



Vat dye sorption onto crude dehydrated sewage sludge

H. Dhaouadi *, F. M'Henni

Faculté des Sciences, Département de Chimie, Laboratoire de Chimie Appliquée et Environnement, Bvd de l'Environnement 5000 Monastir, Tunisia

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ABSTRACT

In this work, sewage sludge is used as a textile dye adsorbent. A sample of crude dehydrated sewage sludge issued from an urban wastewater treatment plant (high-rate aeration, activated sludge process, Sahline, Tunisia) is utilized for vat dye retention. The main objective of this work is to evaluate the “efficiency” of the crude material on vat dye sorption. However, no treatment to modify any of the adsorbent properties was considered. Although the relatively low specific surface area (about $3.2 \text{ m}^2 \text{ g}^{-1}$) compared to more conventional adsorbents, the used material shows very interesting retention capacities when used with water pollutants. The pseudo, first and second order kinetic models have been used to investigate the retention mechanism. When linearized, the pseudo-second order fit, for the both used dyes, in a better way the obtained experimental results than the pseudo-first order kinetic model. For equilibrium dye uptake amount it is found that the used material has a capacity (Langmuir Freundlich monolayer) of 73.1 mg/g to fix the VAT RED 10 and 58.7 mg/g to fix the VAT ORANGE 11.

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1. Introduction

Sewage sludges are by-products of urban and industrial wastewater treatment plants activities. This “waste of the waste”, if it is heavy metals free and after several treatment steps (mainly stabilization and composting) may be disposed through landfills and land reclamation. For the moment, tons of sewage sludges are produced in Tunisia every day and this production is expected to rise (70,000 ton in 2006 against 40,000 ton in 1996). They are now stocked in the municipal wastewater treatment plants, if possible, or discharged in controlled municipal areas. However many legal standards limit the handling or the use of sewage sludge on farmland. Even if many management options for the sewage sludge exist, the utilization of solid waste from one industrial activity to treat the wastewater of another one is environmentally helpful and attractive especially if the used material is cost free. On the other hand, dyes used in the textile industry represent a large and important group of chemicals among the different aqueous pollutants that get mixed in wastewater. The lack of our knowledge of the toxic effects of dyes on environment and human health draws our attention. Activated sludge inhibition process by acid black 1 azo dye discharge is, for example reported by Martin et al. [1]. Textile mill wastewater may contain a substantial amount of dyes which require the adoption of various techniques for their elimination. Liquid phase adsorption remains the most popular

method for dye-containing wastewater treatment. It is especially a promising option for non-biodegradable organic dyes removal. This technology can prove to be attractive in case the adsorbents do not cost much and are ready for use. Many methods show reliance on dye retention using non-conventional materials. Several studies are conducted to evaluate the capacity of such materials to eliminate different kinds of dyes. A quick review of most recent published papers dealing with vat dye retention and sewage sludge based activated carbons used for dye removal is given 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. In the present work, the main objective is the evaluation of the crude dehydrated sewage sludge capacity to fix vat dyes used in the textile industries.

2. Adsorption isotherm and kinetic models

Equilibrium data, commonly known as adsorption isotherms, are basic requirement for the design of adsorption systems used for the retention of organic pollutants. In the removal of dyes from wastewater, it is necessary to know the rate of retention for the design and the quantitative evaluation of adsorbent. Moreover, the kinetics describe the solute uptake rate which, in turn, control the residence time of dye uptake at the solid–solution interface. Therefore it is important to be able to predict the rate at which pollutant is removed from aqueous solutions in order to design appropriate adsorption treatment plant. Various models have been used to describe thermodynamic equilibrium in the present studied systems. The Langmuir adsorption isotherm assumes that adsorption

* Corresponding author. Tel.: +216 98202932; fax: +216 73500278.
E-mail address: hatem.dhaouadi@fsm.rnu.tn (H. Dhaouadi).

Nomenclature

| | |
|----------------|---|
| BOD | biological oxygen demand |
| C | equilibrium dye concentration in solution |
| CHN | carbon/hydrogen/nitrogen |
| IEP | isoelectric point |
| K | model coefficient |
| n | exponent |
| p | pressure |
| q | adsorbed amount of dye |
| R ² | model determination coefficient |
| T | transmittance |
| TOC | total organic carbon |
| V | volume |
| y | data point value |
| \bar{y} | average value of all data points |

Greek letters

| | |
|----------|-----------------|
| α | shape parameter |
| Φ | pore width |

Subscript

| | |
|-----|-------------------------------|
| avr | average |
| eq | equilibrium |
| exp | experimental |
| F | Freundlich |
| HK | Höll-Kirch |
| L | Langmuir |
| LF | Langmuir Freundlich two sites |
| max | maximum |
| mod | model |
| p | partitioning |
| pzc | point of zero charge |
| RP | Redlich–Peterson |
| T | Toth |

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 non-linearity 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 agreement 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.

