Biosorption of an industrial dye (A-BG) by a dairy sludge

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Abstract: Dairy sludge was investigated as potential adsorbent for the removal of hazardous cationic dyes. Biosorption was studied as a function of solution initial pH, biosorbent dose, biosorbent particle diameter and initial dye ion concentration. These parameters were measured in batch experiments. Equilibrium uptake increased with increasing dye concentration with a maximum sorption capacity of a 178.6 mg g^{-1}. Model equations such as Langmuir and Freundlich isotherms were used to analyze the adsorption equilibrium data and the best fits to the experimental data were provided by the first isotherm model. Scanning electron microscopy and energy-dispersive X-ray (SEM-EDX), Brunauer–Emett–Teller (BET), Fourier transform infrared analyses (FTIR) and microbiological characterisation were also performed to characterize the biosorbent. To describe the adsorption mechanism, kinetic models such as pseudo-second-order and the intra particle diffusion were applied.

Keywords: Micropollution, Cationic Dyes, Biosorption, Dairy Sludge, Characterizations

1. Introduction

Colored industrial effluents are one of the most important issues of wastewater treatment, not only because of their high values of biochemistry oxygen demand (BOD), suspended solids and toxicity, but also the color that is considered the first visual contamination (Maurya et al. 2006; Otero et al. 2003). Dyes significantly affect photosynthetic activity in aquatic systems by reducing light penetration and can also be toxic because of the presence within their structure of aromatic compounds, metals, chlorides, etc.. (Gulnaz et al. 2004; Basibuyuk et al. 2003). Having a complex molecular structure and synthetic origin, making them biologically not degradable and resistant to environmental conditions, dyes are stable and difficult to treat (Yeddou 2006).

The use of adsorbents capable of trapping organic micropollutants is interesting in reducing the pollution level of contaminated water (Ho 2004). A number of studies have investigated the use of biosorbent (bacteria, algae and fungi), cheap and efficient, as an alternative or complement to existing techniques that are often expensive, inefficient and generates large amounts of sludge (Weng et al. 2006; Vasanth Kumar et al. 2005). Studies on the use of microorganisms, especially dead, for fixing dyes have been proved successful (Mall et al. 2005). Living cells are susceptible to the toxic effect of organic matter and also require the input of nutrients (Deniz et al. 2010; Gupta et al. 2009). For these reasons, great interest is given to non-living biomaterials (Hameed 2008).

As a result, activated sludge from biological treatment plants is considered good biosorbents of dyes because of their richness in microorganisms (Aksu 2005). It is within this framework that we have studied the biosorption of an industrial dye (A-BG), in aqueous solution, by sludge from the treatment of wastewater of a dairy. The study focused on the influence of pH on biosorption, investigating biosorption's isotherms and kinetics at optimum pH.

2. Materials and Methods

2.1. Acquisition and Preparation of the Sludge and Dye Solutions

The sludge was collected from drying beds (dairy complex Sidi-Khaled Tiaret), dried at 105 ° C, crushed and sieved. The sample was kept in desiccators. The initial concentrations ranging from 5 to 100 mg L^{-1} were prepared from a stock solution of the industrial dye of 2 g L^{-1}.

2.2. Characterization of Biosorbent

The organic fraction was determined by sludge calcinations to constant weight. Microbiological characterization concerns the search for bacteria, fungi and algae. Scanning electronic microscopy (SEM) and X-ray spectrometry were used to characterize the biosorbent. Surface area is determined by the BET method.

2.3. Experimental Protocol

The study of biosorption is achieved by mixing a quantity of sludge (10 mg) with 50 mL of dye solution. The whole is stirred for 2 hours at 120 rpm at 20 ° C then centrifuged for 10 min at 4000 rpm. The unfixed dye in the supernatant was estimated by the spectrophotometric method at specific wavelength (Waranusantigula et al. 2003).

