EQUILIBRIUM STUDY OF METHYLENE BLUE SORPTION FROM AQUEOUS SOLUTIONS BY A LOW-COST WASTE MATERIAL: ALMOND PEEL

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ABSTRACT

In the present work, the usefulness of almond peel as a sorbent material has been investigated for the removal of methylene blue from synthetic aqueous solutions in batch conditions. Isotherm of dye sorption was measured. The influence of different experimental parameters such as: almond peel mass, particles size, temperature, initial pH of solution and NaCl concentration on this isotherm was studied. All these parameters played an important part in sorption phenomenon: the methylene blue sorption increased as these parameters increased. The optimum initial pH for the removal of dye was in the range 6-7. Equilibrium data were mathematically fitted to Langmuir and Freundlich isotherm equations. Langmuir model gave a good fit to the experimental data over the whole equilibrium dye concentrations range. A high dye sorption was observed by this sorbent material: a maximum sorption capacity about 113-140 mg/g was achieved depending on the experimental parameter tested.

Keywords: removal; methylene blue; almond peel; sorption isotherm; modelling.

INTRODUCTION

Synthetic dyes are extensively used by industries including dyehouses, paper printers, textile dyers, colour photography and as additives in petroleum products (Zollinger [1], Selvam et al. [2]). The effluents of these industries are highly coloured and disposal of these wastes into the environment can be extremely deleterious. Their presence in watercourses is aesthetically unacceptable and may be visible at concentration as low as 1 ppm (Zollinger [1]). Moreover, they may also affect photosynthetic activity in aquatic systems by reducing light penetration (O'Mahony [3]). Among the various types of dyes, various cationic dyes, including methylene blue, are used in dye, paint production and in wool dyeing (Bielska and Szymanowski [4]). Methylene blue has wider applications, which include coloring paper, temporary hair colorant, dyeing cottons, wools, coating for paper stock, etc. (Kumar et al. [5,6], Han et al. [7]). Methylene blue is also used in microbiology, surgery, diagnostics, trace analysis of anionic surfactants present in aqueous streams and as a sensitizer in photooxidation of organic pollutants (Bielska, and Szymanowski [4]). Though methylene blue is not strongly hazardous, it can cause some harmful effects. Acute exposure to methylene blue will found cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadripelgia and tissue necrosis in humans (Kumar et al. [5,6]). Due to low biodegradability of dyes a conventional biological treatment process is not very effective in treating a dye wastewater. It is usually treated by physical and/or chemical methods (Garg et al. [8]). Although these treatment methods are efficient, they are quite expensive and have operational problems (Garg et al. [8], Kapdan et al. [9]). Sorption of the molecules onto various sorbents is an ideal option for decolourization, which is evidenced by the effectiveness of sorption for various dye types (Kapdan et al. [9], Porter et al. [10]). The main drawbacks which exist at the present time are the high costs involved in the regeneration of the sorbent. Also, since activated carbon is the most widely used and most effective adsorbent, its high cost tends to increase the cost of adsorption systems (Garg et al. [8], Kapdan et al. [9]). This method will become inexpensive if the sorbent used is of inexpensive material and does not require any expensive additional pre-treatment step (Kumar et al. [5]). As a result, there is a search for low-cost, naturally occurring, abundant sorbent materials that can serve as viable alternatives to activated carbon. The adsorption of methylene blue has a long history of use as a method of surface area determination; it has been adopted widely for solids of a variable nature (oxides, graphite, yeast, activated carbons, calcium carbonate, etc). The method has also been used to assess pore size and distribution in the transitional pore range for charcoals, silica and alumina. In the case of clays, the absorption of MB is currently used for determining either their cation exchange capacities or their surface areas (Ardizzone et al. [11]). Sorption of methylene blue has been extensively studied by many researchers using several low cost materials such as mango seed kernel (Kumar et al. [5]), fly ash (Kumar et al. [6]), cereal chaff (Han et al. [7]), pear millet husk carbon (Inbaraj et al., [12]), *Aspergillus niger* (Fu & Viraraghavan, [13]), rice husk (McKay et al. [14]), Vadivelan & Kumar [15]), hair (McKay et al. [14]), cotton waste (McKay et al. [14]), bark (McKay et al. [14]), perlite (Dogan et al. [16,17]), carbonised press mud (Kumar, [18]), bagasse bottom ash (Kumar, [18]), raw kaolin (Gosh & Bhattacharya, [19]), pure kaolin (Gosh & Bhattacharya, [19]), calcined raw kaoline (Gosh & Bhattacharya, [19]), calcined pure kaoline (Gosh & Bhattacharya, [19]), NaOH treated raw kaolin (Gosh & Bhattacharya, [19]), coir pith (Namasiavam et al. [20]), guava seeds activated carbon (Rahman & Saad, [21]), iron humate (Janos, [22]), neem sawdust (Khattri & Singh, [23]), clay (Gürses et al. [24]), durian shell activated carbon (Chandra et al. [25]), steam activated bitimous coal activated carbon (El Qada et al. [26]), activated carbon (Kumar & Sivanesan,[27]), neem leaf (Bhattacharyya & Sharma [28]), various carbons (Kannan & Sundaram [29]), oxihumolite (Janos et al. [30]), Indian rosewwod sawdust (Garg et al. [31]), palm-tree cobs activated carbons (Avom et al. [32]), water hyacinth root (Low et al. [33]), giant duckweed (Waranusantigul et al. [34]), modified sawdust (De & Basu, [35]). Almond peel waste can be an alternative and favourable sorbent material for pollutants such dyes, heavy metals,… Sorption of cadmium from aqueous solution by almond peel has been studied and this sorbent can be used as a sorbent to remove cadmium(II) from aqueous solutions (Benaïssa, [36]). To date, except the work carried out in our laboratory about the kinetics of methylene blue sorption from synthetic aqueous solution by almond peel (Benaïssa, [37]), no information are available for dyes sorption from aqueous solutions by almond peel in the literature. This low-cost material may be particularly suitable for application in small industries and developing countries.

