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The effect of soaking process of agricultural wastes on the adsorption of methylene blue dye

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Abstract

Locally available agricultural wastes, barely, wheat, and oat straws, were found to be of a low cost and promising adsorbents for the removal methylene blue dye (MB). The effect of soaking process of these straws in water has been investigated for 20 days. The adsorption of MB has been studied by using batch techniques. The influences of sorbent concentration adsorption time and initial dye concentration have been considered. The equilibrium adsorption capacities of straws for MB were obtained by using linear Freundlich, Langmuir, and Tempkin isotherms. The maximum dye adsorption capacity, q_{max}, for the straws before soaking follows the order; barely > oat > wheat, with the values; 27.72, 17.54, and 8.34 mg/g, respectively. While the order of q_{max} for the soaked straws is; oat > barely > wheat, with values equals; 50.34, 22.22, and 11.11 mg/g, respectively. Thermodynamic values of ΔG corresponding to the MB uptake were evaluated from Langmuir model. The negative values of ΔG indicated that the adsorption of MB by these straws is spontaneous and favorable process.

Introduction

Water pollution by high levels of pollutant dyes from textile industry is a serious problem owing to the toxicity effect of these compounds. Over than 7×10^5 ton and approximately 10,000 different dyes and pigments are produced annually world-wide, about 10% of which may be found in wastewater (Deveci *et al*., 2004). Color of these dyes interferes with penetration of sunlight into waters, retards photosynthesis, inhibits the growth of aquatic biota and interferes with gas solubility in water bodies (Banat *et al*., 1996). Complete removal or at least decolorization of these compounds from the environment is, therefore, an important issue.

Although several; physical, chemical, and biological methods have been applied for the treatment of dyes effluents. These methods have earlier been extensively reviewed (Hao *et al*., 2000; Robenson *et al*., 2001; Forgaes *et al*., 2004) and including biological and physico-chemical technologies such as anaerobic treatment, coagulation, electrocoagulation, flotation, filtration, ion exchange, membrane separation, and advanced oxidation (Delee *et al*., 1998; Rai *et al*., 2005; van der Zee and Villaverde, 2005; Mondal, 2008). However, all of those methods have suffered from disadvantages such as incomplete removal of colored effluent, relatively high operating cost, regeneration problem, and high energy requirement.

At present, there is a growing interest in using low cost adsorbents for dye adsorption. If an adsorbent is inexpensive and ready for use, the adsorption process will be a promising technique (Namasivayam *et al*., 2001). Numerous studies on the adsorption properties of naturally occurring and low-cost adsorbents, such as agricultural by-products or natural fibers, have been documented. Namely, barley straw, tree bark, peanut skins, human hair, waste tire rubber, moss peat, etc. have been reported in recent years (Chuah *et al*., 2005; Crini, 2006; Crini and Badat, 2008, Nigam *et al*., 2000). The adsorption capacity of an adsorbent is determined not only by its textural properties, but also by the chemical nature of the surface, i.e., the amount and nature of surface functional groups (Faria *et al*., 2008). It is also dependent on the properties of the adsorptive, such as molecular size, polarity, and functional groups. The nature of the surface functional groups can be modified through physical and chemical treatments. Barley straw composed of many constituents such as: cellulose, lignin, hemicelluloses, and wax. Cellulose is a long chain of glucose molecules, linked to one another primarily with β-(1-4) glycosidic bonds.

Chemical modification of barley straw by a cationic surfactant, hexadecylpyridinium chloride monohydrate (CPC) has been reported. The modified

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surface was employed as an adsorbent to remove emulsified canola oil from aqueous solution (Shariff Ibrahim *et al*., 2010). Moreover, few investigations have been reported using barley straw for other pollutant removal including dye adsorption. The adsorption of artificial dye effluent onto three different agricultural residues including barley husk, sugarcane bagasse, and wheat straw has been reported (Chandran *et al*., 2002; Robinson *et al*., 2002). They were found that pre-treatment would increase the surface area and higher percentage of dye removal was achieved at a faster rate by the milled samples.