2.3.1. Effect of pH

To determine the wavelength corresponding to maximum absorption of the dye we prepared a solution of 5 mg L-1 and using the spectrophotometer, we measured the optical density by varying the wavelength from 500 to 700 nm. To study the effect of pH on the absorption peak we performed the same way by varying each time the medium pH by adding a few drops of NaOH (1N) or HCl (1N) (Pala et al. 2002).

2.3.2. Biosorption Isotherms

This experiment is to evaluate the distribution of the solute (dye) at the adsorption equilibrium between the two phases present: (a) the liquid phase (dye in the solution with concentration, Ce) and the solid phase (dye adsorbed on the substrate, q). Evaluation of dye concentration on the support q (mg g-1) is carried by material balance:

$$q = \frac{V(Co-Ce)}{m} \quad \text{(Demirbas et al. 2009).}$$

Co is the initial dye concentration in the aqueous phase (mg L^{-1}), V the solution volume (L) and m the mass of adsorbent used (g).

2.3.2.1. Procedure

A series of capped flasks containing 50 mL of dye solution of known concentrations, varying from 10 to 100 mg/L were prepared. Identical amounts (10 mg) of sludge were added to the flasks and the resulting suspensions were agitated magnetically at 120 rpm and 20 °C for 2 h at a constant pH of 5 and then centrifuged for 10 min at 4000 rpm. The unfixed dye in the supernatant was estimated by the spectrophotometric method at specific wavelength.

2.3.3. Kinetic Studies

In order to examine the adsorption controlling mechanism, kinetic models such as pseudo-second-order and the intra particle diffusion were applied to experimental data of the studied dye (Hameed et al. 2009). Kinetic experiments were conducted for different initial quantities (10 mg, 50 mg, 100 mg 150 mg and 200 mg) of sludge to which identical volumes of dye solution (50 mg/L) were added in stirred flasks for 2 h at a speed of 200 rpm, a pH of 5, and a temperature of 20 °C. Solution samples were withdrawn at regular intervals, centrifuged and the dye concentration measured. Similar tests were performed by varying the initial concentration of dye (50, 100 and 200 mg/L) and the average particle diameter (<80, 125–250 and 250–500 μm).

3. Results and Discussion

3.1. Characterization of Biosorbent

The analysis of the sludge gave a 65% of organic matter content and a presence of aerobic germs, total coliforms, staphylococcal, the streptococcus lactic ones, bacterial spores, yeasts and moulds, algae and protozoa.

Table 1. *Chemical composition of the sludge, (SEM/DEX)*

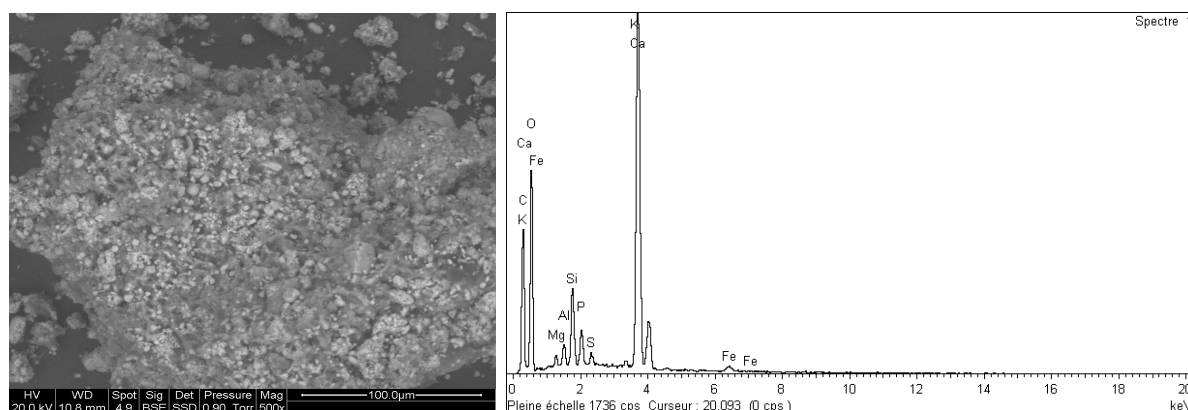| Element	%Mass	%Atomic
C	32.19	45.17
O	40.72	42.89
Mg	0.42	0.29
Al	0.64	0.40
Si	2.22	1.33
P	1.57	0.85
S	0.45	0.24
K	0.42	0.18
Ca	19.76	8.31
Fe	0.67	0.20
Sn	0.94	0.13
Total	100.00	

