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Eosin Biosorption from Aqueous Solution on Two Types of Activated Sludge

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Abstract – In wastewater treatment processes huge quantities of sludge are produced continuously each year. This work investigated the reuse of two types of sludge as biosorbents of a toxic dye. The potential of granular and filamentous fungus dried sludge for the elimination of eosin from aqueous solution was studied in batch system. The effect of initial concentration and temperature was examined. Maximum uptake was observed at 100 mg l^{-1} and 30 °C. The maximum removal rate was 92% for the granular sludge and 90% for the filamentous one. Equilibrium was attained after 30 min for the studied dye concentrations. The equilibrium uptake increased with the initial eosin concentration. The Freundlich and Langmuir adsorption models were also investigated. The reuse of disposed sludge as adsorbent could be a solution for the valorization of such dangerous waste to resolve two environmental problems at the same time.

Key words: Biosorption, Eosin Y, Wastewater, Activated sludge

1. Introduction

Removal of harmful substances from liquid effluents is one of the preoccupations at present. Huge quantities of dyes are used by different industries to improve the appearance of their products. Eosin Y is applied in many industries for dyeing leather, biological stain, printing and fluorescent pigment [1-3]. It is a heterocyclic dye attached to bromine atoms as shown on Fig. 1. Eosin Yellow is an anionic acid dye that belongs to fluorescein class. It is a red crystalline powder, highly water soluble dye used frequently in textile dyeing, ink manufacturing because of its vivid color [4-6].

This dye may cause severe health problems in different organs like kidney, liver, lungs and cornea. Also, eosin incites damage in gastrointestinal DNA, and its metabolites are also highly toxic and carcinogenic [7]. Therefore, this compound is not completely removed by conventional wastewater treatment systems, such as activated sludge processes, due to their high resistance to biodegradation [5,7].

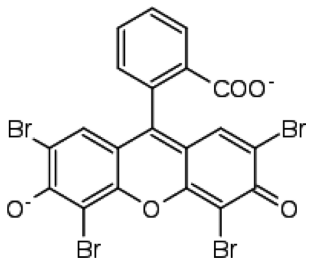

Fig. 1.Chemical structure of eosin.

Various techniques, such as chemical oxidation, froth flotation, adsorption and coagulation, have been applied for the removal of pollutants from wastewaters. Adsorption has the most potential due to its remarkable efficiency to remove a wide range of dangerous compounds [8].

It is a well-established method for treating industrial wastewaters, where the most used adsorbent is activated carbon [9]. However, its high cost makes it less economically practical as an adsorbent. Because of this, the use of cheap and efficient adsorbents for the elimination of dyes to substitute activated carbon is of great interest [10].

In sewage treatment processes huge quantities of sludge are produced continuously. In Algeria the estimated quantity of sludge produced in 2017 exceeded 90.000 tons per year [11]. Sludge disposal and carrying are becoming an economic and environmental concern. In this work, a solution to resolve this problem is proposed by the valorization of sludge used as biosorbent for the elimination of a toxic colorant. Using activated sludge as adsorbent represents a potential alternative to actual methods for wastewater treatment [12]. The micro-organism cell wall consisted essentially of a variety of organic compounds such as amino acids, lipids, chitin, could show a passive affinity towards reactive dyes [13]. Some studies have demonstrated that biomasses possess interesting adsorption properties for a variety of heavy metals, organics and dyes [5,14].

The toxic nature of eosin is still not quantified much but its high content in living systems has proved to be harmful. Many works have investigated the efficiency of low cost adsorbents to eliminate eosin, such as date palm seeds, goethite and their composite [6], rice husk [2], waste material of soya [7]. Compared to these materials, the present study proposes a lower cost adsorbent considered as harmful wastes for the environment: the sludge of wastewater processes used after a simple cleaning.

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This work focused on the ability of two dead sludge biomasses to remove this dye from aqueous solution. The effects of some parameters, namely time of contact, initial adsorbate concentration and temperature of the solution, on the adsorption of eosin on granular and filamentous biomasses were investigated. Kinetic study was performed to investigate the mechanism of the adsorption using the pseudo-first-order and pseudo-second-order models. Also, equilibrium isotherms of Freundlich and Langmuir were tested. The interaction of eosin with both adsorbents is described through isotherm assessments. The suitability of the isotherms equations on the adsorption data was compared using the regression coefficient.