This work studies the possibility of using a certain natural waste: almond peel as an inexpensive sorbent material for the removal of methylene blue from synthetic aqueous solutions, in single dye solutions, as a continuation to our previous work. This sorbent material is abundantly available through our country and the world. The present study reports its sorption potential through tests of sorption equilibrium, in batch conditions. During this investigation, the effect of different experimental parameters such as: almond peel mass, particle size, temperature, initial pH of solution and NaCl concentration on the sorption isotherm was studied. In order to describe the sorption isotherms mathematically and to obtain information about the maximum sorption capacities, the experimental sorption equilibrium data were then analysed using Langmuir and Freundlich equations. The results from this work are useful to communities that lack advanced cleanup facilities for industrial waste.

MATERIALS AND METHODS

1. Sorbent material and dye

In this work, an agricultural by-product waste: almond peel has been employed as a low-cost sorbent material in the removal of methylene blue from synthetic aqueous solutions. This waste was collected in summer 2004 from the region of Bensekrane, in Tlemcen-Algeria-, in the form of large flakes, cut in small particles of size 1-5 mm and sun/air dried at ambient temperature. It was used as a sorbent material after the following treatment chosen arbitrary: 10 g of almond peel were contacted with 2 L of distilled water in a beaker agitated vigorously (at a speed of 400 rpm) by a magnetic stirrer at ambient temperature of 25±1°C during 4 hours, then filtered, washed with distilled water for several times until constant pH (4.90-5.75) to remove all the dirt particles, and oven-dried at 80°C for 24 hours after filtration. This material was crushed and sieved into four particles size ranges: 1–1.25; 1.6-2; 2-2.5 and 2.5-3 mm. Except the study of the effect of particle size, only the size 1.6-2 mm was used for further batch sorption experiments.

The basic dye, methylene blue (REACTIF RAL – France Lot N°.169) was used as such without further purification, in single component aqueous solutions. A 1000 mg/L stock solutions of methylene blue were prepared in distilled water. All working solutions of the desired concentration were prepared by successive dilutions.

2- Uptake isotherm

The dye equilibrium isotherms were determined by contacting a constant mass 1 g/L of sorbent material with a range of different concentrations of dye solutions: 5-800 mg/L. The mixture obtained was agitated in a series of 250 ml conical flasks with equal volumes of solution 100 ml for a period of 24 hours at room temperature. The contact time was previously determined by kinetics tests using the same conditions (Benaïssa, [37]). The reaction mixture pH was not controlled after the initiation of experiments. After shaking the flasks for 24 h, the final pH was measured. The equilibrium concentration of unbound dye was determined with a UV-visible spectrophotometer, model Beckman 52, at the λ_{max} = 663 nm value. The equilibrium dye uptake q_e (mg dye/g adsorbent) was determined as follows:

$$q_e = (C_o - C_e) \times V/m \qquad (1)$$

where C_o and C_e are the initial and equilibrium dye concentration (mg/L), respectively, V is the volume of solution (mL), and m is the sorbent weight (g) in dry form.