Fig. 1. Sludge's SEM/EDX

Table 1 summarizes the chemical composition of biosorbent used. Besides carbon and oxygen, high level of calcium was found in this sludge. The dairy wastewater is laden with lactoserum which is rich in calcium complexing proteins as in caseins, for instance. The sludge analysis by scanning electron microscopy coupled with energy dispersive X-ray spectrometry (EDX) is shown in figure 1. The specific surface area obtained by BET method is 1.22 m^2 g^{-1}.

3.2. Dye's Structure

The industrial dye AB-G or BB1 (called setoglaucine) is a cationic dye whose structure (triarylmethane class) is mentioned in figure 2.
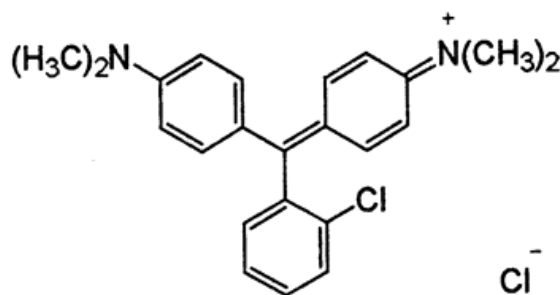

Fig. 2. A-BG structure, [Methanaminium,N-[4-[(2-chlorophenyl][4-(dimethylamino)phenyl]methylene]-2,5-cyclohexadien-1-ylidene]-N-methyl-,chloride (1:1)]

The dye presents the following characteristics:
Raw formula: $C_{23}H_{24}Cl_2N_2$
Chemical Abstracts Service (CAS): 3521 – 6 – O
Colour Index (CI) : 42025

3.3. pH Effect

The pH is a very important parameter that affects not only the ability of biosorption but also the color of the solution and the solubility of dye (Van der Zee 2002). Figure 3 shows the pH effect on the maximum absorption of dye. The maximum wavelength (λ_{max}) of dye is 650 nm. We noticed that the peak absorption is not affected by the change in pH.
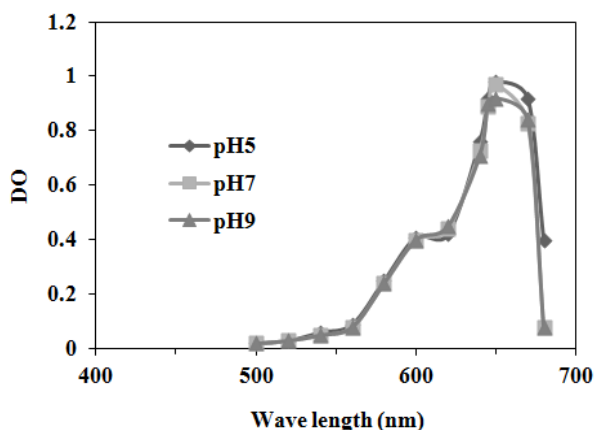

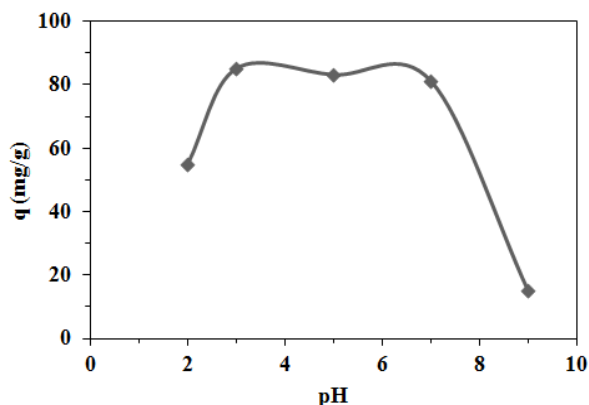*Fig. 3. Maximal optic density according to the pH [A-BG] = 5 mg L^{-1}, T (20 °C), V = 50 mL*