2. Materials and Methods

2-1. Preparation of adsorbate solutions

Eosin dye, also known as Eosin Y, Eosin Yellowish, is a red crystalline powder, with a molecular weight 691.88 ($C_{20}H_6Br_4Na_2O_5$). It was purchased from Merck (Germany) and used without any purification.

A stock solution (1 liter) of eosin was prepared by dissolving a known quantity of dye in distilled water. Further solutions of lower concentrations were prepared by diluting stock solution with distilled water. These solutions were used in biosorption experiments.

2-2. Preparation of biosorbents

Two types of sludge were used. The first is the granular dead biomass (A1) produced from the wastewater treatment system (STEP) directed by the National office of Cleansing (Office National d'Assainissement ONA) of Oued Lahrèche, Médéa, Algeria. It is the sludge from the domestic wastewater treatment processes. The second one is the filamentous fungus dead biomass (A2), produced from the industrial wastewater treatment system of Antibiotical Complex of Médéa (SAIDAL), Algeria. These biomasses were directly taken from their disposal. The morphology of the biomasses was examined by optical microscope (40 × magnifications) and given in Fig. 2. Infra-red spectroscopy analysis of these materials was carried out with a

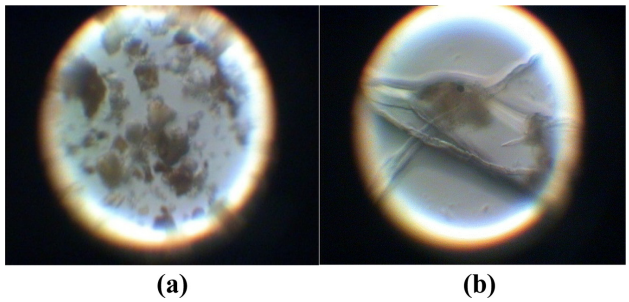

Fig. 2. Optical microscope images (40 × magnification). (a) (A1) and (b) (A2).

Shimadzu 8400S Fourier transform infrared FTIR spectrometer (Shimadzu, Europe).

The granular and the filamentous fungus sludge were cleaned by distilled water many times, and then centrifuged at 5000 rpm for 5 min till the absorbance of the supernatant approached that of water. After that, both materials were dried at 60 °C for 24 h, then milled and sieved through a 2 mm sieve.

Fig. 2(a) shows the dispersed particles of a heterogeneous size of the granular sludge (A1). However, on Fig. 2(b), the filamentous aspect of the (A2) sludge is obviously observed.

In general, *Basidiomycota* and *Ascomycota* were the dominant fungal communities detected in most activated sludge from the wastewater processes. The infra-red spectrum revealed the presence of similar functions on both biomasses' surface as illustrated on Fig. 3(a, b). Both of them gave sharp and strong absorption bands in the range 1033-1118.6 cm^{-1}, confirmed there by the presence of fatty acids and saccharides (C-O stretching vibration). Also, the occurrence of peaks at 1427 is an evidence of polyalcohol (O-H stretching) presence. The broad bands observed between 2858 and 3541 revealed the existence of proteins and peptides (N-H stretching vibration). The sharp peaks found at 1643 and 1620 for A1 and A2, respectively, are due to the conjugated bound C=C and amid functions. Whereas C-H found in benzene derivative are only found in granular sludge spectrum and confirmed by the peaks observed at 709 and 1797 cm^{-1}. The bands from 783 to 875 cm^{-1}, are characteristics for C-H bending