Experiments were carried out/done by varying the different experimental conditions/ the main system variables: sorbent mass (0.5-2 g/L), particle size (1-3 mm), agitation speed (250-800 rpm), temperature (10-50°C), NaCl concentration (0.2-1 g/L) and the initial pH of solution (2-9), to investigate their effects on the sorption kinetics. The initial pH value of solution was adjusted within this range by adding 0.5 N HCl or 0.1N NaOH.

Blank runs, with only the sorbent in distilled water, were conducted simultaneously at similar conditions to account for any colour leached by the sorbent and sorbed by the glass container. Blanks were also run simultaneously, without any sorbent to determine the impact of pH change on the dye solutions.

All studies were carried out in duplicate: each experimental point was an average of two independent sorption tests. Duplicate tests showed that the maximum standard deviation of the results was ± 5 %.

Preliminary experiments had shown that dyes adsorption losses to the container walls were negligible.

RESULTS AND DISCUSSION

1- Sorption equilibrium

Equilibrium experiments were carried out to evaluate the potential of almond peel, as a sorbent material, for commercial applications. Different parameters related to the sorbent, to dye and the medium can influence the isotherm of methylene blue sorption by almond peel. In this context, the influence of various experimental parameters such as: mass of almond peel, particle size, temperature, initial pH of solution and NaCl concentration on the isotherm of methylene blue sorption have been studied in a goal of optimisation.

Figs. 1-5 presented below, show the dye sorption isotherms by almond peel obtained at different experimental conditions. For all isotherms, the amount of dye sorbed increases initially with the dye concentration at equilibrium but then reaches saturation. These isotherms obtained are of type-2 class L type (Langmuir type) according to the classification of isotherms of Giles et al. [38] for sorption from solution, implying strong preferential sorption of the solute, and, are generally associated with the coverage of a solid surface by a monolayer of flat sorbate molecules (Ardizzone et al., [11]).

During all experiments of dye sorption equilibrium (results not presented here), except those of initial pH effect (see below), it was observed that the initial pH of the solution increased, and, the equilibrium pH varied with the initial concentration of dyes and the experimental parameter tested. The same observations were obtained during the experiments of methylene blue sorption kinetics (Benaïssa, [37]).

1.1- Effect of sorbent mass

In the goal to determine the necessary almond peel mass for a maximal sorption of methylene blue, the effect of almond peel mass on the kinetics of methylene blue sorption was studied. Fig. 1 shows that the maximum amount of methylene blue sorbed by almond peel decreases with the increase of the mass of almond peel used: about 140 mg/g (m = 0.5 g) and 92 mg/g (m = 2g): this can be explained by the formation of aggregates at higher almond peel doses, which decreases the effective sorption area (Benaïssa, [37]).

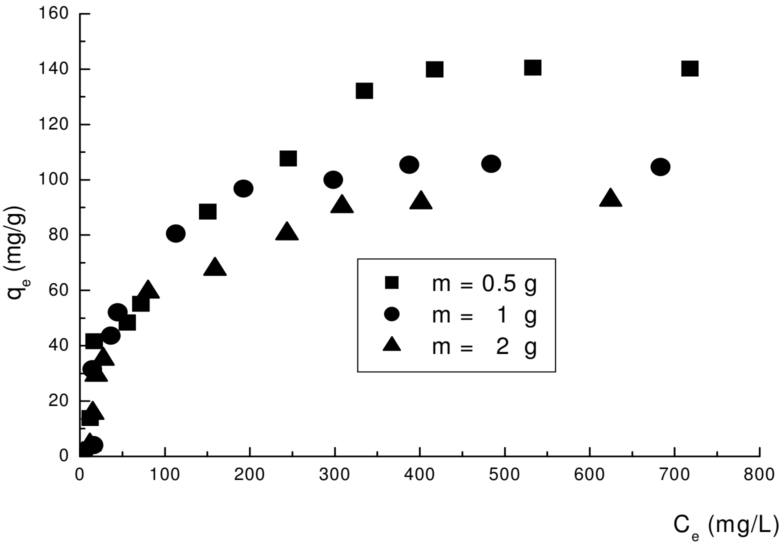

Figure 1. Effect of almond peel mass on methylene blue sorption isotherm.
(dp = 1.6 – 2 mm, original initial pH of solution, agitation speed = 400 rpm, T= 25°C)