The use of biosorbent for dye removal has been intensively investigated as an alternative, economical, and feasible method (Allen *et al*., 2003; El Qada *et al*., 2006; Sulak *et al*., 2007). Examples of these biosorbent are; bagasse pith for the adsorption of Basic Blue 69, Basic Red 22, Acid Red 114, and Acid Blue 25 (McKay *et al*., 1987); banana pith for the adsorption of wastewater containing basic violet (Namasivayam and Kanchana, 1992); palm-fruit bunch for the adsorption of Basic Yellow, Basic Red, and Basic Blue (Nassar and Magdy, 1997); wheat straw, corncobs and barley husks for the adsorption of Cibacron Yellow C-2R, Cibacron Red C-2G, Cibacron Blue C-R, Remazol Black B, and Remazol Red RB (Robinson *et al*., 2002); duckweed for the adsorption of Methylene Blue (Waranusantigul *et al*., 2003); and date pits for the adsorption of Methylene Blue (Banat *et al*., 2003). The present work intends to study the influence of the soaking process of the barely, oat, and wheat straws on the color removal of methylene blue dye. Surface structure, initial dye concentrations, and adsorption capacity were also investigated. .

Materials and Methods

Materials

Barely, wheat and oat straws were obtained from local farms (Misurata) and were subjected to repeatedly washing with water to remove dust and soluble impurities. They were cut into small pieces, about 1 cm length, and washed again thoroughly with distilled water and were dried overnight at 65 ^{o}C. The dried straws were divided into two parts. First one was used on the adsorption process, while the other was soaked in water. Soaking process was achieved by immersing a known amount of straw in a sufficient volume of water at room temperature for 20 days. Throughout this period, it could be expected that some microorganisms from air would be grown on the surface of these straws, which could change the surfaces structure. Moreover, it was found that the color of soaked water was changed into pale brown. This change of color could be attributed to the following; (i) some of the straw composition are released from the surface and dissolved in water. (ii) the microorganisms presented in soaking medium fragmented some straw into soluble materials. The soaked straws were then separated from water and washed with distilled water several times to remove superficially retained dissolved materials. Finally, the straws were dried in an oven at 60 ^{o}C overnight and stored in an airtight glass container and labeled as soaked straws. Methylene blue dye was purchased from Fluka.

Adsorption experiments

The adsorption experiments were carried out in a batch process. The flasks containing 0.3 g of the dry soaked straw and 50 ml of dye solution were placed in a shaker thermostate operating at 130 r/min. Experimental data were collected at 30 ± 1°C by varying the initial concentration of dye in aqueous solution from 1 to 25 mg/L. When the equilibrium was established supernatant was carefully filtered through Whatmann filter paper (no. 1). Samples were taken to measure the dye concentration after 180 min. At this time 3 ml of aqueous sample were taken out and the concentration of the sample was measured using UV/Vis spectrophotometer (Jenway, England) at λ_{max} = 665 nm. Beer's law was used to determine the equilibrium concentration of dye, C_e. The amount of dye adsorbed (mg/g) at equilibrium (q_e) was determined as;

$$q_e = [(C_o - C_e) \text{ x } V] / m \qquad (1)$$

where, C_e is initial dye concentration, C_e is the equilibrium concentration, V is the volume of the solution (0.05 L), and m is the mass of straw (0.3 g).

Results and Discussion

Adsorption isotherm

To optimize the design of an adsorption system for the adsorption of dye wastewater, it is important to establish the most appropriate correlation for the equilibrium curves. Langmuir, Freundlich, and Tempkin models were used to describe the equilibrium characteristics of adsorption.

