FEASIBILITY STUDY OF ACID DYE REMOVAL FROM SYNTHETIC AQUEOUS SOLUTIONS BY SORPTION USING TWO VARIETIES OF ORANGE PEEL IN BATCH MODE

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ABSTRACT

The ability of two varieties of orange peels namely: tomson navel and clementine, as an inexpensive sorbent for the removal of two acid dyes: bemacid blue and bemacid yellow from synthetic aqueous solutions has been studied. The dyes sorption kinetics and equilibrium isotherms have been investigated at acid initial solution pH (2.20) in batch conditions. The effects of some parameters such as: contact time, initial dye concentration and dye type on the kinetics of dye sorption, have been studied. For each system dye-sorbent, the quantity of dye sorbed at equilibrium depends on contact time, initial dye concentration and increases with an increase of these two parameters. The sorption process of each dye by the two varieties of orange peel followed a pseudo second – order rate kinetics. The Langmuir model was found to provide a good fit to the experimental data of dye sorption equilibrium than the Freundlich model for both dyes. Under the experimental conditions tested here, acceptable maximum dye sorption capacities were obtained: about 32.34 and 31.39 mg/g, respectively, for bemacid yellow and bemacid blue using the clementine variety, and, 30.71 and 29.59 mg/g, respectively, for bemacid blue and bemacid yellow using the tomson navel variety under the experimental conditions tested here.

Keywords: Removal, Sorption, Acid dyes, Orange peels, Kinetics, Isotherms

INTRODUCTION

Synthetic dyes are extensively used for dyeing and printing in industries. Their presence in watercourses is aesthetically unacceptable and may be visible at concentration as low as 1 ppm [1]. Moreover, they may also affect photosynthetic activity in aquatic systems by reducing light penetration [2]. Among the various types of dyes, various acidic dyes are used to color nylon, wool, sole in textile industries, paper and leather. This class of dyes is the most problematic, because they tend to pass through conventional treatment systems unaffected [3-5]. Although different physical and / or chemical treatment methods are efficient in treating a dye wastewater, they are quite expensive and have operational problems [6-7]. As a result, there is a search for low-cost, naturally occurring, abundant sorbent materials that can serve as viable
alternatives to activated carbon used in adsorption process.

This work explores the possibility of using an agricultural waste namely: two varieties of orange peels (tomson navel and clementine), as an inexpensive sorbent for the removal of two acid dyes: bemacid blue and bemacid yellow, as models of acid dyes, from synthetic aqueous solutions. This material is abundantly available in Algeria, hence cost effective sorbent. Dyes sorption equilibrium and kinetics tests were performed at acid pH (2.20) of solutions in batch conditions. The effect of some parameters such as: contact time, initial dye concentration and dye type on dye sorption kinetics, has been studied. Two simplified kinetic models including a pseudo first-order and pseudo second-order models were selected to analyse the dye sorption kinetics. In order to describe the dye sorption isotherms mathematically and to obtain information about the maximum dye sorption capacity of this sorbent tested, the equilibrium data were analysed using Langmuir and Freundlich models.

MATERIALS AND METHODS

1 Sorbents and dye: Two varieties of orange peels: tomson navel and Clementine, used as a sorbent material in this work, are cheap and highly available lignocellulosic wastes in Algeria. This waste was collected from a local market in autumn-winter 2011 in the form of large flakes. Firstly, this waste was cut in small pieces and sun/air dried at ambient temperature during many days, oven-dried at 80°C. To be used as a sorbent material, this material was used washed thoroughly with tap water to remove all the adhering dirt particles until no colour was observed, rinsed using a distilled water until a constant pH of solution was stabilized, filtered and then oven-dried at 85 ± 5 °C for 24 h. Then, it was crushed and sieved to keep only the size range 1.25-2.

Bemacid blue E-TL and bemacid yellow E-TL (Bezema Suisse), as commercial salts with unknown structures, were kindly donated by SOITEX Company located in the City of Tlemcen-Algeria. There were used as received without further purification, in single component aqueous solutions. 2000 mg/L stock solutions of each dye were prepared in distilled water. All working solutions of the desired concentration were prepared by successive dilutions.

