Environment and Ecology 36 (1A) : 255—261, January—March 2018
Website: environmentandecology.com ISSN 0970-0420

A Kinetics and Isotherm Study of Alizarin Red S Adsorption on Sugarcane Bagasse: Batch Studies

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Received 1 October 2017; Accepted 3 November 2017; Published on 23 November 2017

Abstract The aim of this study was to assess the decolorization efficiency of alizarin red S using sugarcane bagasse under optimal conditions. The physico-chemical parameters such as initial dye concentration (100-500 mg/l), adsorbent dose (0.1–0.6 g/l), contact time (1–7 days), pH (2–10) and temperature (20–60°C) were employed to assess the decolorization of ARS. Further, to design the equilibrium data of adsorption process, Langmuir and Freundlich isotherm models were carried out. The treated and untreated samples were subjected to UV-vis spectrophotometer to evaluate the extent of decolorization by SCB. The phytotoxicity study using untreated and treated alizarin red S solutions on *Zinnia elegans* was assessed. The results indicated that maximum removal of alizarin red S (85%) occurred at pH 3 with 100 mg/l dye concentration at room temperature (30°C) within 5 days of incubation using 500 g/l adsorbent dose. It was found that dye adsorption onto the adsorbent followed by both Langmuir and Freundlich isotherm and the adsorption kinetics was found both pseudo-first order and pseudo-second order kinetics. UV-vis absorption spectra also confirm the decolorization of alizarin red S by the disappearance of peaks in the treated solution. In phytotoxicity study, the germination percentage, root and shoot lengths of *Z. elegans* was high in control and treated dye solution when compared with untreated dye solution which proved that the treated dye solution was nontoxic to plants.

Keywords Decolorization, Sugarcane bagasse, Alizarin red S, Optimization, Phytotoxicity.

Introduction

Water contamination with textile dyes is a burning environmental issue which poses a severe threat to human beings. Synthetic dyes are widely used by the food, cosmetics, paper printing, leather, plastic and textile industries because of their ease and cost-effectiveness in synthesis, high wet fastness profiles, high stability to light, temperature, detergent, microbial attack and variety in color compared with the natural dyes [1, 2]. Textile industries use the variety

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Table 1. Isotherm models for adsorption of ARS from aqueous solution.

	Langmuri isotherm			Freundlich isotherm		
Adsorbent	Q_0 (mg/g)	K_L (mg/L)	R^2	K_F	I/n	R^2
SCB	1.437	0.0532	0.997	0.1527	0.5482	0.996

of dyes and chemicals to color their products and release an enormous amount of wastewater during finishing processes [3]. Discharge of synthetic dyes from textile units into aquatic ecosystem significantly affects the aquatic flora and fauna by inducing carcinogenic and mutagenic effects on them. Exposure of these dyes to human beings cause severe damage to skin, liver, kidney, brain, reproductive and central nervous system. The release of the untreated dye solution into land also affects the fertility of the soil and decreases the water retention capacity. Hence it is very important to verify the quality of water before disposal into an aquatic or terrestrial ecosystem [4].

A variety of physico-chemical treatment methods such as adsorption, chemical precipitation, flocculation, coagulation, chemical oxidation, membrane separation process, electrochemical and aerobic and anaerobic microbial degradation was employed in the removal of contaminants from the textile dyeing wastewater. But these methods are not successfully used due to its high cost and excessive sludge generation [5]. Nowadays adsorption using natural bisorbents are becoming an area of high interest in the removal of dyes from wastewater. Agricultural wastes are available in large quantities and seem to be the most available renewable resources in the world. These waste materials have no economic value and often presents disposal problem [6]. Many agricultural waste products are subjected to decolorization studies and in the present study sugarcane bagasse (SCB) has been selected due to its easy availability and low-cost.

Table 2. Linearized kinetic coefficients for dye adsorption onto SCB.

