

INFLUENCE OF pH ON METHYLENE BLUE SORPTION KINETICS FROM AQUEOUS SOLUTIONS USING ORANGE PEELS AS A LOW-COST SORBENT: EXPERIMENTAL AND MODELLING STUDIES AND ATTEMPTS OF DESORPTION.

M. Boumediene^{1,2}, H. Benaïssa*¹, B. George³, S. Molina³, A. Merlin³

¹Laboratory of Sorbent Materials and Water Treatment, Department of Chemistry-Faculty of Sciences, University of Tlemcen, P.O. Box. 119 13 000 Tlemcen - ALGERIA – Tel./Fax: 00 (213) 43 28 63 08; E-mail.: ho_benaïssa @ yahoo.fr

² Department of Hydraulics, Faculty of Technology, University of Tlemcen, P.O. Box. 230 13 000 Tlemcen - ALGERIA –Tel: 00 (213) 43 28 56 86, Fax : 00 (213) 43 28 56 85
E-mail.: m_boumd@yahoo.fr

³ LERMAB E4 4370, Faculty of Sciences and Techniques, University of Nancy, Boulevard of aiguillettes, P.O. Box 70239 54506 Vandoeuvre-les-Nancy, France.

ABSTRACT

In the present work, the effect of initial pH of methylene blue solution on the kinetics of dye sorption from synthetic aqueous solution by a natural waste material namely: orange peels, was studied. Kinetic data were measured in batch conditions. Methylene blue uptake was time contact and solution initial pH dependent. Maximum dye sorption was found to occur at initial pH 9. Two simplified kinetic models including a first-order rate equation and a pseudo second-order rate equation were selected to describe the dye sorption kinetics. The process followed a pseudo second – order rate kinetics. A multiple-stage diffusion of methylene blue onto orange peel particles was observed indicating that intraparticle diffusion was not a fully operative mechanism for this systems and reflects some degree of boundary layer control. The desorption of methylene blue from dye-laden-orange peels was performed to an extent of 84 % by a distilled water which solution initial dye was adjusted to 2.

Keywords: Removal, sorption, methylene blue, orange peels, kinetics, modelling, desorption.

INTRODUCTION

The effluents of various industries using extensively synthetic dyes 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, 1991). Moreover, they may affect the nature of water, inhibit sunlight penetration and have a derogatory effect on photosynthesis (O'Mahony et al., 2002). Among the various types of dyes, various cationic dyes including methylene blue, are used for dyeing cotton, wool and silk (Rafatullah et al., 2010; Bielska and Szymanowski, 2006) Though methylene blue is not strongly hazardous, it can cause some harmful effects (eye burns, nausea, vomiting, etc. (Rafatullah et al., 2010). Thus, the treatment of effluent containing such dye is of major scientific interest, decolourization of dye-containing effluent becoming an obligation both environmentally and for water re-use. 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. Although these treatment methods are efficient, they are quite expensive and have operational problems ((Garg et al., 2003; Kapdan et al., 2000). Adsorption processes using suitable adsorbents are proved to be an effective and attractive technique for removal of various dye types from wastewater (Robinson et al., 2001; Aksu, 2005). Most systems use activated carbon as adsorbent to remove dyes because of its excellent adsorption ability (Garg et al., 2003; Kapdan et al., 2000; Wang et al., 2005). Nevertheless, its widespread use is limited due to its cost and the problem of regeneration (Janos et al., 2003). In recent years, it has led to the search

of alternative low cost adsorbents including biosorbents, waste from agriculture or industry and natural materials. Orange peels, an agricultural solid waste, can be an alternative and favourable sorbent material for the removal of pollutants such dyes from aqueous solutions.

