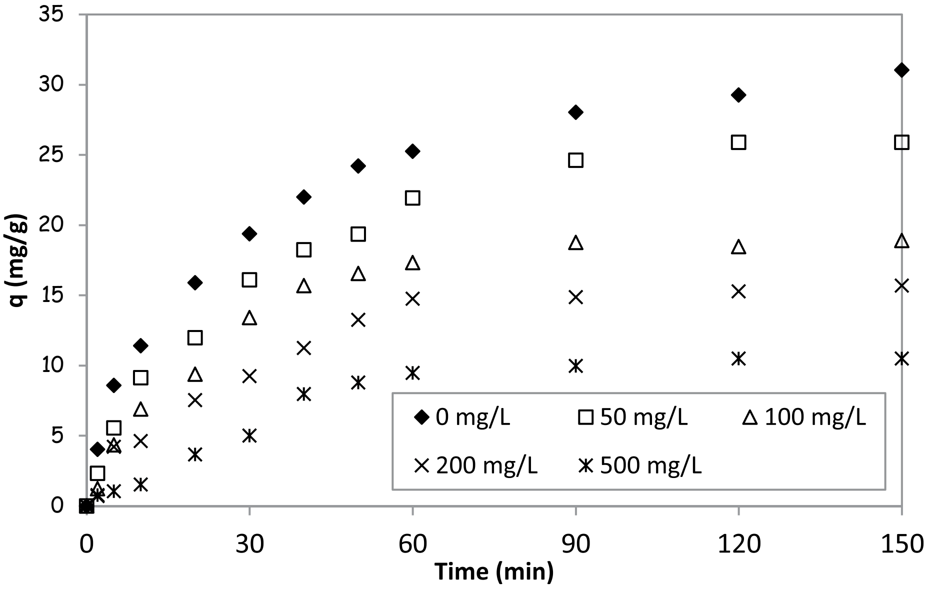


Fig. 4. Effect of salt (Na_2SO_4) concentration on the biosorption of MB by JS (conditions: initial dye concentration = 50 mg L^{-1}; biosorbent dosage = 0.4 g/400 mL; stirring speed = 300 rpm; T = 25°C; pH 5.3).

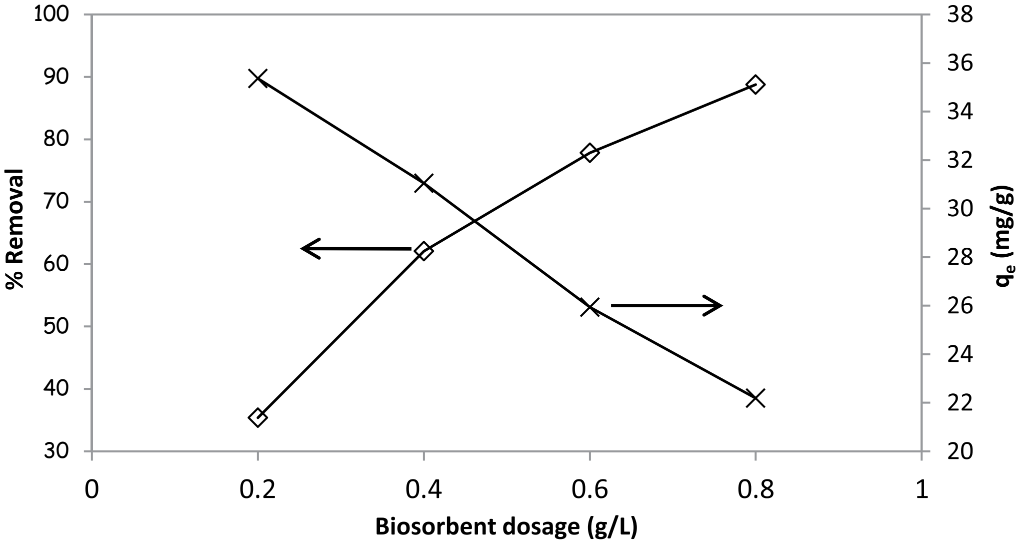


Fig. 5. Effect of biosorbent dosage on the removal of MB and sorption capacity of JS (conditions: initial dye concentration = 50 mg L^{-1}; stirring speed = 300 rpm; T = 25°C; pH 5.3).

decreased from 35.37 to 22.19 mg g^{-1}. By increasing the biosorbent dosage, the number of active sites available for sorption increased, facilitating the uptake of dye, which explain the increase of removal percentage. The decrease of sorption capacity by increasing the biosorbent dosage (higher weight of sorbent per dye ratio) may be due to the unsaturation of biosorbent sites [30], during the sorption process. Similar results have been reported by other authors [30–32,37–39].