2 Sorption experiments

2.1 Uptake kinetics: In each sorption experiment, 2L of dye solution of known concentration in the range of 50-300 mg/L were added to 2 g of the sorbent in a beaker agitated vigorously by a magnetic stirrer at 400 rpm using a water bath maintained at a constant temperature 25 °C. Firstly, for both dyes at initial dye concentration of 100 mg/L, the working pH was that of the original solution in the range 5.86-6.82 and was not adjusted. Secondly, from the first results obtained and for both dyes, the initial solution pH was adjusted to 2.20 for all initial dye concentrations tested by adding small amounts of HCl 1 N after determination of the pH<sub>pzc</sub>. Samples from the clear supernatant, at appropriate time intervals, were pipeted from the beacker by the aid of
the very thin point pipette, which prevented the transition of sorbent samples to solution. Their dye concentrations were determined using UV-visible spectrophotometer (Lange Hach, model DR 5000, USA) at $\lambda_{\text{max}}$ 390 and 604 nm for bemacid yellow and bemacid blue, respectively. The dye uptake $q_t$ (mg dye/g sorbent) was determined as follows:

$$q_t = (C_0 - C_t).V/m$$  \hspace{1cm} (1)

where: $C_0$ and $C_t$ are the initial and time dye concentration (mg/L), respectively, $V$ is the volume of solution (mL), and $m$ is the sorbent weight (g) in dry form.

Preliminary experiments had shown that dye sorption losses to the container walls were negligible.

2.2. Uptake equilibrium: The dye equilibrium isotherms were determined by contacting a constant mass 0.200 g of the sorbent material with a range of different concentrations of dye solutions: 25-700 mg/L with an initial solution pH adjusted to 2.20 by adding small amounts of HCl 1 N. The mixture obtained was agitated in a series of 250 ml conical flasks with equal volumes of solution 200 ml for a period of 24 h at a constant temperature $25 \pm 1 \, ^\circ C$. The contact time in the range 7-10 h for both dyes was previously determined, but, in order to avoid sorption error i.e. a pseudo-equilibrium, 24 h was chosen to study the dyes sorption equilibrium. The mixture pH was not controlled after the initiation of experiments. At equilibrium, the final pH was measured. The equilibrium concentration of each unbound dye was determined with a UV-visible spectrophotometer. The equilibrium dye uptake $q_e$ (mg dye/g. sorbent) was determined by difference between concentrations: initial and at equilibrium, respectively.

RESULTS AND DISCUSSION

1- Kinetics studies

1.1.Effect of contact time: For each dye tested, preliminary dye sorption experiments were performed for an initial dye concentration 100 mg/L and at natural solution in the range 5.86-6.82 to determine the equilibrium time. From, the first results obtained (Fig. no shown here), the amounts of dye sorbed at equilibrium were low/negligible: 0.38 and 0.50 mg/g for bemacide yellow, respectively, using clementine and tomson navel as a sorbent, and, 0-0.21 and 0-0.42 mg/g for bemacid blue respectively using tomson navel and clementine. Facing this situation and in order obtain some information about the surface charge, the pH$_{pzc}$ of both varieties of orange peel were determined as: 4.43 and 4.96 respectively for tomson navel variety and clementine variety. From this last result and in order to obtain appreciable amounts of dyes sorbed by these varieties of orange peel, dyes sorption experiments at acid initial solution pH about 2.20 chosen arbitrary were performed.
According to Fig. 1 obtained for an initial dye concentration 100 mg/L, the sorption kinetics of both dyes tested by the both varieties of orange peels present a same shape characterized by a strong increase of the amount of dye sorbed during the first minutes of contact solution – sorbent, follow-up of a slow increase until to reach a state of equilibrium. The necessary times to reach this equilibrium are in the range 9-10 h for bemacid yellow and bemacid blue using the both varieties of orange peels, and, an increase of removal time to 24 h did not show notable effects.

![Figure 1. Kinetics of dyes sorption from aqueous solution by two varieties of orange peels: A) Bemacid blue, B) Bemacide yellow. (Experimental conditions: C₀= 100 mg/L, sorbent dose= 1g/L, particle size= 1.25-2 mm, agitation speed= 400 rpm, initial solution pH= 2.20, T= 25 °C)](image)

Under these experimental conditions, the amounts of dye sorbed at equilibrium are about 22.70 and 19.21 mg/g, respectively, for bemacid yellow and bemacid blue using clementine variety, and, 20.37 and 16.40 mg/g, respectively, for bemacid yellow and bemacid blue using tomson navel variety During the course of each dye sorption by both varieties of orange peels, a slight increase in the initial pH value of the solution between the initial and equilibrium time was observed (Fig. no shown here). This suggests that dye binding to date pedicels is associated with the fixation of H₃O⁺ ions from solution by the sorbent surface or a release of OH⁻ ions from the sorbent surface.
into the solution.