In this research, the effect of initial pH of methylene blue solution on the kinetics of dye sorption by a natural waste material namely: orange peels, was studied. This sorbent material is abundantly available through our country and the world. The present study reports its sorption potential through kinetics tests in batch conditions. The experimental data of methylene blue sorption kinetics by this material tested were fitted by two current models namely: first-order and pseudo- second-order models. To identify the main rate controlling steps in the overall uptake mechanism, a single intra-particle mass transfer diffusion model was tested. Furthermore, attempts of desorption of methylene blue from dye-laden-orange peels were also performed.

MATERIALS AND METHODS

1. Sorbents and dye

Orange peels used as a sorbent material, is a cheap and highly available lignocellulosic waste in Algeria. It was collected from the region of Mohammadia (Mascara -Algeria) during spring 2007 in the form of large flakes. The peels were sun/air dried at ambient temperature during many days, crushed with a Moulinex Easy power R68 mill and sieved with an Automatic Sieve Shaker D403 device (Controlab) to keep only the size range 1.25-2 mm. These materials obtained were used as sorbent materials after the following treatment chosen arbitrary: 10 g of orange 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 $25 \pm 1^\circ\text{C}$ during 4 h, filtered, washed thoroughly with distilled water to remove all the adhering dirt particles until constant pH and no colour observed, then oven-dried at $85 \pm 5^\circ\text{C}$ for 24 h.

Methylene blue MB (chemical formula: $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}\cdot 3\text{H}_2\text{O}$; molecular weight: 319.86 g/mol; maximum absorption wavelength: 664 nm; chemical structure given in Fig. 1) was

purchased from Janssen Chimica and used as such without further purification, in single component aqueous solutions. 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.

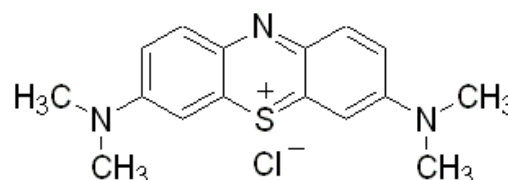


Fig.1. Chemical structure of methylene blue.

2. Sorption experiments

2.1. Uptake kinetics

In each sorption experiment, 1L of solution of known initial methylene blue concentration 100 mg/L and initial pH value adjusted to the required value in the range 3-11 by adding small amounts of 0.1N HNO_3/NaOH , was added to 1g of sorbent in a beaker agitated vigorously by a magnetic stirrer at 400 rpm using a water bath maintained at a constant temperature 25°C . Samples from the clear supernatant, at appropriate time intervals, were carefully pipeted from the beaker to prevent the transition of sorbent samples to solution. Their dye concentrations were determined using UV-visible spectrophotometer (UV-2550 Shimadzu) at λ_{max} 664 nm. The dye uptake q_t (mg dye/g sorbent) was determined as follows:

$$q_t = (C_0 - C_t) \cdot V/m \quad (1)$$

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.

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

2.2. Desorption tests

In these tests, methylene blue was desorbed from orange peels, which were exposed to a concentration of 100 mg l⁻¹ of this dye for 24 h at a natural solution initial pH, by utilizing a distilled water. The sorption of dye by orange peels was carried out by the similar method shown previously. After equilibrium, the sorbent was filtered and oven dried during 24 h. Then the weighted dried methylene blue-loaded orange peels containing 90 mg/g of dye was added to 1L of distilled water with an initial pH adjusted to different values in the range 3-11 using small amounts of 0.1N HNO₃/NaOH in a beaker agitated vigorously by a magnetic stirrer at 400 rpm using a water bath maintained at a constant temperature 25 °C. Samples from the clear supernatant, at appropriate time intervals, were carefully pipeted from the beaker to prevent the transition of sorbent samples to solution. Their dye concentrations were determined using UV-visible spectrophotometer (UV-2550 Shimadzu) at λ_{max} 664 nm. The desorption percentage of methylene blue is defined by

$$DP (\%) = C_t/C_e \times 100 \quad (2)$$

where DP is the pourcentage of dye desorbed into solution; m_e is the mass of methylene blue sorbed by orange peel at equilibrium; m_t is the mass of methylene blue desorbed from the sorbent by the various solutions.