3.6. Effect of ultrasound for different biosorbent dosages

To compare the conventional method (stirring) and the combined technique (simultaneous sonication and stirring), sorption experiments were carried out at different biosorbent dosages (0.2–0.8 g/400 mL) with 25°C temperature, natural pH (5.3), 50 mg L^{-1} initial dye concentration and 300 rpm stirring speed, and when ultrasound was used, the acoustic power was 60 W. It was observed from Fig. 6 that, similar to the conventional method, the amount of MB dye sorbed per unit mass of biosorbent decreased from 71.12 to 23.54 mg g^{-1} in the combined method (combining ultrasound and mechanical stirring) and from 59.32 to 22.89 mg g^{-1} in the presence of ultrasonic irradiation alone with the increase in sorbent dose from 0.2 to 0.8 g/400 mL, respectively.

For all biosorbent dosages, it was observed that the sorption was more effective in the combined technique

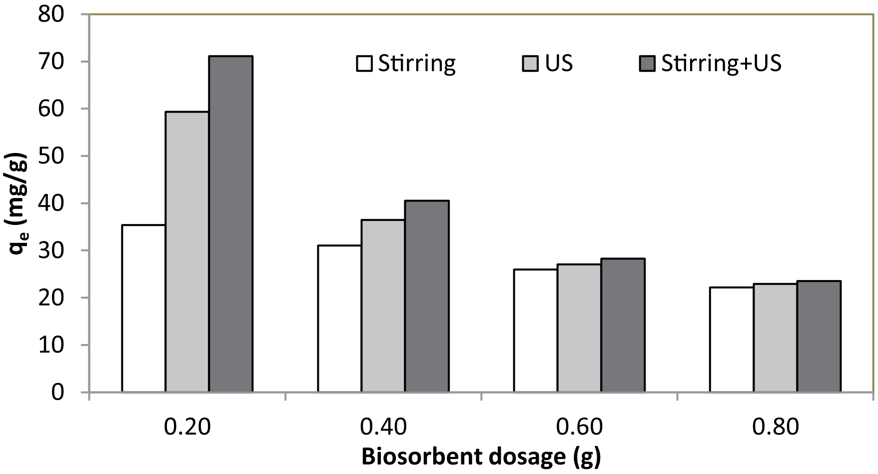


Fig. 6. Effect of biosorbent dosage on MB sorption by JS at equilibrium in the absence and presence of ultrasound (conditions: 400 mL of solution; initial MB dye concentration = 50 mg L^{-1}; ultrasonic power = 60 W; stirring speed = 300 rpm; natural pH (5.3); temperature = 25°C).

than in the conventional method. For the higher biosorbent dosage, the increase of sorption in the presence of ultrasound is low that is due to the high availability of sorption sites. On the other hand, the improvement in the presence of ultrasound is significant for the lower biosorbent mass; the enhancement is 6.1% in the combined method and 3.2% in the presence of ultrasound alone for a sorbent mass of 0.8 g, while it is more than 100% in the combined technique and 33.4% in the presence of ultrasonic irradiation for a sorbent mass of 0.2 g. This behavior could be explained by the intensification of mass transfer phenomena through acoustic vortex microstreaming, shockwaves, microjets, and thermal effects of ultrasound. The asymmetric collapse of bubbles in a heterogeneous system produces high-speed microjets. Additionally, symmetric and asymmetric collapses generate shockwaves, which cause extremely turbulent flow at the liquid-solid interface, increasing the rate of mass transfer near the solid surface [40].