1.2- Effect of particle size

The surface of contact between any sorbent material and the liquid phase plays an important role in the phenomena of sorption. The effect of particle size of almond peel on the isotherm methylene blue sorption was studied using four particle size groups: 1-1.25; 1.6-2; 2-2.5 and 2.5-3 mm. As can be seen in Fig. 2, the curves of dye sorption isotherm obtained have an identical shape. The maximum amount of methylene blue sorbed increases with the decrease of almond peel particle sizes: about 130 mg/g (1-1.25 mm) and 86 mg/g (2.5-3 mm) indicating that methylene blue sorption occurs by a surface mechanism [37].

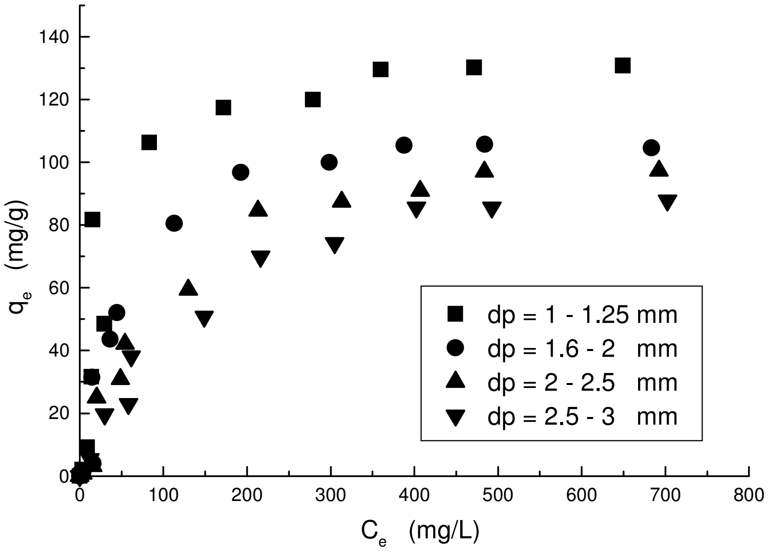

Figure 2 . Effect of almond peel particles size on methylene blue sorption isotherm. (m = 1 g/L, original initial pH of solution, agitation speed = 400 rpm, T= 25°C)

1.3- Effect of temperature

The results obtained and presented on the Figure 3, indicate that an increase of the temperature in the interval 10-50°C deals to an increase in the maximum amount of dye sorbed: about 77 mg/g (T = 10 °C) and 118 mg/g (T= 50 °C). The increase of methylene blue sorption in the interval of temperature 10-50 °C, means that the process of dye sorption by almond peel is endothermic. If this sorption of methylene blue by almond peel is governed only by physical phenomena, an increase in temperature will be followed by a decrease in sorption capacity (Benaïssa, [37]).

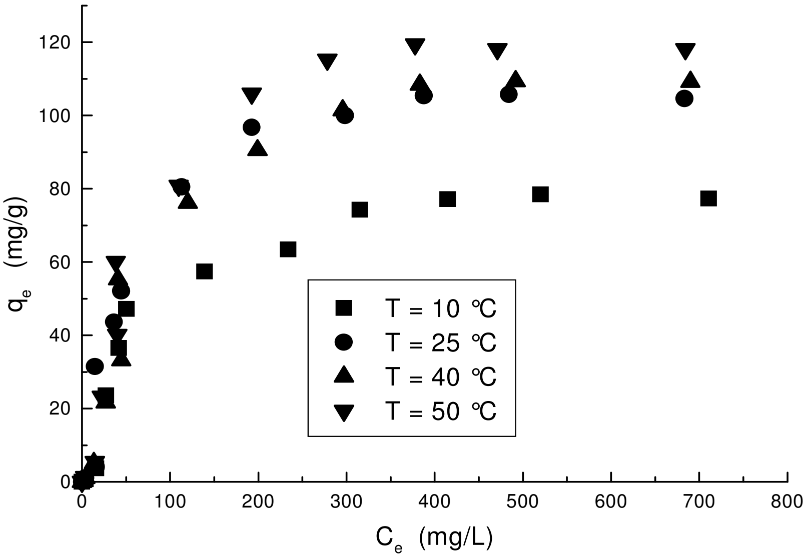

Figure 3. Effect of temperature on methylene blue sorption isotherm by almond peel. (m = 1 g/L, dp = 1.6 – 2 mm, original initial pH of solution, agitation speed = 400 rpm)