RESULTS AND DISCUSSION

1. Effect of solution initial pH on dye sorption kinetics: Several sorption experiments were undertaken to study the effect of solution pH initial in the range 3-11, on the methylene blue sorption kinetics from synthetic aqueous solution by orange peels. As shown in Fig. 1, for all solution initial pH values tested, the obtained curves 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. Under these experimental conditions, from the results obtained at equilibrium, the initial pH of methylene blue solution has an influence on the kinetics of methylene sorption by orange peels. The amount of dye sorbed at the equilibrium increases with the solution initial pH value: 45.22 mg/g (pH₀ = 3) to 101.97 mg/g (pH₀= 11). The necessary time to reach equilibrium was depending on initial pH of solution: it increases from 3 to 8 h as the initial pH of solution increases from the value 3 to 11, and

an increase of removal time to 24 h did not show noticeable effects. In the course of methylene blue sorption by orange peels, for all values of solution initial pH tested except the one of 3, a decrease in the initial pH value of solutions followed by some equilibrium state (Fig. not shown here). This suggests that methylene blue binding to the sorbent tested is associated with the release of H₃O⁺ ions into the solution or a fixation of OH⁻ ions by the sorbent surface. At this stage, further investigations are required to understand the mechanisms involved in dye sorption by this type of complex natural materials.

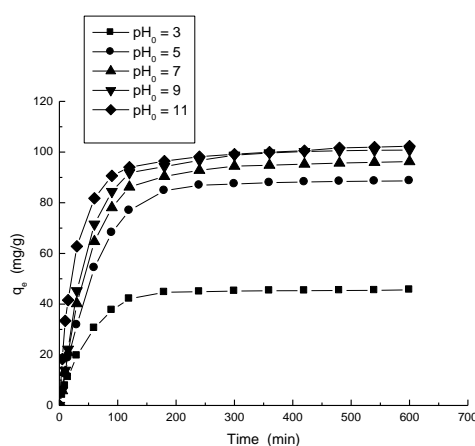


Fig. 1 Effect of solution initial pH on the kinetics of methylene blue from aqueous solution by orange peels. (Experimental conditions: C₀= 100 mg/L, sorbent dose= 1g/L, particle size= 1.25-2 mm, agitation speed= 400 rpm, T= 25 °C)

2. Modelling

To analyze the kinetic data of methylene blue sorption by orange peels under the experimental conditions tested, two common models from the literature, namely, the first-order rate model of Lagergren (1898) and the pseudo second-order rate model (Ho and McKay, 2000) were chosen and shown below as Eqs. (3) and (4) in their linear forms:

$$\log (q_e - q_t) = \log q_e - k_L t / 2.3 \quad (3)$$

$$t/q_t = 1 / k \cdot q_e^2 + t / q_e \quad (4)$$

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 solution initial pH tested, 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. not shown here) are summarized in the Table 1.

Table 1. Models rate constants for methylene blue sorption kinetics by orange peels: effect of solution initial pH.

First-order kinetics model		Pseudo second-order kinetics model		
pH_0	$q_{e,exp.}$	$q_{e,cal.}$	$k_L \cdot 10^2$	R^2
$q_{e,cal.}$	$k \cdot 10^4$	(mg/g)	R^2	(min^{-1})
(mg/g)	$(g \cdot mg^{-1} \cdot min^{-1})$	(mg/g)		
3	45.22	47.48	2.21	0.9933
49.43		5.27	0.9966	
5	88.00	94.77	1.84	
0.9939		99.11	1.89	
0.9943				
7	95.40	82.76	1.48	
0.9918		106.61	1.88	
0.9937				
9	100.38	83.06	1.41	
0.9806		111.36	1.88	
0.9931				
11	101.61	54.13	1.04	
0.9190		105.71	4.83	
0.9998				

The results obtained and presented in Table 1 confirm that the kinetic data obtained follow the pseudo second-order kinetic model. Compared to the first-order rate model ($0.9806 < R^2 < 0.9939$), the pseudo second-order rate model acceptably described the kinetics of dye sorption with acceptable correlation coefficients ($0.9931 < R^2 < 0.9998$). The equilibrium dye sorption capacity, q_e , increases with the increase in the solution initial pH value. The values of q_e obtained from the fitting to the pseudo second-order rate model are approximately similar to the experimental values obtained from the sorption kinetics at equilibrium, in spite some deviations observed for both low and high initial pH values of solutions.