Langmuir adsorption isotherm

The basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a dye molecule occupied a site, no further adsorption

Table 1. Langmuir isotherm constants for the adsorption of MB onto different straws

Straw	Before soaking			After soaking		
	q_{max} (mg/g)	b (l/mg)	R^2	q_{max} (mg/g)	b (l/mg)	R^2
barely	22.22	0.027	0.999	27.72	0.043	0.994
oat	17.54	0.029	0.998	50.32	0.016	0.889
wheat	8.32	0.122	0.989	11.11	0.112	0.976

Table 2. Gibbs's free energy for the adsorption process of MB

Straw	Before soaking			After soaking		
	K (L/mol)	ln K	ΔG kJ/mol	K (L/mol)	ln K	ΔG kJ/mol
barely	8621.60	9.062	-22.817	13720.43	9.526	-23.985
oat	9251.74	9.132	-22.993	5104.34	8.537	-21.495
wheat	34719.10	10.45	-26.320	35842.69	10.480	-26.387

Table 3. Freundlich isotherm constants for the adsorption of MB onto different straws

Straw	Before soaking			After soaking		
	(1/n)	K_F $[(mg/g)/(mg/l)^{1/n}$	R^2	(1/n)	K_F $[(mg/g)/(mg/l)^{1/n}$	R^2
barely	1.583	0.305	0.988	1.181	0.573	0.998
oat	1.392	0.285	0.964	0.972	0.702	0.956
wheat	1.185	0.573	0.987	1.023	0.983	0.975

Table 4. Tempkin isotherm constants for the adsorption of MB onto different straws

Straw	Before soaking			After soaking		
	B_1	K_T (l/mg)	R^2	B_1	K_T (l/mg)	R^2
barely	2.89	0.63	0.972	1.52	1.50	0.976
oat	0.59	0.41	0.999	0.92	3.72	0.969
wheat	0.65	0.41	0.999	1.03	4.10	0969

can take place at that site. Theoretically, therefore, a saturation value is reached beyond no further sorption can take place. The linear form of Langmuir model is represented by equation (2)

$$1/q_e = 1/q_{max} + 1/q_{max}\, b\, C_e \qquad (2)$$

where C_e is the residual concentration of dye in the solution at equilibrium (mg /l), q_e is the adsorption capacity at equilibrium (mg/g), q_{max} is the maximum adsorption capacity (mg/g), b is the affinity coefficient (l /mg). When $1/q_e$ is plotted against $1/C_e$ a straight line is obtained, Figs (1, 2), for the three adsorbents. The Langmuir constants qmax and b are calculated and the values of these constants are tabulated in Table (1).

The maximum dye adsorption capacity, q_{max}, for the straws before soaking is follows the order; barely > oat > wheat, with the values; 27.72, 17.54, and 8.34 mg/g, respectively. While the order of qmax for the soaked straws is: oat > barely > wheat, with values equals; 50.34, 22.22, and 11.11 mg/g, respectively. This indicated that the soaking process led to increase the adsorption capacity of straws. Furthermore, when comparing b values for unsoaked straws, the follows the order; wheat > oat > barely, while for soaked straws the order is: wheat > barely > oat.

In addition, Gibb's free energy change, ΔG, of adsorption can be estimated from the b constant (Liu, 2006). The b (l/ mg) had to be converted to K (l/ mol) by using the molecular weight of MB (Mol. wt = 319) before calculating ΔG as in Eq. (3). Where R is the universal gas constant (8.314 J K^{-1} mol^{-1}) and T is temperature (K) (Raymon, 1998).

$$\Delta G = -\, R\, T\, In\, K \qquad (3)$$

The values of K and ΔG are determined and are listed in Table (2). Negative values of ΔG indicate that the MB dye adsorption by the straws were spontaneous and a favorable process. Thus, adsorption of MB onto wheat straw (with a more negative value) is more favored although others straws have comparable values.

Freundlich isotherm

Freundlich isotherm is driven by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. The logarithmic linear form of Freundlich model is given by the equation (4);

$$In\, q_e = In\, KF + (1/n)\, In\, C_e \qquad (4)$$

where KF is the Freundlich constant related to the capacity (l/mg), and 1/n is the unit-less Freundlich constant related to the heterogeneity factor. Figs (3, 4) show the plots of ln q_e versus ln C_e for the removal of MB by the adsorbents under investigation are linear, thereby confirming that the Ferundlich isotherm is followed in the adsorption process. The values of Freundlich constants are calculated from the slope and intercept of the linear regression and are listed in Table (3). The 1/n value range between 0 and 1; the more heterogeneous the surface, the closer 1/n value is to 1) (Kumar and Sivanesan, 2007).