All the used mathematical models for dye adsorption isotherm are summarized in Table 2 where 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. Concerning the kinetic study, several models can be used to check out the mechanism of solute adsorption onto an adsorbent [17,18]. In order to investigate this adsorption mechanism, characteristic constants were determined using a pseudo-first order equation of Lagergren based on solid capacity with the assumption that the adsorption mechanism is diffusion controlled and a pseudo-second order equation based on solid phase adsorption with the assumption that the rate-limiting step may be chemical sorption (chemisorption) involving valency forces through sharing or exchange of electrons between adsorbent and adsorbate [18]. The used kinetic model expressions are presented in Table 3 where k_1 and k_2 are the kinetic rate constants of respectively the pseudo-first and second order, q is the adsorbed amount of dye at any time t and q_{eq} is the solute adsorbed at equilibrium state. For isotherm and kinetic model parameters determination, the non-linear method is preferred to the linear one [19–24]. While the non-linear method, based on a trial and error procedure, uses the “raw” experimental data for model parameter determination, the linear method assumes that the scattered points around the line follows a Gaussian distribution and the distribution error are the same at every value of the abscissa. This is rarely true or virtually impossible with equilibrium isotherm models (as most of the isotherm models are non-linear) as the error distribution gets altered after transforming the data to a linear form.

2.1. Material and methods

A sample of dehydrated sewage sludge issued from Sahline (Tunisia) urban wastewater treatment plant (high-rate aeration activated sludge) is 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 SEM (scanning electron microscopy) technique was used to analyze the external aspect of the adsorbent and its shape. The Energy Dispersive (ED) X-ray spectrometre was used to reveal the surface qualitative mineral components. An SCA-CNRS organic elemental analyzer is used to check out the Carbon, Hydrogen and Nitrogen (C, H, N) 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 which are performed with a Thermo Electron® SORPTOMATIC 1990 device. Fourier transform infrared spectroscopy (FT-IR) spectra of the sewage sample is scanned ($16\times$) in the range of 400–4400 cm^{-1} using a PerkinElmer® FT-IR spectrophotometre model RX I with potassium bromide (KBr) disks at the weight ratio of 1:50 (dehydrated sewage sludge/KBr). The sewage sludge surface charge distribution was characterized by titrating the crude suspension sample with acid, starting with a pH value above 10, then adding incremental amounts of acid down to a pH value below 4 [6]. The amount of acid that was required to cause a given amount of pH change was proportional to the surface charge. This experiment was conducted in two electrolytes concentration, 0.1 M NaCl and 0.01 M NaCl under nitrogen at 25 °C. A blank titration was also performed at the two electrolyte concentrations under the same condition. The relative surface charge can be calculated from the difference between the volume of titrant used in titration of solid suspension on the one hand, and in blank titration on the other hand, leading to the same pH value. Theoretically, the pH_{pzc} can be taken as the crossover point of two suspension surface charge curves in different ionic strength electrolytes, since it is

Table 2
Mathematical models for sorption isotherms

| Isotherm | Equation | Parameter (dimension) |
|--|--|--|
| Langmuir | $q = q_{\max} \frac{K_L C_{\text{eq}}}{1 + K_L C_{\text{eq}}}$ | q_{\max} (mg/g) K_L (mg/L) ⁻¹ |
| Freundlich | $q = K_F C_{\text{eq}}^n$ | K_F (mg/g) × (mg/L) ⁻ⁿ n |
| Redlich–Peterson | $q = \frac{K_{\text{RP}} C_{\text{eq}}}{1 + \alpha_{\text{RP}} C_{\text{eq}}^n}$ | K_{RP} (mg/g) × (mg/L) ⁿ⁻¹ α_{RP} n |
| Höll-Kirch (Langmuir Freundlich monolayer) | $q = q_{\max} \frac{K_{\text{HK}} C_{\text{eq}}^n}{1 + K_{\text{HK}} C_{\text{eq}}^n}$ | q_{\max} (mg/g) K_{HK} (mg/L) ⁻ⁿ n |
| Toth | $q = q_{\max} \frac{C_{\text{eq}}}{(1 + \alpha_T C_{\text{eq}}^n)^{1/n}}$ | q_{\max} (mg/g) α_T n |
| Langmuir–Freundlich two site | $q = q_{\max} \frac{K_{\text{LF}} C_{\text{eq}}^n}{1 + K_{\text{LF}} C_{\text{eq}}^n} + K_p C_{\text{eq}}$ | q_{\max} (mg/g) K_{LF} (mg/L) ⁻ⁿ n K_p (mg/L) ⁻¹ |