Fig. 4. Effect of pH on A-BG's biosorption. Sludge (10 mg); [A-BG] 50 mg L^{-1}; T (20 °C) ; Stirring (120 rpm) ; Stirring time (2h)

According to Figure 4, dye fixation remains maximal (q = 80 mg g^{-1}) from pH 3 to pH 7. We can say that the pH does not affect the biosorption of A-BG.

However we must consider the behavior of the dye and sludge at different pH values (Gibbs et al. 2003)[20]. Indeed, the Figure. 5 shows that the sludge tends to alkalize the medium for initial pH values between 5 and 8. A similar case was found while fixing heavy metals (Cr) by the sludge (Volesky 1995). According to Duangrat et al. (2004), the pH values between 3 and 7 has no significant effect on the binding of Astrazon (6B), which is explained by the fact that at this pH interval the cationic dye is always positively charged. The increase in dye uptake at low pH 2 may be due to the high concentration of H+ ions in the aqueous solution competing with the dye molecules for the available sites on the adsorbent surface (Nemchi et al. 2012). Beyond pH 7, the binding decreases significantly which could be explained by the discoloration of the dye.
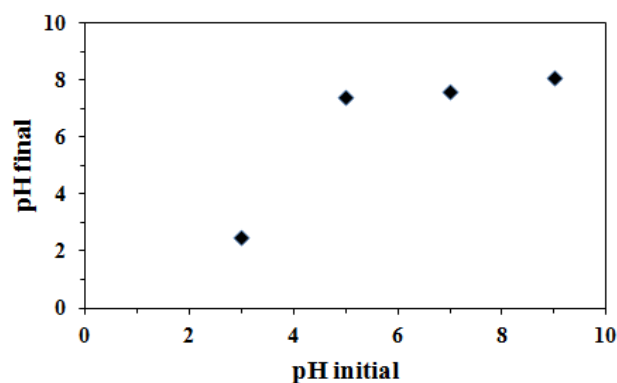

Fig. 5. Final pH variation according to initial pH. Sludge (10 mg) ; [A-BG] 50 mg L^{-1}; T (20 °C) ; Stirring (120 rpm) ; Stirring time (2h)

3.4. Biosorption Isotherm

In order to evaluate the applicability of biosorption as a means of removing A-BG dye from aqueous solutions, two frequently used single-component adsorption isotherm models were considered in this study to describe the interaction between the adsorbate and the biosorbent, viz. the Langmuir and Freundlich isotherms. Both models represent

the affinity of the adsorbate for the biosorption sites on the biosorbent surface. These isotherms (Sassi et al.2010) are represented by the following linearized equations:

Langmuir equation:

$$\frac{C_e}{q} = \frac{1}{q_m} \times C_e + \frac{1}{bq_m}$$

where q is amount of solute biosorbed per unit weight of biosorbent (mg/g). Ce is the concentration of solute remaining in solution at equilibrium (mg/L). q_m (mg/g) is the maximum biosorption capacity corresponding to complete monolayer coverage and b is a constant related to the energy or net enthalpy.

Freundlich equation:

$$\log q = \log k + \frac{1}{n}\log C_e$$

where k and n are the Freundlich constants related to biosorption capacity and biosorption intensity that can be obtained from the intercept and slope of log q vs. log Ce plot

Figure 6, representing the amount of fixed dye depending on its concentration at equilibrium, shows an increase in the discoloration reached a limit value (120 mg g^{-1}) obtained for an equilibrium concentration of 20 mg L^{-1}.