Adsorption (g/l)	Pseudo-first order q_e	K_1	R^2	Pseudo-second order q_e	K_1	R^2
0.1	28.5271	0.0111	0.9930	43.8715	0.0069	0.9942
0.2	21.8264	0.0081	0.9992	30.5294	0.0120	0.9963
0.3	15.3422	0.0128	0.9964	22.2163	0.0242	0.9981
0.4	11.7568	0.0248	0.9981	16.0461	0.0434	0.9945
0.5	4.05316	0.0043	0.9942	11.5279	0.0029	0.9994
0.6	10.3857	0.0065	0.9931	17.3176	0.0434	0.9997

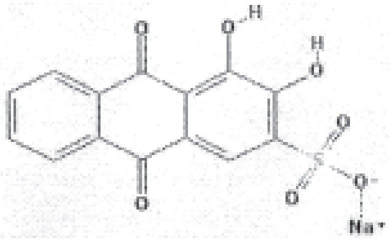

Fig. 1. Chemical structure of alizarin red S.

Sugarcane bagasse, an agro-industrial waste is the largest natural fiber resource which is basically built by macromolecules with humic and fulvic substances, lignin, cellulose, hemicellulose and proteins. It has adsorption sites such as carbonyl, carboxylic, amine and hydroxyl groups on its surface and has a high capacity to absorb the dye by ion exchange phenomena or by complexation process [7]. Thousands of tons of sugarcane bagasse have been produced daily by the sugarcane processing industries and these can be utilized for the environmental cleanup process [8]. Alizarin red S is a prominent red anionic dye belonging to anthraquinone group of dye is widely used in large quantities in textile industries. These dyes are not completely degraded by the conventional process because of the presence of complex aromatic rings which offer high thermal, optical and physico-chemical stability. It was observed that the effluent released from textile industries contain an adequate amount of alizarin red dye [9]. The consumption of waters containing residual amounts of alizarin red cause several harmful effects such as gas-

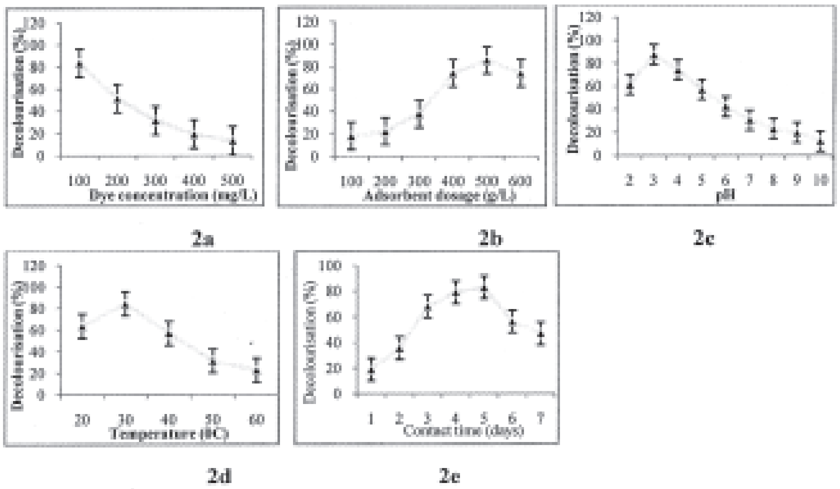

Fig. 2. Effect of physico-chemical parameters on ARS decolorization: (2a) Dye concentration, (2b) Adsorbent dosage, (2c) pH, (2d) Temperature, (2e) Contact time.

tritis, malfunctioning of lungs, severe headache, painful micturition and methemoglobinemia [10]. The parent compounds are less harmful whereas the degradation products may be more harmful and persist [11]. Hence with this background, an attempt has been made to study the effect of sugarcane bagasse on alizarin red S under optimized conditions.

Materials and Methods

Collection of adsorbent and adsorbate

SCB was collected from local juice market, Coimbatore, Tamil Nadu. It was washed throughly with running tap water to remove the color and dried in sunlight for a week. The dried bagasse was powered and sieved to obtain uniform particle size (0.25 mm) and stored for adsorption studies. ARS a water-soluble dye was used in this study was purchased from the local dye market Coimbatore, Tamilnadu. It is synthesized by sulfonation of alizarin which is natural dye obtained from madder (*Rubia tinctorum*, L. *Rubiaceae*) plant. The molecular structure shown in Fig. 1.