1.4- Effect of initial pH of solution

As shown in Fig. 4, the initial pH of solution has an influence on the isotherm of methylene blue sorption by almond peel. The maximum amount of methylene blue sorbed increases when the initial pH of solution increases: about 39 mg/g ($pH_0 = 2$) and 114 mg/g ($pH_0 = 6$). Beyond this last value of pH_0, we noticed a decrease in the maximum amount of dye sorbed: 110 mg/g ($pH_0 = 7$) and 108 ($pH_0 = 9$).

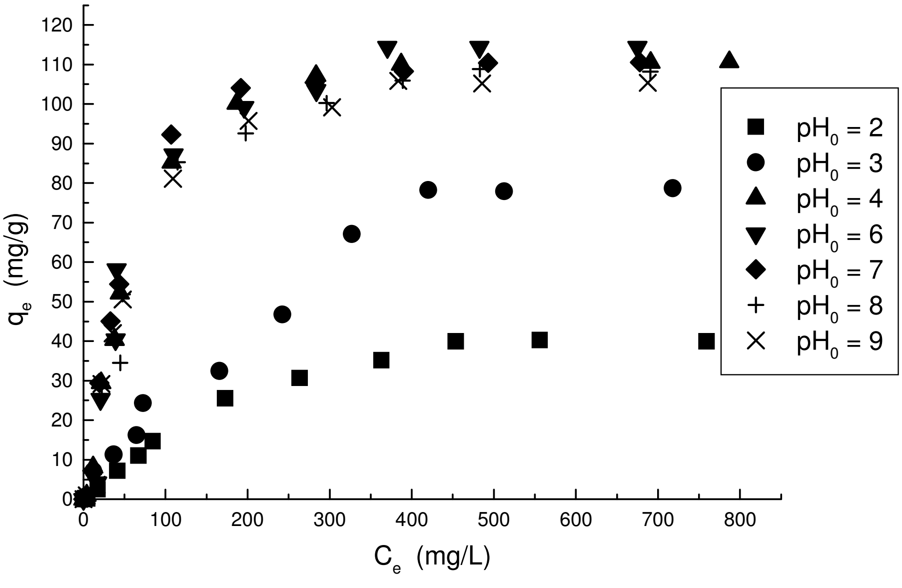

Figure 4. Effect of initial pH of solution on methylene blue sorption isotherm by almond peel. (m = 1 g/L, dp = 1.6 – 2 mm, agitation speed = 400 rpm, T = 25 °C)

During these experiments (results not presented here), we noticed two opposite phenomenon: an increase in the initial pH value of solutions for initial pH of solution ranging from 2 to 4, and, a decrease for initial pH of solution ranging from 6 to 9 (Benaïssa, [37]).

1.5- Effect of NaCl concentration

The effect of NaCl concentration on the isotherm of methylene blue sorption by almond peel was analysed with 3 concentrations: 0.2, 0.5 and 1 g/L , respectively. As shown in Fig. 5, this range of NaCl concentration used has an influence on the isotherm of dye sorption by the sorbent. The maximum amount of methylene blue sorbed increases when the NaCl concentration of solution increases: about 113 mg/g ([NaCl]= 0.2 g/L) and 130 mg/g ([NaCl] = 1 g/L).