Table 2 allows us to determine the parameters for the two models. These data were well fitted by Langmuir isotherm model with R^2 = 0.91.
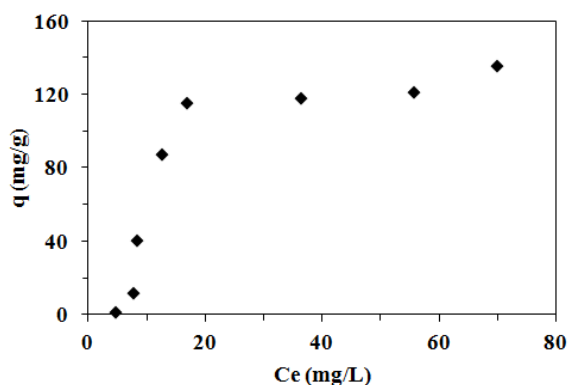

Fig. 6. A-BG's isotherm of fixation Sludge (10 mg); T (20°C); Stirring (120 rpm); Stirring time (2h)

Table. 2. Langmuir and Freundlich isotherm parametersfor A-BG's biosorption by the sludge at pH5 and 20 °C.

	Langmuir			Freundlich		
q$_{max}$(mg g^{-1})	b	R^2	k	n	R^2	
178.6	0.06	0.91	17.75	1.94	0.64	

3.5. Kinetic Studies

The biosorption of a dye in the liquid phase is controlled by various steps including diffusion processes and phases of fixing itself. If we exclude the movement of solute from the solution to the boundary layer surrounding the adsorbent particle, the process of adsorption in porous solids can be divided into three parts:

a) Transfer of solute from film to the external adsorbent surface. It's the external diffusion.

b) Distribution of solute from the surface to internal sites. It's the intraparticle diffusion.

c) Fixing the solute on the adsorbent sites. This step is the adsorption (Ho et al. 2000).

When more than one step are present, intraparticle diffusion is not the sole limiting step. Sorption itself can be accounted for by several interactions between the metal ions and the sorbent due to the numerous and complex surface functional groups present on the sludge. The kinetics of biosorption, representing the rate of biosorption of the biosorbate controlled by the residence time in the solid–liquid interface is the principal characteristic defining the biosorption efficiency (Crini et al. 2008).

3.5.1. Effect of Sludge Amount

In Figure 7 we noted that the quantity not fixed relative to the initial amount (Ce / Ci) is about 0.5 for quantities of sludge of 10, 50 and 100 mg. It falls below 0.4 for 150 mg of sludge and almost vanishes for the amount of biosorbent 200 mg. In fact, according to Birol (2011), increasing the amount of biosorbent enables high availability of binding sites which results in a rapid decrease in dye concentration in the solution. For different concentrations of sludge maximum dye is removed during the first 20 minutes.
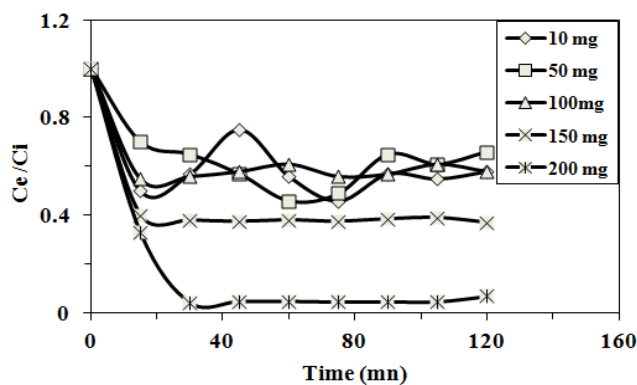

Fig. 7. A-BG's fixation kinetic according to sludge amount [A-BG] 50 mg L^{-1}; T (20 °C) ; Stirring (120 rpm)

3.5.2. Effect of Particles Size

The kinetics of attachment allow the access to speeds of fixation.These kinetics can be controlled by diffusion mechanisms (external, intra-particle). The intra particle diffusion is often the limiting step of the kinetic process, for this reason, experiments will be done based on the particle size.