3. Rate determining steps

From a mechanistic viewpoint, to interpret the experimental data, it is necessary to identify the steps involved during the sorption process. It is generally agreed that there are four consecutive steps which describe the overall sorption process of solute from a solution by a sorbent particle (Furusawa and Smith, 1973). These steps, as adapted to apply to the sorption dye by a sorbent particle, are as follows:

1. Transfer of dye from the solution bulk to the boundary layer recovering the surface of the solid phase: bulk diffusion.
2. Dye diffusion through the boundary film to the surface of the sorbent particle: film diffusion.
3. Diffusion of dye from the solid phase surface to the sorption sites: intraparticle diffusion.
4. Final uptake of dye at the sorption sites, via sorption, ion-exchange, complexation or precipitation, which is fast.

In the process of establishing the rate limiting step, the fourth step is assumed to be very rapid and is therefore not considered in any kinetic analysis (Findon et al., 1993): sorption is a quasi-instantaneous process (Tsezos and Volesky, 1982). The first and the second step are external mass transfer resistance steps, depending on various parameters such as agitation and homogeneity of solution. In this study, the agitation given here to the solution (400 rpm) is considered as sufficient to avoid steps 1 and 2 being controlling steps. In a well – agitated batch system, the boundary layer surrounding the particle is much reduced, reducing the external mass transfer coefficient; hence, the third intraparticle diffusion resistance step is more likely to be the rate controlling step (Sag and Aktay, 2000; McKay, 1983). This possibility was tested in terms of a graphical relationship between q_t and the square root of time, $t^{1/2}$, according to the intraparticle diffusion model proposed by Weber and Morris (1962) which is commonly expressed by the following equation:

$$q_t = K_i t^{0.5} \quad (5)$$

where q_t is the solute concentration in the solid ($mg \cdot g^{-1}$) and K_i is the slope of the plot defined as an intraparticle diffusion rate parameter ($mg \cdot g^{-1} \cdot min^{-1/2}$).

If the intraparticle diffusion is involved in the solute sorption process, then the plot of q_t vs.

$t^{0.5}$ would result in a linear relationship, and the intraparticle diffusion would be the controlling step if this line passed through the origin (McKay and Poots, 1984; Ho, 2003). Fig. 2 shows plots of q_t vs. $t^{0.5}$ for methylene blue sorption kinetics by hard almond peels at different solution initial pH, and Table 2 summarizes the intraparticle diffusion model coefficients.

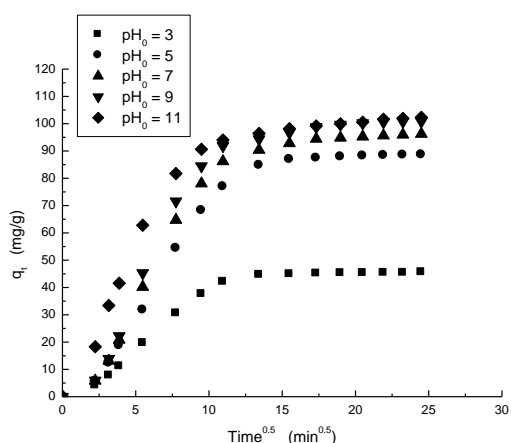


Fig.2. Intraparticle diffusion plots for methylene blue sorption kinetics by orange peels: effect of solution initial pH.

