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Textile mill effluent decolorization using crude dehydrated sewage sludge

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Abstract

Crude dehydrated sewage sludge issued from an urban wastewater treatment plant (High-rate aeration, activated sludge process, Monastir, Tunisia) is used as an adsorbent for the decolorization of a textile mill effluent. The main objective of this work was to evaluate the crude material adsorption capability of the dye contained in wastewater. No treatment to modify any of the adsorbent properties was however considered. Starting with a synthetic effluent, two different kinds of textile dyes had been used: A direct dye, Direct Red 79 and a vat dye from the anthraquinonic class, Vat Blue 4. It was found that the used material, in fact "waste of waste", has a capacity (Langmuir monolayer) of, respectively, 19.6 mg/g to fix the former and 248.3 mg/g to fix the latter. The experiments conducted with the real textile mill effluent to evaluate the material capacity to decolorize it showed that 8 mg/g of the dominant dye (Indigo) gets adsorbed. Langmuir, Freundlich, Redlich-Peterson, Höll-Kirch, Toth and Langmuir–Freundlich two sites equilibrium models were used to fit the experimental results. A sensitivity analysis of the fitted models parameters, made by using Markov Chain Monte Carlo (MCMC) method and the contour plots showed, from statistical point of view, the goodness of the obtained results and the most influential parameter in each used model.

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Keywords: Low cost adsorbent; Textile mill effluent decolorization; Dye retention; Isotherm sensitivity analysis

1. Introduction

Dyes used in the textile industry represent a large and important group of chemicals among the different aqueous pollutants that get mixed in wastewaters (20% of the dyes used for coloring activities might be lost to wastewaters). The lack of our knowledge of the toxic effects of dyes on environment and human health calls our attention. Mutagenic activity of some azo dyes has been recently proven (Umbuzeiro et al. [1]). Textile mill wastewater may contain a substantial amount of dyes which require the adoption of various techniques for their reduction. The conventional methods applied for treating dye-containing wastewater are coagulation and flocculation. These techniques do not show a significant difference in their effectiveness. Moreover, membrane technologies and activated carbon adsorption are also used. However, the high cost and regeneration is one of their major disadvantages. Still, adsorption remains the most popular method for dye-containing wastewater treatment. This

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technology can prove to be attractive in case the adsorbents do not cost much and are ready for use. Utilization of solid waste from one industry to treat the wastewater of another one is environmentally helpful and attractive especially if the used material is cost free. Sewage sludge, waste of the waste, represents a serious problem in the absence of the two main methods of valorisation i.e., agriculture use and incineration. Waiting for a specific sewage sludge local policy for the sector organization, they are now stocked in the municipal wastewater treatment plant, if possible, or discharged in controlled municipal areas.

Many methods show reliance on dye retention using nonconventional materials. Several studies are conducted to evaluate the capacity of such materials to eliminate different kinds of dyes. Some recent results in this field are summarised in Table 1.

In nearly all the mentioned studies and in many other papers, the used adsorbent has been treated to modify some of its physicochemical properties to ensure a higher sorption capacity. Very few of them consider the use of the studied material for industrial application. In the present study, our main objective was the evaluation of the dehydrated sewage sludge capacity to fix dyes contained in a textile mill effluent.

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Nomenclature				
С	equilibrium dye concentration in solution			
CHN	carbon/hydrogen/nitrogen			
D	diameter			
Κ	model coefficient			
n	exponent			
p	pressure			
q_{\perp}	adsorbed amount of dye			
R^2	model determination coefficient			
У	data point value			
\bar{y}	average value of all data points			
Current	1-44			
Greek	teners			
α	snape parameter			
Subscr	ipts			
eq	equilibrium			
F	Freundlich			
HK	Höll-Kirch			
L	Langmuir			
LF	Langmuir–Freundlich two sites			
max	maximum			
р	partitioning			
pr	prediction given by the model			
RP	Redlich-Peterson			
Т	Toth			

1.1. Theoretical aspect of the used mathematical models for adsorption isotherm

Adsorption is a time-dependent process. In the removal of dyes from wastewater, it is necessary to know the rate of adsorption for the design and the quantitative evaluation of adsorbent. Various models have been used to describe thermodynamic equilibrium in the studied systems.