3.7. Effect of initial dye concentration

The effect of initial dye concentration on the sorption of MB from aqueous solutions by JS was studied at varying initial MB concentration from 50 to 200 mg L^{-1} with 0.4 g/400 mL of biosorbent dosage, 25°C temperature, natural pH (5.3), and 300 rpm stirring speed. The results of the experiments are shown in Fig. 7. It can be seen that increasing the initial dye concentration, decreased the percentage of dye removal from aqueous solution from 62.1% to 31.98%, but the sorption capacity at equilibrium was proportional to the initial dye concentration; the amount of MB sorbed at equilibrium increased from 31.05 to 63.95 mg g^{-1} as the initial dye concentration was increased from 50 to 200 mg L^{-1}. This indicates that the biosorbent, at lower dye concentration, is not saturated but the concentration of dye in solid phase is at equilibrium with the residual concentration in the liquid phase [41]. The high initial concentration provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases.

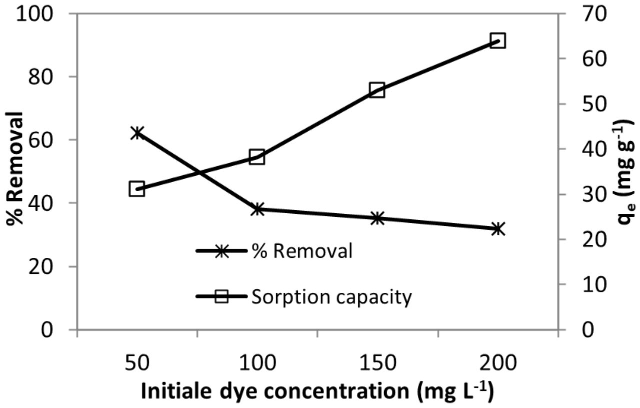


Fig. 7. Effect of initial dye concentration on the removal of MB and biosorption capacity of JS (conditions: adsorbent dosage = 0.4 g/400 mL; stirring speed = 300 rpm; T = 25°C; pH 5.3).

3.8. Effect of ultrasound for different initial dye concentrations

To investigate the effect of ultrasound on the sorption of MB by JS at different initial dye concentrations, experiments were carried out at various MB initial concentrations (50–200 mg L^{-1}) with 0.2 g/400 mL sorbent dosage, 25°C temperature, natural pH (5.3), 300 rpm stirring speed and, when ultrasound was used, the acoustic power was 60 W. Fig. 8a and b shows the biosorption of MB dye in the absence of ultrasound and in the combined process (sonication and mechanical stirring) for different initial dye concentrations as a function of contact time, respectively. It was observed that the sorption capacity increased with time, and at a certain time period, reached a constant value indicating that no dye was further removed from the solution. Ultrasound increased significantly the sorption capacity at equilibrium (Fig. 9) and at any time (Fig. 8) for all initial dye concentrations. For 50 mg L^{-1}, for example, a sorption capacity of about 34 mg g^{-1} was reached after 120 min of contact time by conventional method, while it was reached after only 30 min by combined method. The sorption capacity at equilibrium in the presence of ultrasound was much greater than in the absence of ultrasound and as it has been found that the sorption capacity without ultrasound increases when the initial concentration of the dye increases, also the improvement of the sorption capacity by the assistance of ultrasound increases when the initial concentration of the dye increases. For initial dye concentrations of 50, 100, 150 and 200 mg L^{-1}, ultrasonication improved the sorption capacity from 35.37 to 71.36 mg g^{-1}, from 38.55 to 80.48 mg g^{-1}, from 52.9 to 95.03 mg g^{-1} and from 63.95 to 98.66 mg g^{-1}, respectively, in the combined technique (ultrasound + stirring), and from 35.37 to 55.32 mg g^{-1}, from 38.55 to 65.55 mg g^{-1}, from 52.9 to 79.33 mg g^{-1} and from 63.95 to 83.17 mg g^{-1}, respectively, in the presence of ultrasound alone (Fig. 9). These effects associated with the hydrodynamic phenomena due to cavitation and mechanical stirring are responsible for the perfect mixing of the vessel content [42]. It is obvious from the principle of cavitation that the ultrasound process results in convection of the solution medium through shock waves, microjets, microturbulence and microstreaming. Similar trend was found in the literature [43–45].