Biosorption studies

Batch adsorption experiment was carried out to study the effect of dye removal with different adsorbent doses (100–600 g/l), dye concentration (100–500 mg/l), pH (2–10), temperature (20–60°C) and incubation period (1–7 days). The solution pH was adjusted using 0.1 N NaOH and 0.1N HCl. After adsorption, the adsorbent and the supernatants were separated by centrifugation at 4000 rpm for 10 min and the samples were analyzed for percent decolorization.

$$\text{Percentage decolorization} = \frac{C_o - C_t}{C_o} \times 100 \qquad (1)$$

Where, C_o is the initial concentration of the dye solution and C_t is the final concentration of the dye solution. In order to explain the mechanism of the process of biosorption Langmuir and Freundlich isotherm models were followed. To determine the decolorization efficiency of SCB on alizarin red S, the absorbance values of the untreated and treated dye solution were observed at the wavelength of 200–800 nm using UV-vis spectrophotometer. Phytotoxicity tests

Table 3. Biometric parameters of *Z. elegans* on 7th day.

Treatments	Germination %	Shoot length (cm)	Root length (cm)	Vigor index
T_1	97	20.03	6.76	2595.72
T_2	92	17.56	5.49	2120.6
T_3	25	3.45	0.12	89.25
SEd	–	1.951	0.818	–
CD (5%)	–	1.284	0.734	–

were performed in order to assess the toxicity of the untreated and treated dye solution of ARS on *Z. elegans* seeds at room temperature. Three treatments were set for the present study namely T_1 (control- tap water), T_2 (untreated dye solution) and T_3 (treated dye solution). Ten seeds were sown in each treatment separately and watered regularly with tap water (T_1), untreated dye solution (T_2) and treated dye solution (T_3). At the end of 7th day germination percentage, shoot and root length were recorded in each treatment.

$$\text{Vigor index} = \text{germination percentage} \times (\text{root length} + \text{shoot length}) \qquad (2)$$

Results and Discussion

Effect of dye concentration and adsorbent dosage

The concentration of dye was varied from 100–500 mg/l and maximum removal of 84% occurred at 100 mg/l treated with SCB (Fig. 2a). The decrease in biosorption by raising the ARS indicates that the ratio of the number of ARS molecules to bind to the available active sites on the sugarcane area is fewer and vice versa. Thus the initial concentration of the ARS removal depends on their concentration. Results in Fig. 2b depicts that the adsorption rate increased rapidly with increase in the adsorbent dose and at a certain stage when the dose has increased equilibrium existed and slowly the rate of decolorization was decreased. It can be noted that 0.5 g/l of the adsorbent dose removed 86% of ARS. The increase in percentage removal of ARS with an increased amount of SCB up to 0.5 g/l indicates that the surface area and the adsorption sites to ARS were high. When the amount of adsorbent dose was increased from 0.5 g to 0.6 g/l the adsorption rate was not efficiently enhanced which might be due to the overlapping or aggregation of adsorbent sites at high dose [12].

Effect of pH

pH of a solution is a key factor in the adsorption process because it influences the functional groups on the adsorbent surface and also determines the solubility of the dye in aqueous solution [13]. SCB can effectively remove ARS from aqueous solution (Fig. 2c) at pH 3 (88%) which depicts that the surface of the adsorbent becomes positively charged and favors the uptake of anionic dye and increases the electrostatic force of attraction [14]. Whereas at the alkaline condition, the net positive surface potential of sorbent decreases, resulting in a reduction of electrostatic attraction between the sorbent and the sorbate, which ultimately leads to decrease in percentage dye adsorption. The results of the present study corroborate with earlier findings [15] who showed that the activated carbon derived from the stems of *A. aspera* removed 80% of ARS at pH 3.