Tempkin isotherm

Tempkin isotherm contains a factor that explicitly takes into account adsorbing species-adsorbate interactions. This isotherm assumes that; (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate-adsorbate interactions, and (ii) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy (Tempkin and Pyzhev 1940). Tempkin isotherm model is represented by the equation (5);

$$q_e = B1\, In\, KT + B1\, In\, C_e \qquad (5)$$

A plot of q_e versus ln C_e, Figs (5, 6), enables the determination of the isotherm constants KT and B1, where KT is the equilibrium binding constant (l/mg)

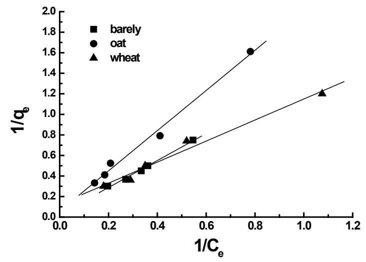

Figure 1. Langmuir isotherm plots for adsorption of MB by unsoaked straws (temperature= 30°C, contact time =180 min)

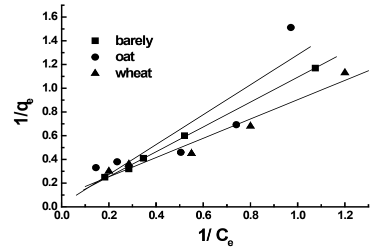

Figure 2. Langmuir isotherm plots for the adsorption of MB by soaked straws (temperature= 30 °C, contact time =180 min)

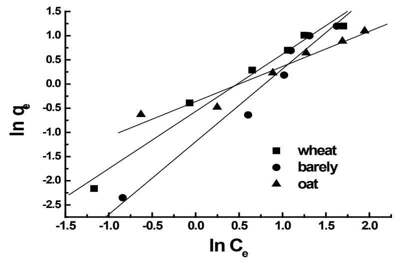

Figure 3. Freundlich isotherm plots for the adsorption of MB by unsoaked straws (temperature = 30 °C, contact time =180 min)

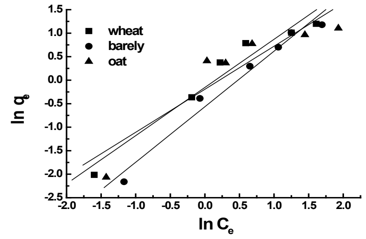

Figure 4. Freundlich isotherm plots for the adsorption of MB by soaked straws (temperature = 30 °C, contact time =180 min)

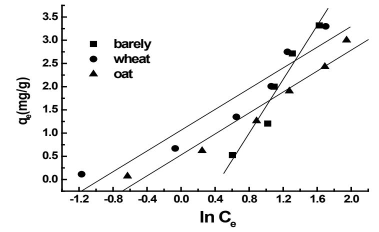

Figure 5. Tempkin isotherm plots for the adsorption of MB by unsoaked straws (temperature = 30 °C, contact time =180 min)

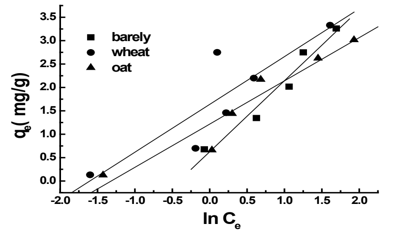

Figure 6. Tempkin isotherm plots for the adsorption of MB by soaked straws (temperature= 30 °C, contact time =180 min)

corresponding to the maximum binding energy, and B1 is related the heat of adsorption. The values of B1 and KT were determined from the slope and intercept of the linear regression and are listed in Table (4).

Conclusions

In this work, the unwanted barley and wheat straws were proven to be useful as biosorbent which were able to uptake methylene blue dye. The experimental data showed that the adsorption capacities were a function of adsorbate, and initial dye concentration. The adsorption equilibrium could be explained by both Freundlich and Langmuir isotherms. Comparison between the adsorption capacities of these straws emphasized that the soaked straws had a reasonably high adsorption capacities for MB. This validates the application of soaked straws for the color removal in textile industry.

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