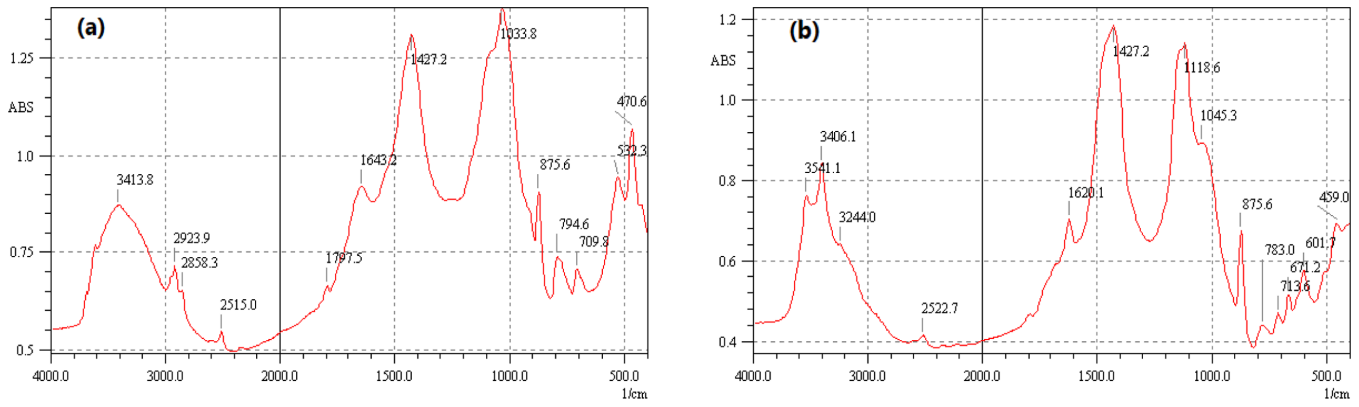

Fig. 3. IR spectra of (a) (A1) and (b) (A2).

in *di, tri or tetra*-substituted compounds. And the last analyzed region from 532 to 672 cm^{-1} indicated the presence of halogenated molecules on the surface of both sludge.

2-3. Adsorption process

The adsorption isotherms were established by putting a series of Erlenmeyer flasks in a thermostatic bath under continuous stirring at 500 rpm. Each bottle contained a quantity of adsorbent (m) and a volume (V) of eosin solution of an identified concentration.

The concentration of eosin inside the supernatant solution had underwent an analysis by means of a UV (Shimadzu UV Mini-1240) spectrophotometer at a wavelength of an utmost absorbance of 515 nm.

The quantity adsorbed *per* unit mass of adsorbent (q) is given by Equation 1.

$$q = (C_0 - C)V/m \quad (1)$$

q: is the quantity adsorbed of Eosin Y at time *tper* gram of adsorbent (mg/g),

C: is the concentration of Eosin Y at time t (mg/l),

C_0: is the initial concentration (mg/l),

V: is the solution volume (l), and $m$is the adsorbent mass (g).

The equation of isotherms of sorption is: q(mg/g) = f(C(mg/l))

3. Results and Discussion

3-1. Influence of time and initial concentration

Influence of time and initial concentration is shown in Fig. 4. Experiments were realized for 120 minutes. It was found that the quantity of adsorbed eosin increased initially with time. Then it reached saturation at the equilibrium time. A large amount of dye was removed from the liquid during the first minutes of contact and equilibrium was established after 30 min for the two waste activated sludges.

The impact of the initial concentration on the removal of dye using the two waste activated sludges was examined. Two values

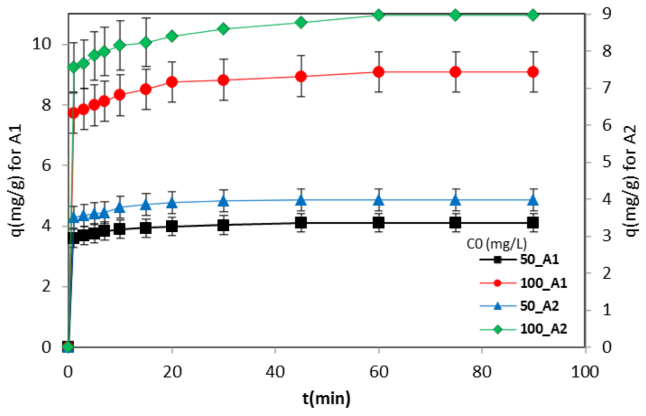

Fig. 4. Influence of time and initial concentration (Relative standard deviation was less than 4.54% in all cases).

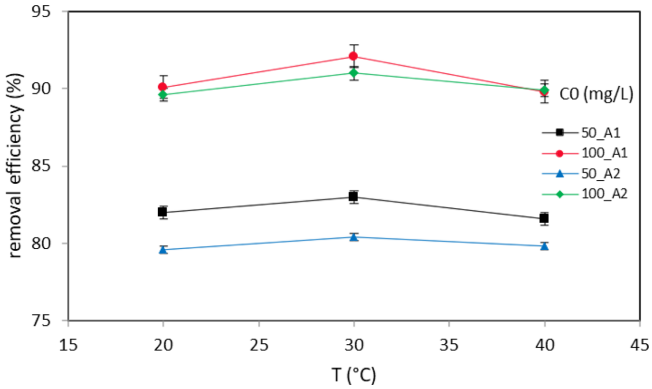

Fig. 5. Influence of temperature.

of C_0 (50 and 100 mg/l) were tested. The results show that q increases from 4.1 to 9.09 mg/g for A1 and from 3.98 to 8.96 mg/g for A2 with increasing initial eosin concentration from 50 to 100 mg/l. This increase may be due to important interactions between eosin and biomasses.