In Table 2, "q" is the adsorbed amount of dye and " C_{eq} " is the equilibrium concentration of dye in solution and those are the only measured parameters. All the others are fitting ones. The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous surface sites within the adsorbent and has found successful application in many sorption processes of monolayer adsorption. The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. It assumes neither homogeneous site energies nor limited levels of sorption. The Freundlich adsorption isotherm constant is indicative of the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively. The Redlich-Peterson isotherm model combines elements from both the Langmuir and Freundlich equation and the mechanism of adsorption is a hybrid one and does not follow ideal monolayer adsorption. It is used as a compromise to improve the fit by Langmuir or Freundlich equation. The exponent "n" ranges between 0 and 1. For "n" = 1, Redlich-Peterson equation leads to Langmuir one. The Höll-Kirch model is essentially a Freundlich isotherm, which approaches an adsorption maximum at high concentration of adsorbate. An equation mathematically equivalent to the Höll-Kirch equation can also be obtained by assuming that the surface is homogeneous, but the adsorption is a cooperative process due to adsorbate–adsorbate interactions. The Toth isotherm model, similar to the Redlich-Peterson model, combines the characteristics of both the Langmuir and Freundlich isotherm. It approaches the Freundlich model at high concentration and is in accord with the low concentration limit of the Langmuir equation. The Langmuir–Freundlich two site isotherm model combines an adsorption component (e.g., Langmuir) with a linear partitioning component.

2. Materials and methods

A sample of dehydrated sewage sludge issued from Monastir (Tunisia) urban, high-rate aeration activated sludge, wastewater treatment plant was collected. The samples were used as they were. Neither mechanical nor chemical treatment method was used to modify any of their physicochemical or mechanical characteristics. The scanning electron microscopy (SEM) technique was used to analyze the external aspect of the adsorbent and its shape. The energy dispersive (ED) X-ray spectrometer was used to reveal the surface qualitative mineral components before and after dye retention. A Perkin-Elmer 240/A/B/C series organic elemental analyser was used to check out the CHN elemental composition of the adsorbent. The "Malvern" mastersizer was used to characterize the used adsorbent size distribution. The Brunauer Emmett Teller (BET) method was used for the adsorbent specific surface area measurements.

"AHIBA" thermo-regulated shaker was used to perform the batch experiments. Temperature was set to 25 °C during 24 h dye/adsorbent aqueous contact. The equilibrium time was determined by preliminary kinetic investigation. It was found that the sorption equilibrium could be established in quite less than 20 h. Two dyes (Direct Red 79 and Vat Blue 4) and a third one, Indigo, contained in an industrial effluent were used in this work. The Chemical formula and some other specific characteristics of the used dyes are summarized in Table 3. All the batch experiments are carried out at constant pHs which are 6.4, 9.2 and 12.3 for, respectively, the DR79, VB4 and Indigo.

The dye concentration was determined using CECIL UV-Visible spectrophotometer by measuring the absorbance at different wavelengths corresponding to the used dye. The used wavelengths were 600, 515 and 650 nm, respectively, for the Direct Red 79, the Vat Blue 4 and the Indigo. A calibration curve obtained at each massic dye concentration ranging between 0 and 100 mg/L was used for initial and final concentration determination. A control flask containing only the studied dye with no adsorbent was used to determine the extent of dye removal by non-adsorptive mechanism. The samples were centrifuged at 5000 rpm ($3500 \times g$) for nearly 5 min to remove the adsorbent from the aqueous solution before the spectrophotometric analysis.

Typically, the VAT dyes are used in the industry in a reduced form according to the following three steps. Transformation of the vat dye dispersed into a reduced form, using the hydrosulTable 1