1.2. **Effect of initial dye concentration**: To study the effect of the initial dye concentration on the sorption kinetics of each dye from synthetic aqueous solution by the both varieties of orange peel tested here, sorption experiments were performed at different initial dye concentration: 50, 100 and 300 mg/L. According to Figs. 2 and 3 as typical examples, for all dye concentrations studied, the curves obtained for both dyes present the same shape characterized by a strong increase of the amount of dye sorbed during the first minutes of contact solution–sorbent, follow-up of a slow increase until to reach a state of equilibrium.

**Figure 2.** Effect of initial dye concentration on sorption kinetics of bemacid yellow by clementine variety, as a typical example. (Experimental conditions: sorbent dose = 1g/L, particle size: 1.25-2 mm, agitation speed= 400 rpm, acid initial solution pH= 2.20, T= 25 °C)

**Figure 3.** Effect of initial dye concentration on sorption kinetics of bemacid blue by tomson navel variety, as a typical example. (Experimental conditions: sorbent dose = 1g/L, particle size: 1.25-2 mm, agitation speed= 400 rpm, acid initial solution pH= 2.20, T= 25 °C)
Under these experimental conditions, from the results obtained at equilibrium, the necessary time to reach equilibrium is in the range 7-10 h respectively for both dyes, dependent on initial dye concentration, and an increase of dye removal time to 24 h did not show notable effects. The amount of dyes sorbed at the equilibrium increases with the initial dye concentration. During the course of each dye sorption by both varieties of orange peels (Fig. no shown here), a slight increase in the initial pH value of the solution followed by some equilibrium state was also observed.

1.3 Modelling: To analyze the sorption kinetic data of each dye by the date pedicels under the experimental conditions tested, two common models from the literature, namely: the first-order rate model of Lagergren [8] and the pseudo second-order rate model [9,10] were chosen and shown below as Eqs. (2) and (3) in their linear forms:

\[
\log (q_e - q_t) = \log q_e - k_L t / 2.3
\]  
\[
t/q_t = 1 / k \cdot q_e^2 + t / q_e
\]

where: \(k_L\) is the Lagergren rate constant of sorption (min\(^{-1}\)) and \(k\) the pseudo second-order rate constant of sorption (g.mg\(^{-1}\).min\(^{-1}\)); \(q_e\) and \(q_t\) are the amounts of dye sorbed (mg.g\(^{-1}\)) at equilibrium and at time \(t\), respectively. For all initial dye concentrations, the different values of constants from the slope and intercept of linear plots of \(\log (q_e - q_t)\) vs. \(t\) and \(t/q_t\) vs. \(t\) (Fig. no shown here) are summarized in the Table 1.

The results obtained confirm that the kinetic data obtained follow the pseudo second-order kinetic model. Compared to the first-order rate model (\(R^2 = 0.8606-0.9745\)), the pseudo second–order rate model adequately described the kinetics of dye sorption with good correlation coefficients (\(R^2 = 0.9651-0.9949\)). The equilibrium dye sorption capacity, \(q_e\), increases with the increase in the initial dye concentration. The values of \(q_e\) obtained from the fitting to the pseudo second-order rate model are very similar to the experimental values obtained from the sorption kinetics at equilibrium.
Table 1. Models rate constants for bemacid yellow and bemacid blue sorption kinetics by both varieties of orange peel: effect of initial dye concentration.

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<th>Pseudo second order kinetics model</th>
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<td>qₑexp. (mg/g)</td>
<td>qₑcal. (mg/g)</td>
<td>kₑ.10³ (min⁻¹)</td>
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<td></td>
<td></td>
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<td>k.10⁴ (g.mg⁻¹.min⁻¹)</td>
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<tr>
<td>Clementine</td>
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<td>C₀ (mg/L)</td>
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<td>50</td>
<td>15.32</td>
<td>15.57</td>
<td>7.66</td>
<td>0.9612</td>
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<tr>
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<td>22.70</td>
<td>20.09</td>
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</tr>
<tr>
<td>300</td>
<td>29.30</td>
<td>21.86</td>
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<td>0.9604</td>
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<tr>
<td>Tomson navel</td>
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<td>C₀ (mg/L)</td>
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<td>50</td>
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<tr>
<td>300</td>
<td>27.95</td>
<td>20.66</td>
<td>4.69</td>
<td>0.9509</td>
</tr>
</tbody>
</table>
2- Equilibrium study

2.1 Sorption isotherms: Fig. 4 shows the sorption isotherms, \( q_e \) vs. \( C_e \) of both dyes by the both varieties of orange peel at acid initial pH of solutions which are of L type according to the classification of Giles et al. [11] for liquid-solid adsorption. Under these experimental conditions and from the plot of these isotherms, the maximum capacities of dyes sorbed by both varieties of orange peels are about: 29.40 mg/g for bemacid blue and 30.50 mg/g for bemacid yellow using clementine variety, and, 28.70 mg/g for bemacid blue and 28.25 mg/g for bemacid yellow using tomson navel variety.