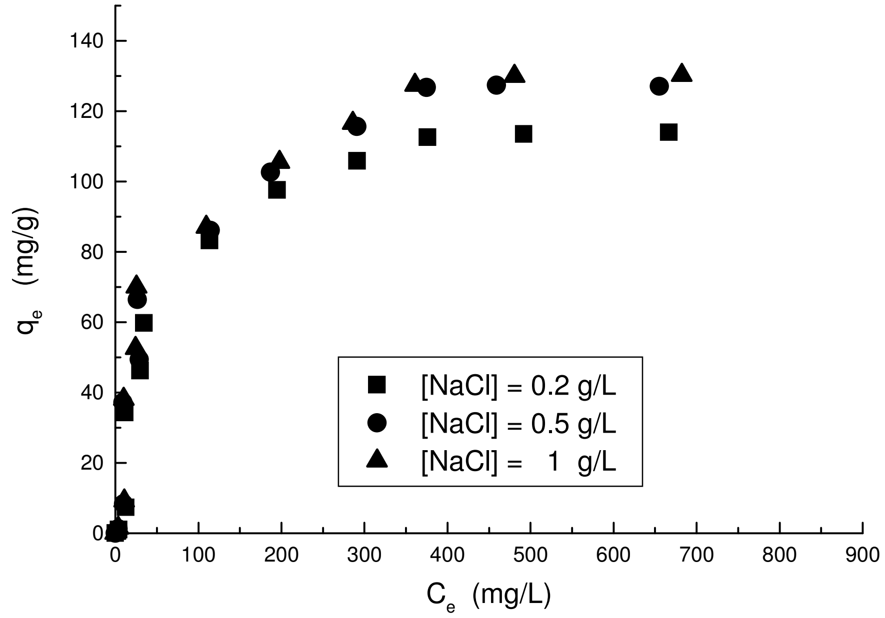

Figure 5. Effect of NaCl concentration on methylene blue sorption isotherm by almond peel. (m = 1 g/L, dp = 1.6 – 2 mm, original initial pH of solution, agitation speed = 400 rpm, T = 25 °C)

2- Modelling

In order to optimise the design of a sorption system to remove pollutants from effluents, it is important to establish the most appropriate correlation for the equilibrium curve. Two isotherm equations commonly used to fit experimental data when solute uptake occurs by a monolayer sorption, have been tested in the present study, namely, Langmuir [39] and Freundlich [40] and given as follows:

Langmuir: $q_e = q_m K_L C_e/(1+K_L Ce)$ (2)

Freundlich: $q_e = K_f C_e^n$ (3)

The linearized forms on these equations can be written as follows:

$$C_e/q_e = 1/K_L q_m + C_e/q_m \quad (4)$$

$$Log\ q_e = Log\ K_f + n\ Log\ C_e \quad (5)$$

where: q_e is the amount of dye sorbed at equilibrium per g of sorbent (mg/g); C_e the equilibrium concentration of dye in the solution (mg/L); q_m and K_L are the Langmuir model constants; K_f and n the Freundlich model constants. If the equation of Langmuir is valid to describe the experimental results, it must verify the linearized shape of the basis equation, in system of coordinates C_e/q_e vs. C_e, that will permit us to obtain the constants q_m and K_L from the intercept and slope. If the equation of Freundlich is also verified, we must obtain a straight line in the system of coordinates Ln q_e vs. Ln C_e, the slope and the intercept to the origin give n and K_f respectively. Results of the modelling of isotherms of dyes adsorption by the sorbent used, according to these models, are presented in Table 1.

It appears that the Langmuir model acceptably fits the experimental results over the experimental range with good coefficients of correlation (R^2: 0.8808-0.9986). A high dye sorption was observed by this sorbent material confirming the previous tendencies observed in the kinetics sorption (Benaïssa, [37]). According to the coefficients of correlation (R^2: 0.7145-0.9535), the model of Freundlich is not adequate for modelling isotherms in all the studied equilibrium concentrations domain. As shown in Table 2, the maximum capacity of methylene blue sorption obtained is also very high compared to those reported by other authors with other methylene blue – sorbent systems, although this direct comparison is difficult due to the varying experimental conditions used in these studies. In identical experimental conditions, differences in dye uptake are due to the properties of each sorbent material such as structure, functional groups and surface area.

Table 1: Model constants for the sorption of methylene blue by almond peel at T = 25 °C.