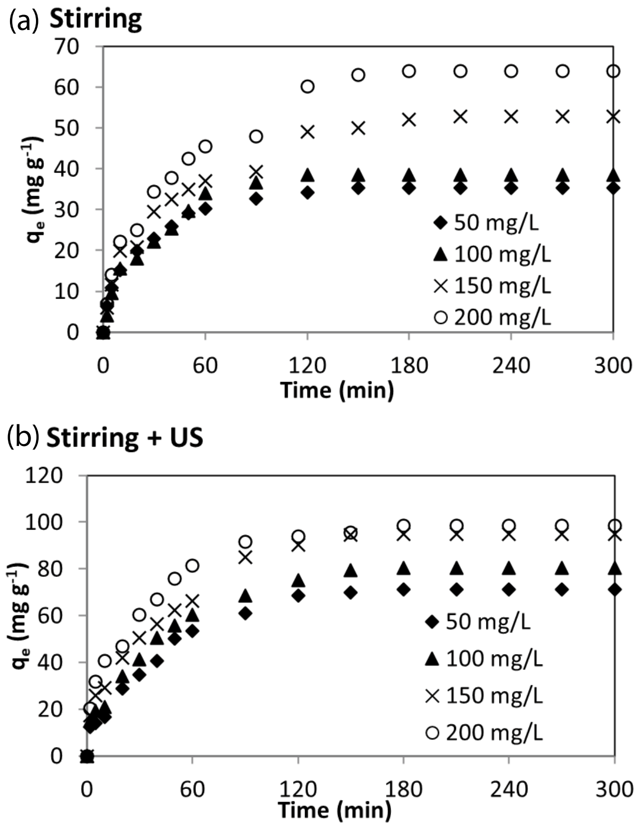


Fig. 8. Kinetics of MB uptake by JS for various initial dye concentrations; (a) conventional method and (b) combined technique (conditions: biosorbent dosage = 0.2 g/400 mL; stirring speed = 300 rpm; T = 25°C; pH 5.3; ultrasonic power = 60 W).

3.9. Effect of ultrasonic power

The influence of ultrasonic power on the sorption of MB by JS was studied under the following operating conditions: 50 mg L^{-1} initial MB concentration, 0.2 g/400 mL sorbent dosage, 25°C temperature, natural pH (5.3), 300 rpm stirring speed and when ultrasound was used, the acoustic power was 30 or 60 W. Fig. 10 shows that the sorption capacity of MB by the JS increased from 35.37 to 58.24 mg g^{-1}; an increase of 64.7% when the ultrasonic power increased from 0 W (stirring alone) to 30 W (stirring + ultrasound (30 W)), respectively. This capacity increased by 101.1% (71.12 mg g^{-1}) compared to conventional method, when the suspension is simultaneously agitated and sonicated at 60 W. Also, the initial sorption rate increases with increasing ultrasonic power. This is due to the physical effects of ultrasound mainly micro-mixing, microjets and shock waves. In addition, the extreme conditions produced by acoustic cavitation leading to very high pressures and temperatures on the surface of the solid can change the morphology of the surface and the particle size of the biosorbent [46].

3.10. Biosorption kinetics

The kinetics of biosorption of MB by JS was studied on the basis of two simplified kinetic models, including

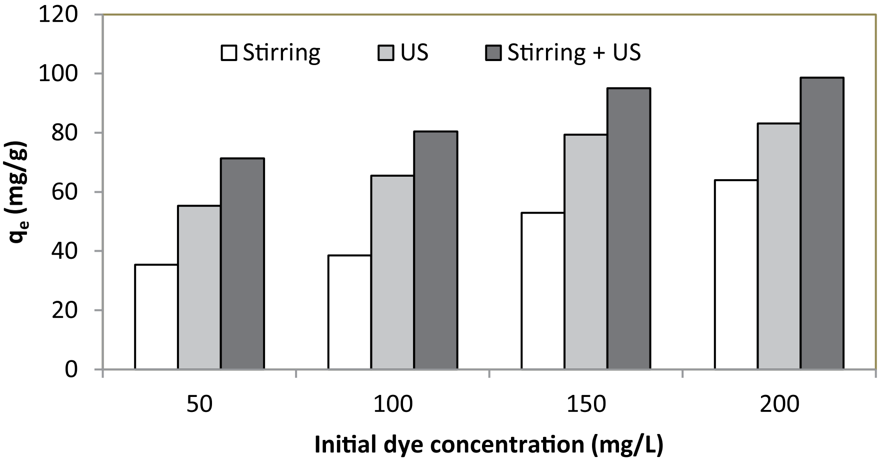


Fig. 9. Effect of initial dye concentration on MB sorption by JS at equilibrium in the absence and presence of ultrasound (conditions: sorbent dosage = 0.2 mg/400 mL; ultrasonic power = 60 W; stirring speed = 300 rpm; natural pH (5.3); temperature = 25°C).