![Figure 4. Isotherms of dye sorption by two varieties of orange peels at 25 °C: A) Tomson navel, B) Clementine](image)

From these results, both varieties of orange peel tested here appear to be effective to remove bemacid yellow and bemacid blue from synthetic aqueous solution under the experimental conditions tested here (i.e. acid medium). During the experiments of dyes sorption equilibrium by both varieties of orange peels, for all initial dye concentration used, a slight increase in the initial pH value of the solution between the initial and saturation time was also observed.
2.2 Modeling: To analyze the sorption equilibrium data obtained of bemaci yellow and bemacid blue by both varieties of orange peels, two simple isotherm equations have been tested in the present study, namely, Langmuir [12] and Freundlich [13]. The quality of the isotherm fit to the experimental data is typically assessed based on the magnitude of the correlation coefficient for the regression; i.e. the isotherm giving an $R^2$ value closest to unity is deemed to provide the best fit.

a) The linearised Langmuir model has the following form:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$$

(4)

with: $q_e$: amount of dye sorbed at equilibrium per g of sorbent (mg/g), $q_m$: maximal dye sorption capacity of sorbent material (mg/g), $C_e$: equilibrium dye concentration in the solution (mg/L) and $K_L$: constant of equilibrium (L/mg) depending on temperature and the applied conditions. If the model of Langmuir is valid to describe the experimental results, it must verify the linearised shape of the basis equation, in system of coordinates $C_e/q_e = f (C_e)$, that will permit to obtain the constants $q_m$ and $K_L$ from the intercepts and slopes.

b) The linearised Freundlich model has the following form:

$$\ln q_e = \ln K_F + n \ln C_e$$

(5)

where: $q_e$ and $C_e$ are as described before, $K_F$ and $n$: positive constants depending on the nature of system solute-sorbent and temperature, $n < 1$. If this equation is verified with data of sorption equilibrium, we must obtain a straight line in the system of coordinates $\ln q_e = f (\ln C_e)$, the slope and the intercept to the origin give the values of constants $n$ and $K_F$ respectively.

Table 2. Parameters of Langmuir and Freundlich models for dyes sorption isotherms by two varieties of orange peels at 25 °C.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Langmuir model</th>
<th>Freundlich model</th>
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<tbody>
<tr>
<td></td>
<td>$q_{\text{max}}$ (mg/g)</td>
<td>$K_L$ (L/mg)</td>
</tr>
<tr>
<td>Clementine</td>
<td></td>
<td></td>
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<tr>
<td>Bemacid yellow</td>
<td>32.34</td>
<td>0.036</td>
</tr>
<tr>
<td>Bemacid bluel</td>
<td>31.39</td>
<td>0.029</td>
</tr>
<tr>
<td>Tomson navel</td>
<td></td>
<td></td>
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<tr>
<td>Bemacid yellow</td>
<td>29.59</td>
<td>0.043</td>
</tr>
<tr>
<td>Bemacid bluel</td>
<td>30.71</td>
<td>0.026</td>
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</table>
From results obtained (Figs. not shown here) and the model parameters determined by least squares fit of the experimental sorption data presented in Table 2, it appears that the Langmuir model reasonably fits the experimental results over the experimental dye concentration range with acceptable coefficients of regression ($R^2 = 0.9971-0.9990$). According to coefficients of correlation ($R^2 = 0.7397-0.9676$) obtained, the model of Freundlich is not adequate for modelling the isotherms of dyes sorption by both varieties of orange peel in all the domain of studied concentrations.

CONCLUSIONS

The present study shows that both varieties of orange peel tested here can be acceptably used as a sorbent material for the removal of acid dyes from synthetic aqueous solutions but in acidic medium. For each system dye-sorbent, the quantity of dye sorbed at equilibrium depends on contact time, initial dye concentration and increases with an increase of these two parameters. The sorption kinetics of both dyes was well described by a pseudo-second order rate model. An acceptable fitting of dye sorption equilibrium data was obtained with Langmuir model in all the range of concentrations studied. Under the investigated experimental conditions, the maximum dye sorption capacities obtained by both varieties of orange peels followed the order: bemacid yellow (32.34 mg/g) > bemacid blue (31.39 mg/g) using Clementine variety, and, bemacid blue (30.71 > bemacid yellow (29.59 mg/g) using tomson navel variety. The results obtained stimulate the prosecution of this research because there are still several very important aspects to clarify.

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REFERENCES