Parameter	Langmuir model			Freundlich model		
	q_m(mg/g)	K_L(L/mg)	R^2	K_F	n	R^2
m (mg/L)		Sorbent mass				
0.5	166.39	0.009	0.9815	5.41	0.533	0.9317
1	113.77	0.023	0.9979	14.16	0.334	0.9360
2	103.41	0.016	0.9947	7.37	0.427	0.9024
dp (mm)		Particle size				
1 – 1.25	140.85	0.042	0.9667	24.52	0.296	0.7167
1.6-2	113.77	0.023	0.9979	14.16	0.334	0.9360
2 – 2.5	112.62	0.011	0.9923	7.15	0.424	0.9492
2.5 – 3	110.25	0.007	0.9772	1.85	0.626	0.7145
T (°C)		Temperature				
10	85.18	0.017	0.9964	10.67	0.338	0.8804
25	113.77	0.023	0.9979	14.16	0.334	0.9360
40	128.04	0.011	0.9859	6.43	0.465	0.8832
50	135.14	0.014	0.9891	8.77	0.437	0.8478
pH_0		Initial pH of solution				
2	57.41	0.004	0.9385	0.46	0.727	0.9400
3	121.21	0.003	0.8808	0.46	0.854	0.9495
4	122.70	0.018	0.9962	10.94	0.388	0.8952
6	128.53	0.016	0.9952	10.18	0.406	0.8698
7	120.05	0.022	0.9977	13.04	0.359	0.8777
8	123.15	0.013	0.9927	8.57	0.422	0.8821
9	116.28	0.018	0.9977	11.37	0.371	0.9100
[NaCl] (mg/L)		NaCl				
0.2	121.80	0.024	0.9986	1.94	0.716	0.7206
0.5	136.43	0.023	0.9952	20.75	0.297	0.9535
1	138.31	0.024	0.9951	32.08	0.222	0.8822

Table 2: Maximum sorption capacities of low cost sorbents for the removal of methylene blue from its aqueous solutions.

Sorbent material	Maximum sorption capacity, q_m (mg/g)	Reference
Bark	914.58	(McKay et al., [14])
Activated bitimous coal activated carbon	580	(El Qada et al., [26])
Activated carbon	343-400	(Kumar & Sivanesan, [27])
Coal	323.68	(McKay et al., [14])
Rice husk	312.26	(McKay et al., [14])
Cotton waste	277.78	(McKay et al., [14])
Durian shell activated carbon	237.13-289.26	(Chandra et al., [25])
NaOH treated raw kaolin	204.00	(Gosh & Bhattacharya, [19])
Hair	158.23	(McKay et al., [14])
Mango seed kernel	142.86-153.85	(Kumar et al., [5])
Bagasse bottom ash	142	(Kumar, [18])
Almond peel	113-140	Present work
NaOH treated pure kaolin	122.01	(Gosh & Bhattacharya, [19])
Unexpended perlite	67.45-266.14	(Dogan et al, [17])
Carbonized press mud	50	(Kumar, [18])
Pure kaolin	91.9	(Gosh & Bhattacharya, [19])
Pear millet husk carbon	66	(Inbaraj et al., [12])
Calcined pure kaolin	56.3	(Gosh & Bhattacharya, [19])
Expended perlite	17.39-30.79	(Dogan et al., [17])
Raw kaolin	27.50	(Gosh & Bhattacharya, [19])
Aspergillus niger	15.5	(Fu & Viraraghavan, [13])
Calcined raw kaolin	13.4	(Gosh & Bhattacharya, [19])
Neem leaf	8.76	(Bhattacharyya & Sharma [28])
Clay	5-6.3	(Gürses et al. [24])
Fly ash	5.72	(Kumar et al. [6])
Neem sawdust	2.12-3.62	(Khattri & Singh, [23])
Guava seeds activated carbon	0.62-0.67	(Rahman & Saad, [21])

The applicability of these models should be considered as a mathematical representation of the sorption equilibrium over a given dye concentration range. The mechanistic conclusions from the good fit of the models alone should be avoided. In spite of the above limitations, these models can provide information on dye uptake capacities and differences in dye uptake between various species (Kapoor & Viraraghavan [41]). At this stage, we have not enough information about the mechanism of dyes sorption by this material. The sorption of dyes by this kind of materials might be attributed to different kinds of sites present on the sorbent surface.

CONCLUSION

This work shows the interest of a concept based on the waste to treat another waste or to resolve an environmental problem. The results obtained confirm that almond peel can remove methylene blue from aqueous solution. Parameters studied such as: sorbent mass, particle size, temperature, initial pH of solution, and NaCl concentration play an important part in sorption phenomenon: the maximum methylene blue sorption increased as these parameters increased. Langmuir model gave a good fit to the experimental data over the whole equilibrium dye concentrations range. However, we have not enough information about the mechanism of methylene blue sorption by this sorbent. Additional work will be also required in order to optimize the overall process, to improve these actual capacities of sorption obtained and to identify the different functional groups responsible for the dye binding.

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