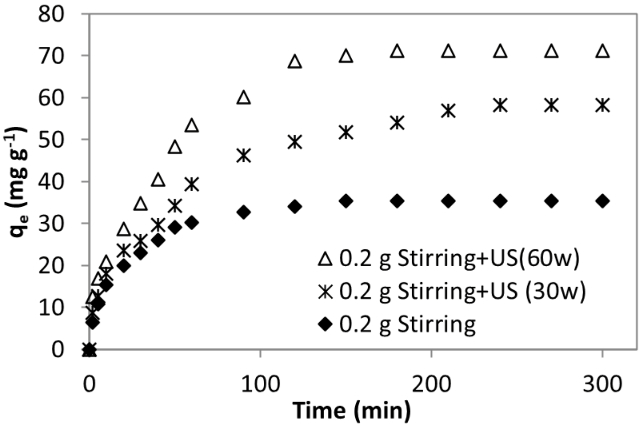


Fig. 10. Effect of ultrasonic power on the biosorption of MB by JS (conditions: biosorbent dosage = 0.2 mg/400 mL, initial dye concentration = 50 mg L^{-1}; stirring speed = 300 rpm; natural pH (5.3); temperature = 25°C).

pseudo-first-order [47] and pseudo-second-order equations [48,49]:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{5}$$

where q_e and q_t are the amounts of MB sorbed (mg g^{-1}) at equilibrium and at time t (min), respectively, k_1 is the rate constant of pseudo-first-order (min^{-1}) and k_2 is the rate constant of pseudo-second-order (g mg^{-1} min^{-1}).

k_2 was calculated from the slope and intercept of the plot t/q_t vs. t.

k_1 was calculated from the slope of the plot $\ln(q_e - q_t)$ vs. t.

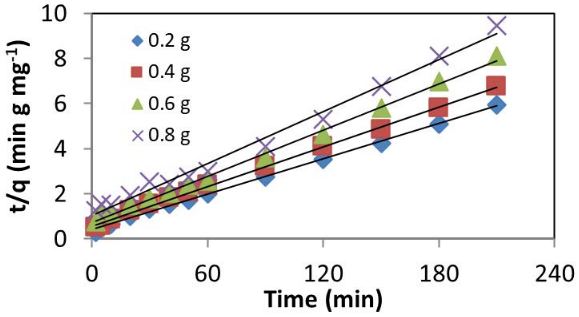
The initial sorption rate of pseudo-second-order kinetics, h (mg g^{-1} min^{-1}), is expressed as:

$$h = k_2 q_e^2 \tag{6}$$

The sorption kinetics of MB by JS using conventional method and combined technique at various biosorbent dosages and different initial dye concentrations were analyzed using the pseudo-first-order model equation (figures not shown). Fig. 11a and b shows the pseudo-second-order plots for the biosorption of MB by JS employing conventional method and combined process, respectively, at various biosorbent dosages. Finally, Fig. 12a and b displays the pseudo-second-order plots for the sorption of MB by JS employing conventional method and combined technique, respectively, at various initial dye concentrations.

The corresponding kinetic constants along with regression coefficients and APE values, for the sorption of MB by JS at various sorbent dosages and different initial dye concentrations, are presented in Tables 2 and 3, respectively. Based on the high regression coefficients and low APE, pseudo-second-order model fit the experimental

(a) Stirring



(b) Stirring + US (60W)