3-2. Influence of temperature

The effect of temperature on A1 and A2 efficiency was tested in the range of 30~40 °C at an initial eosin concentration of 20 mg/l and 100 mg/l. Fig. 5 demonstrates the negligible effect of temperature on the removal efficiency for both waste activated sludges. However, the removal efficiency for eosin was maximum at 30 °C and C_0 = 100 mg/las 92 % for activated sludge 1 and 90% for activated sludge 2. A similar observation was reported for the sorption of acid dye eosin onto date palm seeds, Goethite and their composite [6]. Furthermore, the negligible effect of temperature could be an indicator of the chemisorption phenomenon that could be confirmed later.

3-3. Kinetics of adsorption

The pseudo-first-order and the pseudo-second-order model were tested to examine the mechanism of the sorption process.

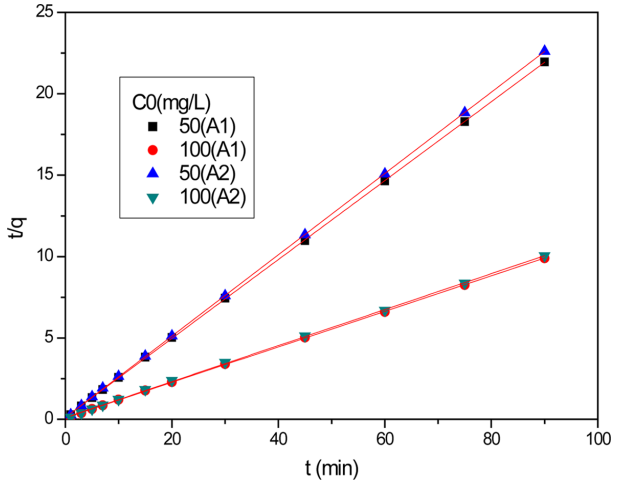

Fig. 6. Pseudo-second order kinetic for adsorption of eosin on A1 and A2.

Table 1. Kinetic Parameters

Eosin/Biosorbent (A1, A2)		First-order model				Second-order model			
Eosin/A1 C_0/mg/l	q_{exp}/mg/g	$q_{e,cal}$/mg/g	k_1/min^{-1}	R^2	SD	$q_{e,cal}$/mg/g	k_2/g/mg·min	R^2	SD
50	4.10	4.31	0.0239	0.572	1.495	4.12	0.46	0.999	0. 248
100	9.10	9.60	0.0314	0.479	2.560	9.18	0.13	0.999	0. 824
Eosin/A2 C_0/mg/l	q_{exp}/mg/g	$q_{e,cal}$/mg/g	k_1/min^{-1}	R^2	SD	$q_{e,cal}$/mg/g	k_2/g/mg·min	R^2	SD
50	3.98	4.26	0.022	0.555	4.545	4.00	0.52	0.999	0.405
100	8.96	9.72	0.033	0.483	2.820	9.04	0.11	0.999	0.920

The equation of the first one was proposed by Lagergren and Svenska [15] as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (2)$$

where k_1 (min^{-1}) is the rate constant of adsorption. $k_1$values (at 20 °C) are given in Table 1. It is observed from Table 1 that the pseudo-first-order model fits not well ($R^2 < 0.57$), pointing out the non-suitability of this model (Table 1).

The equation of pseudo-second order [16-17] is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad (3)$$

where k_2 (g/mg.min) is the rate constant of adsorption. The linear plot of t/q_t *versus* t at 20 °C, as demonstrated in Fig. 6 that R^2 values were superior than 0.99 for all eosin concentrations. The values of standard deviation (SD) and R^2 illustrated a good conformity of the experimental values with the theoretical q_e values (Table 1).The pseudo-second-order model showed the best concordance with the experimental data compared to the pseudo-first-order model (Fig. 6 and Table 1).

3-4. Isotherm of adsorption

The isotherm of adsorption is featured by some parameters that tell about the sorption capacity and properties. These properties may also be utilized in comparing the capacity of adsorption of the adsorbent for various pollutants. Generally, isotherms are fitted with Freundlich and Langmuir models [18-19]. The sorption isotherm of eosin on dried biomass was examined by these two models based on the correlation coefficient R^2 values.