Dye retention capacities of some non-conventional adsorbents

Dye	Adsorbent	Performances and observations	Reference
Eosin Y	Chitosan hydrobeads	70–80 mg/g	Chatterjee et al. [2]
Bismark brown Activated carbons		1000–2000 mg/g depending on initial dye concentration	Prakash Kumar et al. [3]
Basic Blue 9 Cyclodextrin-based material		60 mg/g	Crini et al. [4]
Methylene blue	Sand (untreated)	Up to 92% of the dye can be retained Salt presence decreases the sorption capacity	Bukallah et al. [5]
Direct Red 23 Direct Red 80	Orange peel	More than 90% of the used dyes are retained	Arami et al. [6]
Methylene blue	Fly ash	6 mg/g (at pH=8)	Kumar et al. [7]
Basic Red 22KudzuBasic Yellow 21PeatBasic Blue 3		150–210 mg/g 200–500 mg/g	Allen et al. [8] and [11]
4-Bromoaniline-azo-1,8- dihydronaphthalene-3,6- disodiumsulphate	Palm kernel fibre	39 mg/g	Ofomaja and Ho [9]
Direct red 80 Direct red 81 Acid blue 92 Acid red 14	Soy meal hull	100–200 mg/g	Arami et al. [10]
Methylene blue Rhodamine B	Dead macro fungi	200 mg/g 30 mg/g	Maurya et al. [12]
Methylene blue Congo red	Flyash	90–100% Removal at lower concentration	Basava Rao et al. [13]
Malachite green	Raw fresh water alga – <i>Pithophora</i> sp. Activated fresh water alga – <i>Pithophora</i> sp.	20 mg/g 118 mg/g at 30 °C	Vasanth Kumar et al. [14]
Remazol Black BB Remazol Red RR Remazol Golden Yellow RNL	Chlorella vulgaris	BB: 270–470 mg/g RR: 140–200 mg/g RNL: 50–70 mg/g	Aksu et al. [15]
Reactive Yellow 22	Green algae (Spirogyra species)	70–90% color removal	Venkata Mohan et al. [16]
Safranine TJalshakti (a novelMethylene bluepolymer)Crystal violet		93%, 98%, 84% (maximum removal for pH of 6.0)	Dhodapkar et al. [17]
Methylene blue Rhodamine B Congo red Acid brilliant blue	Raw Coir pith (lignocellulosic agricultural waste)	Mean value of 20 mg/g	Namasivayam et al. [18]
Acid violet Procion Red Procion orange	Activated Coir pith	Mean value of 130 mg/g	
Basic violet 7 Basic blue 3 Direct yellow 50 Acid red 37	Maize starch	6-8 mg/g 4-10 mg/g 1-3 mg/g 2-5 mg/g	Abdel-Aal et al. [19]

phite salt and addition of cleaning agent. The dying step usually made at a temperature of 50–60 °C, is conducted in basic conditions using caustic soda salt, followed by 'rinse and oxidize phase' using air or H_2O_2 , eventually ending in 'the soap off and rinse phase' to eliminate the unused dye (this step is the main source of the polluted wastewater). In this study and for the vat

dye, caustic soda and hydrosulphite salts are used for aqueous solution preparation.

3. Results and discussion

The main objective of this work was to study a real textile mill effluent decolorization using an available, abundant and

Table 2			
Mathematical	models	for sorption	isotherms

Isotherm	Equation	Parame	ter and dimension	Note
Langmuir	$q = q_{\max} \frac{K_{\rm L} C_{\rm eq}}{1 + K_{\rm L} C_{\rm eq}}$	$q_{ m max} \ K_{ m L}$	(mg/g) (mg/L) ⁻¹	Capacity at monolayer coverage Langmuir coefficient related to the free energy of adsorption
Freundlich	$q = K_{\rm F} C_{\rm eq}^n$	K _F n	$(mg/g) (mg/L)^{-n}$ (-)	Freundlich affinity coefficient Exponent
Redlich-Peterson	$q = \frac{K_{\rm RP}C_{\rm eq}}{(1+\alpha_{\rm RP}C_{\rm eq}^n)}$	K _{RP} α _{RP} n	(mg/g) (mg/L) ⁿ⁻¹ (-) (-)	Redlich-Peterson affinity coefficient Heterogeneity or shape parameter Exponent
Höll-Kirch (Langmuir-Freundlich monolayer)	$q = q_{\max} \frac{K_{\rm HK} C_{\rm eq}^n}{1 + K_{\rm HK} C_{\rm eq}^n}$	q _{max} K _{HK} n	(mg/g) (mg/L) ⁻ⁿ (-)	Maximum sorption capacity Höll-Kirch affinity coefficient Exponent
Toth	$q = q_{\max} \frac{C_{\text{eq}}}{(1 + \alpha_{\text{T}} C_{\text{eq}}^n)^{1/n}}$	$q_{ m max} \ lpha_{ m T} \ n$	(mg/g) (-) (-)	Maximum sorption capacity Heterogeneity or shape parameter Exponent
Langmuir–Freundlich two site	$q = q_{\max} \frac{K_{\text{LF}} C_{\text{eq}}^n}{(1 + K_{\text{LF}} C_{\text{eq}}^n)} + K_{\text{p}} C_{\text{eq}}$	q _{max} K _{LF} n K _p	(mg/g) $(mg/L)^{-I}$ (-) $(mg/L)^{-1}$	Maximum sorption capacity Langmuir–Freundlich affinity coefficient Exponent Partitioning coefficient