Table 2 Parameters obtained from the intraparticle diffusion model for methylene blue sorption by orange peels: effect of solution initial pH.

pH_0	K_i ($mg\ g^{-1}\ min^{-0.5}$)	C ($mg\ g^{-1}$)	R^2
3	4.20	-3.42	0.9855
5	3.17	42.20	1.0000
7	1.46	70.38	0.9894
9	1.10	79.74	0.9989
11	0.74	86.25	0.9780

In Fig.2 except for solution initial pH 3, two linear portions are observed in the same experiment, before achieving the equilibrium confirming that straight lines do not pass through the origin with correlation coefficients ranging from 0.9780 to 1 values (see Table 2). These observations are indicative of a multiple-stage diffusion of methylene blue onto orange peel particles: external-mass transfer followed by intraparticle diffusion in pores (Ho and

McKay, 1998). Such a multiple nature of the curve confirms that intraparticle diffusion is not a fully operative mechanism for this system and reflects some degree of boundary layer control.

4. Desorption tests

The results of the kinetics of methylene blue desorption from dye loading orange peels by utilizing a distilled water which its initial pH was adjusted to various values in the range 2-11, are shown in Fig. 3. Except the curves obtained with distilled water initial pH values 7 and 9, all other curves present the same shape characterized by a strong increase of the extent of dye desorbed during the first minutes of contact solution – sorbent, follow-up of a slow increase until to reach a state of equilibrium. Under these experimental conditions, from the results obtained at equilibrium, the initial pH of distilled water has an influence on the kinetics of methylene blue desorption from dye-laden- orange peels. The extent of dye desorbed at the equilibrium increases with the decrease in the solution initial pH value: 0.29% ($pH_0 = 9$) to 83.59 % ($pH_0 = 2$). The necessary time to reach equilibrium was in the range of 4-6 h depending on initial pH of distilled water, and an increase of removal time to 24 h did not show noticeable effects. In the course of methylene blue desorption from dye-laden- orange peels, for the values of distilled water initial pH tested in the range 5-9, a decrease in the initial pH value of solution was observed followed by some equilibrium state. In opposite, a weak increase in its value was observed in the range 2-3 followed by some equilibrium state.

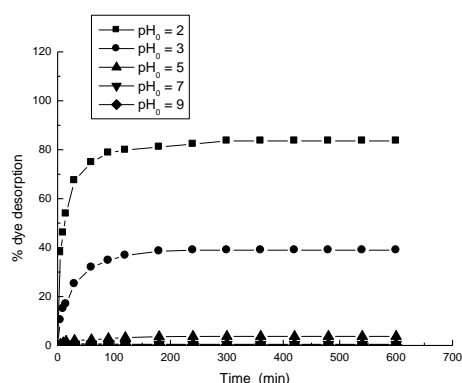


Fig. 3. Kinetics of methylene blue desorption from dye-laden orange peels. (Experimental conditions: sorbent dose= 1g/L, particle size= 1.25-2 mm, agitation speed= 400 rpm,

T= 25 °C)

CONCLUSIONS

The present study shows that orange peels can be efficiently used as a sorbent material for the removal of methylene blue from synthetic aqueous solutions. The amount of dye sorbed at equilibrium was solution initial pH dependent: it increased with an increase of this parameter from 45.22 (pH₀= 3) to 100.38 mg/g (pH₀= 9), respectively. The kinetics of methylene blue sorption was acceptably described by a pseudo-second order rate model. A multiple-stage diffusion of methylene blue onto orange peel particles was observed indicating that intraparticle diffusion was not a fully operative mechanism for this system and reflects some degree of boundary layer control. The desorption of methylene dye from dye-laden- orange peels was performed to an extent of 84 % with a distilled which its initial pH was adjusted to a value of 2. Under the investigated experimental conditions, the orange peel waste tested was shown to be promising a sorbent material for removal of methylene blue from synthetic aqueous solution. From these results, orange peels, low cost and easily available materials, can be an interesting alternative for more expensive adsorbents used for dye removal in waste treatment processes. The results obtained stimulate the prosecution of this research because there are still several very important aspects to clarify.

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