Effect of temperature

The rate of diffusion of dye molecules is a temperature controlled process and variation in temperature alters the equilibrium capacity of the adsorbent for a particular adsorbate. The optimum temperature for decolorization of ARS by SCB was observed at 30°C (Fig. 2d). Beyond 30°C there might be a high resistance offered by viscous forces in the solution which leads to sluggish diffusion of dye molecules across the external layer and internal pores of the adsorbent particles. Bhatti et al. [16] studied the maximum adsorption (89%) of Foron blue B-BL by sugarcane bagasse was recorded at 30°C which supports the present observation.

Effect of contact time

The nature of adsorption process relies on the con-

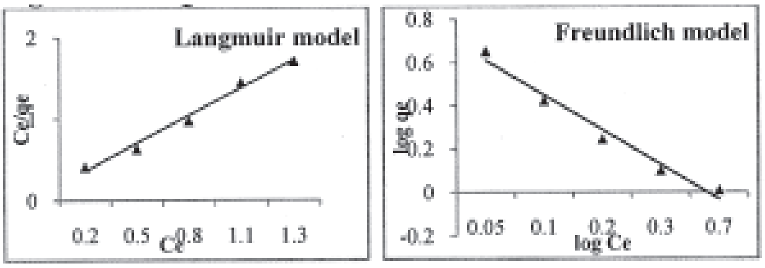

Fig. 3. Langmuir and Freundlich isotherm for ARS onto SCB.

tact time which is evident from the data that the rate of adsorption increases rapidly with contact time up to 5 days and thereafter it gets decreased gradually on 6th and 7th day (Fig. 2e). As the contact time increases there occurs the aggregation of dye molecules with the sorbent surface or it is impossible for the dyes to diffuse deeper into the adsorbent surface at highest energy sites. When the contact time increases the micropores may get filled up and offers resistance to diffusion of aggregated dye molecules in the adsorbents. The same trend was observed in the removal of alizarin red S from aqueous solution using coconut husk at 180 min [17].

Isotherms for the sorption of ARS into SCB

Isotherms are that describe the affinity of the adsorbent in the aqueous solution for the removal of ARS and also based in a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents and interaction between the adsorbate. Adsorption data are usually described by adsorption isotherms, such as Langmuir and Freundlich isotherms. These isotherms relate ARS dye uptake per unit mass of adsorbent (q_e) to the equilibrium adsorbate concentration in the bulk fluid phase C_e. The Langmuir model is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane.

$$\text{Langmuir isotherm} \quad q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \qquad (3)$$

Where q_e, Q_0, K_L, C_e are the amount of dye adsorbed at equilibrium (mg/g), maximum adsorption capacity (mg/g), Langmuir constant (L/g) and the equilibrium concentration of dye in solution (mg/L), respectively. The linear form of Langmuir equation is,

$$C_e q_e = 1/K_L Q_0 + C_e/Q_0 \qquad (4)$$

The Freundlich isotherm is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved or the adsorption process takes place on a heterogenous surface. Freundlich adsorption isotherm is the relationship between the amounts of dye adsorbed per unit mass of adsorbent, (q_e) and the concentration of the dye at equilibrium (C_e).

$$q_e = K_F C_e^{\ 1/n} \qquad (5)$$

where K_F is adsorption capacity at unit concentration and 1/n is adsorption capacity. The logarithmic form of the equation becomes,

$$\log q_e = \log K_F + (1/n) \log C_e \qquad (6)$$

The parameter values related to Langmuir and Freundlich isotherms are calculated from the slope and intercept of the plots (C_e/q_e vs. C_e) and ($\log q_e$ vs $\log C_e$) respectively. The values of Q_0, K_L, K_F, 1/n, R^2

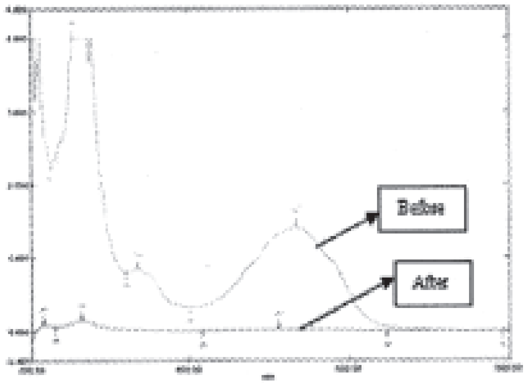

Fig. 4. UV-Vis spectral analysis of ARS after decolorization by SCB.