Table 3

Dyes chemical configuration and characteristics





Fig. 1. SEM of the dehydrated sewage sludge sample.

cost free materiel; crude dehydrated sewage sludge. The first step was the preliminary experiments to characterize the used adsorbent.

3.1. Adsorbent and dyes characterization

The SEM examination (Fig. 1) of the used dehydrated sewage sludge samples showed a regular shape of the material and the presence of silicium, carbon and calcium minerals was revealed by the energy dispersive X-ray spectrometer (Fig. 2a). No additional significant elements appear after the dye retention (Fig. 2b) since the adsorbent elements cover the dye ones (C, O, S and Na). The organic matter fraction of the sewage sludge is about 50% (5.42% moisture, 50.47% volatiles and 44.11% ash). The CHN elemental analysis of the adsorbent is 39.73, 5.38 and 4.76%, respectively. The used material had a mean volumetric diameter (*D*, [4,3]) measured using a "Malvern" mastersizer of 186 μ m (Fig. 3). With the BET method (Fig. 4), it was found that the used adsorbent offered a surface area of 5.28 m²/g. The median pore width was found to be 55.631 nm and the cumulative pore volume was about 0.025 cm³/g (Fig. 5).

The steric energy calculation made using the Molecular Mechanics (MM2) model had been performed using commercial software. The distance in Å found in Table 3 was obtained after atomic calculations and represented the higher distance between the two extreme atoms of the studied molecule. The found distance gave an idea about the steric clogging of the used dyes. For



Fig. 2. (a) ED X-ray of the dehydrated sewage sludge sample before dye retention. (b) ED X-ray of the dehydrated sewage sludge sample after dye retention.



Fig. 3. Size distribution of the dehydrated sewage sludge sample.



Fig. 4. BET of the dehydrated sewage sludge sample.

the Direct Red 79 the distance was observed to be about 24.95 Å and about 18.21 Å for the Vat Blue 4. The INDIGO presented a smaller molecule and was about 12.69 Å.

3.2. Dye retention capacity determination

The first experiments were conducted with a synthetic effluent using two different kinds of dyes: Direct Red 79 and Vat Blue 4. In aqueous solution, the first dye was in a soluble form and presented a sulphonic acid terminal group $(-SO_3^-H^+)$. To retain the soluble form, the addition of a reduction and basic agents is necessary in the case of the vat dye and in aqueous solution, it is found as salt $(-O^-Na^+)$ with a basic character. The adsorbent used in this work, which contained mainly dead biomass, showed different retention capacity, depending on the studied dye. This could be explained in the case of the Direct Red 79 and the Vat Blue 4 by the difference in the chemical struc-



Fig. 5. Pore sizes distribution of the dehydrated sewage sludge sample.



Fig. 6. Applied models for "Direct Red 79" experimental isotherm.

ture and the ensued properties. The dye retention is essentially a surface phenomenon and then the retained amount is strongly dependent on the steric clogging. The average adsorbent pore size is about 55.6 nm. The molecular distance for the three used dyes ranges between 12.6 and 25 Å. This means that all the adsorbent pores are accessible to the dye molecules. However, the retention is not done by pore's inclusion but by an interaction between the active adsorbent sites and the dyes molecules. The steric clogging concerns two or more consecutive active sites which may not be occupied because of the dye molecule size. So the greater the molecule is, the less the probability that two or more consecutive active retention site could be occupied.