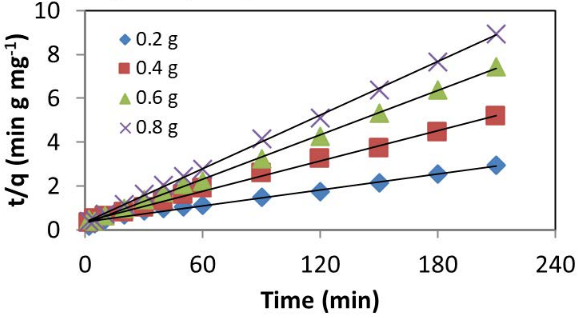
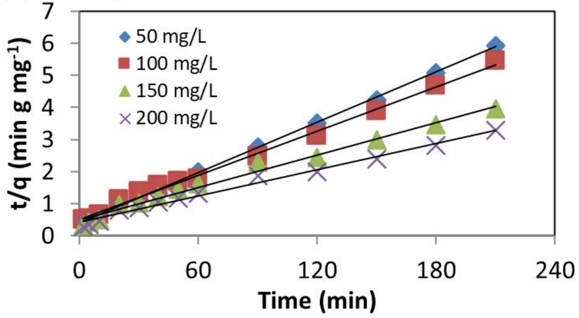


Fig. 11. Pseudo-second-order fit to MB removal by JS at various biosorbent dosages: (a) conventional method and (b) combined technique (conditions: initial dye concentration = 50 mg L^{-1}; natural pH (5.3); temperature = 25°C; stirring speed = 300 rpm; ultrasonic power = 60 W).

(a) Stirring



(b) Stirring+US (60W)

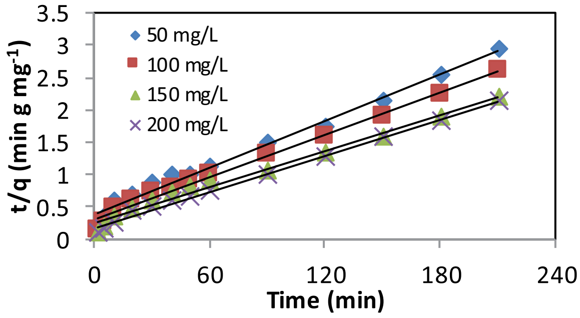


Fig. 12. Pseudo-second-order fit to MB removal by JS at various initial dye concentrations: (a) conventional method and (b) technique method (conditions: sorbent dosage = 0.2 g/400 mL; natural pH (5.3); temperature = 25°C; stirring speed = 300 rpm; ultrasonic power = 60 W).

Table 2
Kinetic constants for the sorption of MB by JS at various biosorbent dosages

		Stirring				Stirring + US (60 W)			
	w (g)	0.2	0.4	0.6	0.8	0.2	0.4	0.6	0.8
Pseudo-first-order	R^2	0.9895	0.9861	0.9891	0.9745	0.9775	0.9030	0.9192	0.8870
	k_1	2.68×10^{-2}	2.35×10^{-2}	3.62×10^{-2}	3.64×10^{-2}	2.54×10^{-2}	1.92×10^{-2}	4.47×10^{-2}	2.86×10^{-2}
	q_e(exp)	35.37	31.05	25.94	22.19	71.12	40.55	28.27	23.54
	q_e(cal)	28.36	25.45	25.89	23.49	72.46	28.59	23.41	14.51
	APE (%)	39.45	38.35	6.67	12.70	17.38	54.14	33.28	59.94
Pseudo-second-order	R^2	0.9984	0.9983	0.9861	0.9900	0.9856	0.9974	0.9990	0.9993
	h	2.47	1.74	1.38	0.96	2.78	2.55	3.27	2.96
	k_2	1.69×10^{-3}	1.49×10^{-3}	1.61×10^{-3}	1.41×10^{-3}	4.17×10^{-4}	1.33×10^{-3}	3.68×10^{-3}	4.90×10^{-3}
	q_e(exp)	35.37	31.05	25.94	22.19	71.12	40.55	28.27	23.54
	q_e(cal)	38.27	34.22	29.27	26.06	81.70	43.71	29.81	24.58
	APE (%)	4.28	4.06	5.75	7.54	10.36	3.67	3.64	3.47

Table 3
Kinetic constants for the sorption of MB onto JS at various initial dye concentrations