3-4-1. Langmuir model

The Langmuir model supposes the presence of a limited amount of compulsory locations which are distributed in a steady way above the solid surface, presenting the same attraction for adsorption of a sole layer, without any interaction between the adsorbed species. The famous Langmuir expression [20] is given as follows:

$$q_e = \frac{Q_0 k C_e}{1 + kC_e} \quad (4)$$

where Q_0 (mg g^{-1}) is the maximum quantity of Eosin Y for each gram of A1/or A2 biomasses to shape one layer on the surface at maximum equilibrium concentration C_e, q_e is the adsorbed quantity of Eosin Y *per* gram of adsorbent at equilibrium (mg/g), k(l/mg). This constant reflects the affinity of the binding sites. The presentation of $1/q_e$ *versus* $1/C_e$ shows a straight curve of slope $1/kQ_0$ and an intercept $1/Q_0$. The R^2 value of 0.99 demonstrates that the adsorption results of Eosin Y onto dried biomass at 20 °C fitted well the Langmuir isotherm model. The Langmuir constants k and Q_0 were calculated from Eq. (2), the obtained values are given in Table 2.

3-4-2. Freundlich model

It is an empirical model founded on the sorption on a heterogeneous surface signifying that binding sites are not similar and/or independent [21].

$$q_e = k_f C_e^{\frac{1}{n_f}} \quad (5)$$

where k_f and n_f are Freundlich parameters correlated with the adsorption capacity and adsorption intensity, respectively.

A value for $1/n_f$ less than one points out the Langmuir isotherm, while $1/n_f$higher than one indicates the cooperative sorption [22]. The plot of $\ln q_e$ *versus* $\ln C_e$ gives a direct line with slope of $1/n_f$ with value of 0.63-0.80, showing a normal Langmuir isotherm. Freundlich constants k_f and n_f were also calculated and are listed in Table 2.

From Table 2, the Langmuir model gave the best fit with the highest R^2 value at 20 °C temperature compared to the Freundlich model. Comparison of the experimental data with Langmuir isotherm showed the identical nature of biomass surface. The outcomes also confirmed the formation of single-layer coverage of eosin by molecules at the external surface of biomass. A similar observation was given by the sorption of methyl orange

Table 2. Constants of isotherm models

T/°C	Isotherm Langmuir model			Isotherm Freundlich model		
20	Q_0 mg/g	K l/mg	R^2	k_f (mg/g(l/mg)$^{1/n}$)	$1/n_f$	R^2
A1	9.174	0.184	0.999	10.23	0.047	0.998
A2	7.806	1.212	0.996	11.97	0.126	0.995

onto NiO and CuO nanoparticles [23] and Blue 56 on activated carbon obtained from *Cordia myxa* [24]. So, based on the temperature effect results and according to the single-layer bonding formation, this adsorption could be a chemical process driven by the possible interactions between the existing functions in the biomasses and the eosin molecules.

4. Comparison with Some Adsorbents Reported in the Literature

According to Wang (2006) [25] Eosin Y biosorption onto raw anaerobic sludge was very low (2.4 mg/g). However, for other biosorbents, it was found that the maximum uptake values were 0.29 mg/g for raw date palm seeds, 27.69 mg/g for goethite and 30.19 mg/g for composite COM)[6]. Note that the sewage sludge was mostly used after carbonization or chemical treatment for the adsorption of metals and organic substances. So, without any further treatment, neither thermal nor chemical, both studied sludge A1 and A2, exhibited good adsorptive performance with low cost (9.09 mg/g for A1 and 8.96 mg/g for A2).

5. Conclusion

The effect of temperature and initial eosin concentration on the batch adsorption of Eosin Y on two different samples of waste activated biomasses, granular and filamentous fungus sludge, was studied. The maximum uptake increased with the initial eosin concentration. The maximum eosin adsorption capacity was obtained at 30 °C, for both activated sludges. The experimental results were analyzed by Freundlich and Langmuir isotherms. The adsorption isotherm corresponding to these biomasses (A1 and A2) follows significantly the Langmuir model. Furthermore, the pseudo-second-order provided the best correlation of the experimental data compared to the pseudo-first-order model. The present work demonstrates the double benefit of the reuse or the recycle of the biomasses originating from urban and industrial wastewater processes for the elimination of a toxic dye.

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