Figure 8 shows that the maximum discolorization (Ce / Ci = 0.5) is obtained again after the first 20 minutes with a slight performance for diameter of 125 microns. Indeed, the low porosity can develop a large area and therefore a better dye binding (Hameeda et al. 2008). However, in order to minimize losses of biosorbent, the diameter of 500 microns is chosen for different experiments.
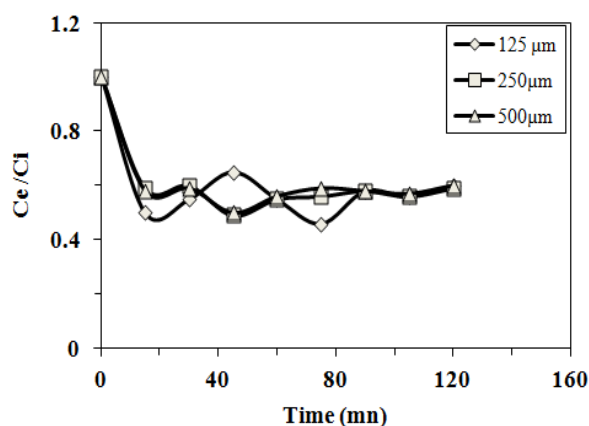
Fig. 8. *A-BG's fixation kinetic according to particle diameter [A-BG] 50 mg L^{-1}; T (20° C); Stirring (120 rpm)*

Fig. 9. *A-BG's fixation kinetic according to its initial concentration*

Table. 3. *A-BG's second order kinetic parameters*

	q_e(mg g^{-1})	k_2(mg g^{-1}mn^{-1}).10^{-3}	R^2
Init. conc. (mg L^{-1})			
50	92.59	3.67	0.97
100	166.67	0.96	0.96
200	256.41	0.71	0.85
Ø particles (µm)			
125	102.04	4.70	0.93
125-250	103.09	1.99	0.96
250-500	98.04	4.86	0.97
Sludge amount(mg)			
50	38.17	6.65	0.99
100	7.24	10.34	0.90
200	12.24	36.57	0.99

3.5.3. Effect of Initial Concentration of Dye

From Figure 9, the kinetic of discoloration is highest during the first 20 minutes and stabilizes beyond and for the initial concentration of 50 mg L^{-1}. For other concentrations the time required to reach equilibrium is slightly elongated (30 to 40 minutes).

The data from kinetic study were analyzed using the second order model described by the following equation:

$$\frac{dq_t}{dt} = k(q_e\text{-}q_t)^2$$

whose integration gives the linear form:

$$tq = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where k_2 is the constant rate of biosorption, q_e the amount of dye attached at equilibrium and q_t the quantity fixed at time.

The kinetic parameters are confined in Table 3. For the concentration parameter, it should be noted that the second order model can be applied especially well for the first two concentrations (50 and 100 mg L^{-1}) with a correlation coefficient exceeding 96 %. However, it should be noted the difference between the value of calculated and experimental q_e (120 mg L^{-1}). For the constant k_2, its value decreases with increasing initial concentration (Basibuyuk et al. 2003). The kinetic study of biosorption according to the particle diameter parameter follows well the second order model. This is confirmed by the value of R^2 and that of q_e calculated. In the case of the third parameter, despite a correlation coefficient that reached 99 %, the calculated value of q_e is much away of the experimental value.
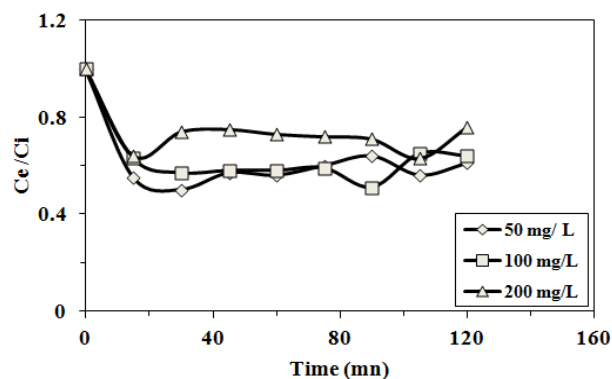
3.6. Study of Intra-Particle Diffusion