With regard to dye found in aqueous solutions, it seems that the used material has higher affinity to retain the basic dyes than the acidic ones. In spite of its reduced specific area $(5.28 \text{ m}^2 \text{ g}^{-1})$ compared to the activated carbon (may reach $1300 \text{ m}^2 \text{ g}^{-1}$) and the relative high clogging of the studied dyes, the used adsorbent shows interesting retention capacities. The Langmuir monolayer retention capacity was found to be 19.6 mg/g for the Direct Red 79 and 248.3 for the Vat Blue 4. The adsorbent used in this work has a retention capacity comparable to nearly all the non-conventional materials listed in Table 1. In the textile mill wastewater case, 8.1 mg/g of the dominant dye (Indigo) was found retained. This capacity is of the same order than some material retention capacity found in the literature (fly ash, palm kernel fibre, raw fresh water alga – *Pithophora* sp., coir pith and maize starch).

3.3. Modelisation study of the dye adsorption

The experimental isotherms modelisation is made using the most common mathematical adsorption models (Langmuir, Freundlich, Redlich-Peterson, Höll-Kirch, Toth and Langmuir–Freundlich two sites). The obtained results are summarized in Table 4. Figs. 6 and 7 gather in the same graph the experimental isotherm and its representation by four from the six used models. It was found that the Freundlich, Redlich-Peterson, Höll-Kirch and Toth gave exactly the same curves. The best fit was obtained using Langmuir–Freundlich two sites model. The high parameter number, four, easily explained this fact. In the textile mill wastewater case, the salt presence notably affected the dye adsorption. The effluent was well clarified and the color

 Table 4

 isotherm models estimated parameters for the three studied dyes

Isotherm model	Parameter	Direct Red 79	Vat Blue 4	Indigo
Langmuir	$\begin{array}{c} q_{\max} \ (\text{mg/g}) \\ K_{\text{L}} \ (\text{mg/L})^{-1} \\ R^2 \ (\%) \end{array}$	$ 19.6 4.7 \times 10^{-2} 90.2 $	248.3 2.4×10^{-3} 93.7	8.1 9.2×10^{-2} 83.6
Freundlich	$K_{\rm F} \ ({\rm mg/g}) \ ({\rm mg/L})^{-{\rm n}}$ $n \ (-)$ $R^2 \ (\%)$	2.1 4.8×10^{-1} 95.5	9.4×10^{-1} 8.5×10^{-1} 94.4	1.7 3.5×10^{-1} 93.2
Redlich-Peterson	$K_{\rm RP} \ ({\rm mg/g}) \ ({\rm mg/L})^{n-1}$ $\alpha_{\rm RP} \ (-)$ $n \ (-)$ $R^2 \ (\%)$	276 131 5.2×10^{-1} 95.4	311 330 1.5×10^{-1} 94.4	285 169 6.5×10^{-1} 93.1
Höll-Kirch	$q_{\max} (mg/g) K_{HK} (mg/L)^{-n} n (-) R^2 (\%)$	2700 7.7×10^{-4} 4.8×10^{-1} 95.4	$\begin{array}{c} 4569 \\ 2.0 \times 10^{-4} \\ 8.5 \times 10^{-1} \\ 94.3 \end{array}$	$1295 \\ 1.3 \times 10^{-3} \\ 3.5 \times 10^{-1} \\ 93.1$
Toth	$q_{ m max} \ (m mg/g) \ lpha_{ m T} \ (-) \ n \ (-) \ R^2 \ (\%)$	6001 8.5 × 10 ⁻¹ 7.7 × 10 ⁻² 95.2	$145 1.5 \times 10^{-1} 2.8 \times 10^{-2} 94.3$	60000 1.45 8.5 × 10 ⁻² 92.7
Langmuir–Freundlich two sites	$q_{\max} (mg/g)$ $K_{LF} (mg/L)^{-n}$ $n (-)$ $K_{p} (mg/L)^{-1}$ $R^{2} (\%)$	5 1.4×10^{-2} 1.5×10^{-1} 1.7×10^{-1} 98.5	1.9 9.1 9.5×10^{-2} 4.9×10^{-1} 95.5	$3.87.1 \times 10^{-1}15.3 \times 10^{-2}94.7$



Fig. 7. Applied models for "Vat Blue 4" experimental isotherm.