are shown in Table 1. The R^2 values show that the dye adsorption isotherm using SCB follows both Langmuir and Freundlich isotherms (Table 1). The linear fit between (C_e/q_e verses C_e) and (log q_e verses log C_e) with calculated R^2 values for Langmuir and Freundlich models shows that the dye adsorption can be approximated as both Langmuir and Freundlich models (Fig. 3). This means that the adsorption of dye takes place at both homogeneous and heterogeneous adsorption onto SCB surface.

Adsorption kinetics

Adsorption kinetic using pseudo-first order equation and pseudo-second order equation was determined in order to investigate the mechanism of ARS dye adsorption onto SCB. A linear form of pseudo-first order model

$$\log (q_e - q_t) = \log (q_e) - (k_1/2.303)t \qquad (7)$$

where q_e, q_e, k_1 are the amount of dye adsorbed at equilibrium (mg/g), amount of dye adsorbed at time t (mg/g) and the equilibrium rate constant of pseudo-first order kinetics (1/min) respectively. The linear fit between the log ($q_e - q_t$) and contact time (t) can be approximately as pseudo-first order model kinetics. Linear form of pseudo-second order model was illustrated as

$$t/q_t = 1/K_2 q_e^2 + (t/q_e)t \qquad (8)$$

where K_2 is the equilibrium rate constant of pseudo-second order (g/mg/min).

To understand the applicability of the kinetics models for the dye adsorption onto SCB, linear plots of log ($q_e - q_t$) versus t, t/q_t versus t are plotted. The values of K_1, K_2, R^2 (correlation coefficient values) and the calculated q_e are shown in Table 2. The linearity of the plots (R^2) demonstrates that pseudo-first order and pseudo-second order kinetic models play a significant role in the uptake of the ARS by SCB. The linear fot between (log (q_e – q_t) versus t) and (t/q_t versus t) are calculated R^2 values for pseudo-first order and pseudo-second order kinetics model show that the dye removal can be approximated as both pseudo-first order and pseudo-second order kinetics.

UV-vis spectroscopic analysis

Supernatants were analyzed by UV-vis spectroscopic analysis of the supernatants of untreated and treated ARS solution confirms that the decolorization was due to the biodegradation. The absorption spectra of treated ARS showed a constant decrease in intensity (534, 335 and 252 nm) with time indicating efficient degradation. The dye removal is attributed to biodegradation, either the major visible absorbance peak would completely disappear or a new peak will appear [18]. The results indicate that the color removal by SCB may be attributed to bioadsorption.

Phytotoxicity study

The seeds of *Zinnia elegans* treated with tap water – control (T_1) showed 97% germination, untreated ARS solution (T_2) exhibited 25% germination and ARS dye solution treated with SCB (T_3) revealed 92% germination which was close to that of control plants. Similar such results were observed in shoot length and root length of *Z. elegans* treated with tap water, untreated and treated dye solution (Table 3) which confirms that the selected adsorbent significantly reduce the toxic effect of parent dye. Hence, textile dye ARS alone has a lethal effect on the plant as they remain persistent in the environment but the sugarcane bagasse removes the toxicity of ARS dye significantly.

Conclusion

The present study reveals the role of Sugarcane bagasse in bioremediation of alizarin red S. Maximum removal occurred on the 5th day at 100 mg/L dye concentration. Acidic pH with room temperature (30°C) increases ARS dye biosorption. UV-Vis spectroscopy indicated the decolorization was due to the degradation. Phytotoxicity reveals the nontoxicity of the treated solution. The low cost, high efficiency and possibility of dye recovery predict the potentiality of the uses of sugarcane bagasse for commercial exploitation.

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