		Stirring				Stirring + US (60w)			
	C_0 (mg L^{-1})	50	100	150	200	50	100	150	200
Pseudo-first-order	R^2	0.9895	0.9769	0.9644	0.9341	0.9831	0.9716	0.9797	0.9832
	k_1	2.68×10^{-2}	3.19×10^{-2}	1.86×10^{-2}	2.00×10^{-2}	2.56×10^{-2}	2.50×10^{-2}	2.32×10^{-2}	2.33×10^{-2}
	q_e(exp)	35.37	38.55	52.90	63.95	71.36	80.48	95.03	98.66
	q_e(cal)	28.36	37.60	46.30	58.48	73.34	79.94	89.08	78.34
	APE (%)	39.45	15.61	32.38	27.74	15.14	14.78	23.13	39.96
Pseudo-second-order	R^2	0.9984	0.9948	0.9870	0.9858	0.9858	0.9891	0.9859	0.9953
	h	2.47	2.00	2.06	2.38	2.61	3.28	3.98	5.93
	k_2	1.69×10^{-3}	1.06×10^{-3}	5.89×10^{-4}	4.45×10^{-4}	3.78×10^{-4}	3.89×10^{-4}	3.41×10^{-4}	5.15×10^{-4}
	q_e(exp)	35.37	38.55	52.90	63.95	71.36	80.48	95.03	98.66
	q_e(cal)	38.27	43.44	59.10	73.20	83.05	91.74	107.99	107.30
	APE (%)	4.28	6.92	9.46	9.70	9.91	10.05	10.67	8.19

data well and was best than the pseudo-first-order model for the conventional method and combined technique at different initial dye concentrations and various biosorbent dosages. For the pseudo-first-order model equation, it was observed that the values of the sorption capacity at equilibrium determined theoretically were not in the neighboring of the experimental values both for various initial dye concentrations and different biosorbent doses. In contrast, for the pseudo-second-order equation, the variations between the calculated sorption capacity at equilibrium and experimental sorption capacity at equilibrium were very minimal in the combined technique as well as in the conventional method. The determination coefficients for the pseudo-second-order equation obtained at all operating conditions were high (from 0.9856 to 0.9993) and the APE values were low (from 3.47% to 10.36%). Contrariwise, the determination coefficients for the pseudo-first-order equation obtained were low (from 0.8870 to 0.9891) and the APE values were high (from 6.67% to 59.94%). Recently, similar observation was reported in the literature [50].

3.11. Comparison of sorption capacity of JS with other sorbents

Table 4 lists a comparison of the biosorption capacity of JS with those obtained in the literature for the sorption of MB. The biosorption capacities of JS for MB were 82.64 and 104.17 mg g^{-1} for the conventional method (mechanical stirring) and the combined technique (ultrasound + mechanical stirring), respectively. The calculated biosorption capacities show a good capability for MB sorption from aqueous media. These results reveal that the JS is an effective biosorbent for MB from aqueous solutions, especially by combining ultrasound and mechanical stirring. It should be noticed that the values and comparisons reported for MB removal capacity have only a relative meaning because of different testing conditions and methods.

4. Conclusion

The applicability of a new biosorbent, Jujube stone (JS), for the sorption of MB dye from aqueous solution and the effect of ultrasound on the rate and capacity of the sorption

Table 4
Comparison of sorption capacities of various sorbents for MB

Sorbent	q_m (mg g^{-1})	Ref.
Jujube stone (conventional method)	82.64	Present work
Jujube stone (combined method)	104.17	Present work
Palm spathe	74.29	[51]
Potato peel	105.26	[52]
Macrofungus (*Agaricus campestris*)	24.2	[53]
Magnetic peanut husk	32.50	[54]
Magnetic graphene oxide composites	62.70	[55]
Yellow passion fruit waste	44.70	[56]
Dehydrated peanut hull	123.50	[57]
Coffee husks	90.09	[58]
Activated carbon (*Euphorbia rigida*)	114.45	[59]
Rice husk	8.07	[60]
Tomato plant root	83.33	[61]
Activated carbon (fir wood)	70.05	[62]
Activated carbon (*Cocos nucifera L.*)	15.59	[63]
Activated carbon (oil palm wood)	90.90	[64]

process were investigated in batch mode. The biosorption capacity of MB by JS increases gradually with increasing initial pH. By the conventional and the combined methods the removal of MB increased by increasing biosorbent dosage. The amount of MB dye sorbed in the presence or in the absence of ultrasound was improved with the increase of dye initial concentration and ultrasonic power. Ultrasound has a drastic improvement impact on both the rate and the sorption capacity. Kinetic results were adequately fitted by the pseudo-second-order model. The findings revealed that the JS has the potential to be used as a biosorbent for the removal of MB from aqueous solutions and the simultaneous association of ultrasound and stirring leads to a significant intensification of the sorption.

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