The possibility of intra-particle diffusion is exploited using the model of Morris and Weber:

$q_t = k_{id}\ t^{1/2}$ where k_{id} is a rate constant of intra-particle diffusion (mg.g^{-1}.min$^{-1/2}$). According to this equation the representation q_t according to $t^{1/2}$ (Figures 10, 11 and 12) could be linear if the diffusion is involved and if these lines pass through the origin then the movement of the adsorbate is controlled by intra-particle diffusion. Otherwise other kinetic models may be factors limiting the rate of biosorption (Attouti et al. 2013).
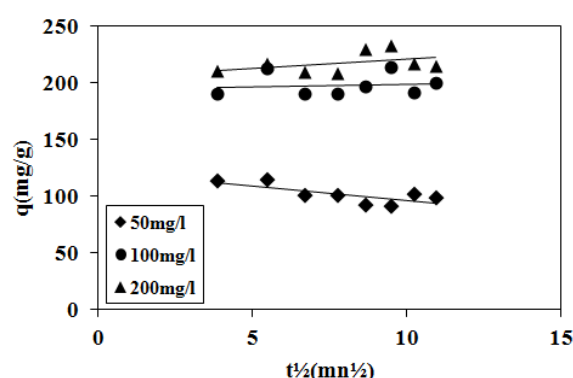

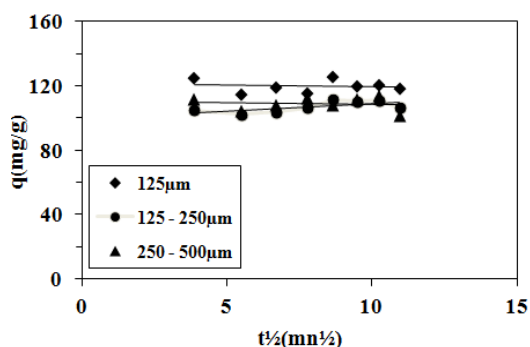**Fig. 10.** *Effect of dye concentration on its intraparticle diffusion*

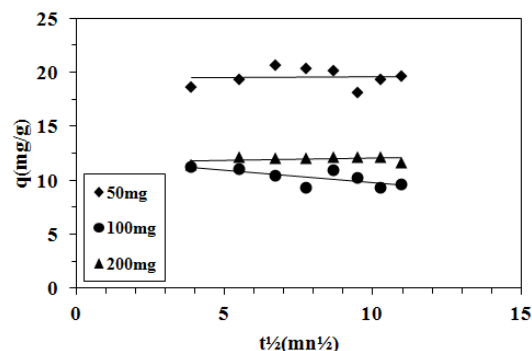***Fig. 11.*** *Effect of particles diameter on the intraprticle diffusion of the dye*

Fig. 12. *Effect of sludge amount on dye's intraparticle diffusion*

4. Conclusion

With the unlimited release of wastewater carrying out pollutants, the treatment has become a priority. Biosorption constitutes a new efficient and inexpensive biological treatment process. This study has shown that dairy sludge is effective biosorbent for the removal of dye used in textile industry due to its richness in microorganisms. Indeed the maximum discoloration is achieved using 10 mg of sludge and during the first 20 minutes. This setting does not seem to be affected by particles diameter and the pH between 3 and 7 did not affect dye biosorption. The initial concentration has little effect on the equilibrium time. Biosorption of this dye follows especially the Langmuir model (R 2 = 0.91) which allowed us to determine the maximum dye fixation that is 178.6 mg g^{-1}. Kinetics studies showed that biosorption process obeyed the pseudo-second- order rate model. The mechanism of dye's biosorption is partly explained by the model of intra-particle diffusion which does not seem to be the only part controlling that process. This study showed that dairy sludge can be an alternative to the commercially available adsorbents for dyes removal from liquid effluents.

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