Fig. 8. Applied models for industrial wastewater (Indigo) experimental isotherm.

intensity decreased notably. Fig. 8 gathers in the same graph the experimental isotherm and the applied equilibrium models for the industrial wastewater case.

For the modelling work, the MODEST[®] software was used to fit the model parameters to the isotherm data. The first criteria retained for the fitting job was that the fitted maximum adsorbed phase concentration should not be smaller than the maximum value derived from experiments. The second one was the sum



Fig. 9. MCMC sensitivity analysis of Langmuir model (Indigo).

of residual squares. It is the most common objective function according to which the parameters are estimated. The goodness of fit is the coefficient of determination, the R^2 -value given by the expression:

$$R^{2} = 100 \left(1 - \frac{||y - y_{\rm pr}||^{2}}{||y - \bar{y}||^{2}} \right)$$

So, $R^2 \le 100$ – the closer the value is to the number 100, the more perfect is the fit.

3.4. Sensitivity analysis

Contour plots and Markov chain Monte Carlo (MCMC) methods are used for sensitivity analysis of the proposed models

to parameter variation around their optimum. In the 'sensitivity' plot using the MCMC method, we sample points in the parameters space, as a 'histogram' of the sampled points, one gets the probability posterior distribution (in the 'Bayesian' sense) of the parameters. These are the 'true' statistical distributions, supposing that the error level of measurements is correctly estimated by the residuals of the MODEST fit. MCMC is applied to the experimental data point of the industrial wastewater case. Fig. 9 shows the obtained result. 1 D plots on the axis: the 'marginal' distributions of each Langmuir parameter and the 2 D plot: the joint posterior. A sensitivity analysis for the Langmuir parameters was also performed. By plotting the contour lines with varying parameter intervals for the R^2 values of the fit, it was found that no crucial intercorrelations exist. So, the identifiability of the two parameters (Langmuir) proved to be good and precise.



Fig. 10. Contour curves sensitivity analysis of Langmuir-Freundlich two sites model (Direct Red 79).

 Table 5

 Isotherm model parameters relative sensitivity

$q_{\rm max} \sim { m K_L}$	Langmuir
$K_{\rm F} \sim n$	Freundlich
$K_{\rm RP} < \alpha_{\rm RP} \sim n$	Redlich-Peterson
$q_{\rm max} \sim K_{\rm HK} \sim n$	Höll-Kirch (Langmuir Freundlich monolayer)
$q_{\rm max} \sim \alpha_{\rm T} \sim n$	Toth
$q_{\max} \gg K_p \gg n > K_{\rm LF}$	Langmuir-Freundlich two site
$q_{\rm max} \gg K_{\rm p} \gg n > K_{\rm LF}$	Langmuir-Freundlich two site

The same analysis using the contour curves was performed for all the obtained model parameters fitted with the Direct Red 79 experimental data. Fig. 10 gathers the obtained results for the best used model: Langmuir–Freundlich two sites. Table 5 summarizes the relative sensitivity of all model parameters. The most influential parameter is q_{max} with its determination being precise. The same comments cannot be made concerning the two other parameters of Langmuir–Freundlich two sites model, n and K_{LF} . For all the other used models, no crucial intercorrelation exists and the parameters identifiability is presented to be good.

4. Conclusion

The decolorization of a real textile mill effluent and two synthetic ones using crude dehydrated sewage sludge as an adsorbent is studied in batch system. Investigating the sorption properties of the crude material has been one of the main objectives of the present work. It was found that the used material behaves differently according to the used dye. Its retention capacity varied from 8 up to more than 200 mg/g and its affinity to retain the basic dyes seemed higher than that of the acidic ones. The lowest retention capacity is obtained with experiments performed using the real textile mill effluent. It may be concluded that the crude dehydrated sewage sludge, in fact waste of waste, and in spite of its low specific area, has undoubtedly a real potential to remove and retain large amounts of different dyes. This process could be adopted as an efficient approach for decolorization of industrial effluents and it may be an alternative to more costly materials such as activated carbons. This work indicated that the locally available and abundant dehydrated sewage sludge could be employed as an adsorbent for the removal of some dyes from textile mill effluents. Several equilibrium models have been applied to fit the experimental data. A sensitivity analysis of the used models showed the goodness of the obtained parameter values and the more influential one between them for each model.

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