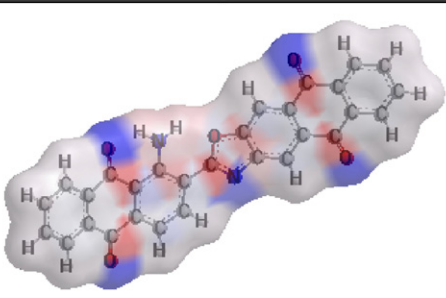
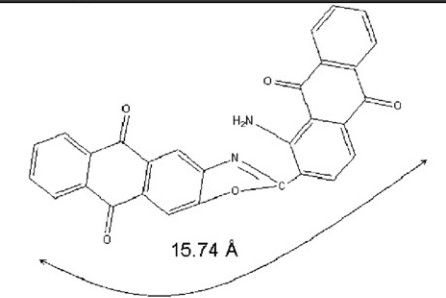
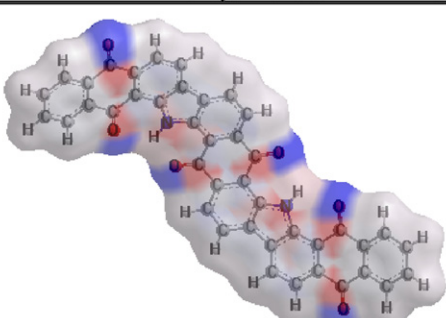
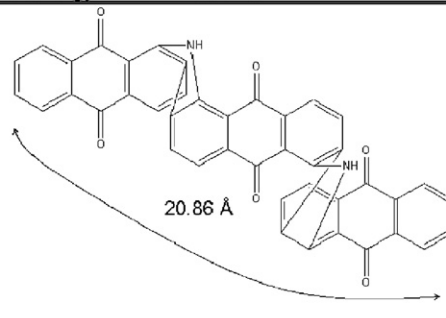
the only point where the surface charge is independent of electrolyte concentration. A MALVERN Zetasizer Nano ZS[®] is used for sewage sludge zeta potential distribution allowing the identification of the isoelectric point (IEP) which is defined as the point of zero zeta potential corresponding also to the point of least stability due to the weakened repulsive forces. The total surface acidity/basicity was determined by the conventional back titration methods [6,25]. To access the total acidity (basicity) of the used adsorbent, about 0.5 g of the crude sewage sludge sample

Table 3
Mathematical models for the used sorption kinetics

| Kinetic model | Non-linear linear and form | Parameters |
|---------------------|---|--|
| Pseudo-first order | $\frac{dq}{dt} = k_1(q_{\text{eq}} - q)$ $\log(q_{\text{eq}} - q) = \log(q_{\text{eq}}) - \frac{k_1}{2.30} t$ | k_1, k_2 : rate constant (min ⁻¹) q_{eq} : solute adsorbed at equilibrium state (mg/g) |
| Pseudo-second order | $\frac{dq}{dt} = k_2(q_{\text{eq}} - q)^2$ $\frac{t}{q} = \frac{1}{k_2 q_{\text{eq}}^2} + \frac{1}{q_{\text{eq}}} t$ | q : solute adsorbed at any time (mg/g) t : time (min) |

was soaked into 50 mL of 0.025N NaOH (0.025N HCl) solution in a closed flask and agitated for 48 h at 25 °C. After filtration, the supernatant was titrated with 0.025N HCl (0.025N NaOH) solution to determine the remaining of NaOH (HCl) in the solution. The surface oxygenated functional groups determination was performed according to Boehm titration [25–28]. 0.5 g sewage sludge sample was placed in 50 mL of the following 0.05N solutions: sodium hydroxide (NaOH), sodium carbonate (Na₂CO₃) and sodium bicarbonate (NaHCO₃). The vials were sealed and shaken for more than 48 h and then filtered. 20 mL aliquots were back titrated pH-metrically with 0.05N NaOH after acidifying with a known amount excess of 0.05N HCl solution. The number of acidic sites was determined under the assumptions that NaOH neutralizes carboxylic, lactonic and phenolic groups; that Na₂CO₃ neutralizes carboxylic and lactonic groups; and that NaHCO₃ neutralizes only carboxylic groups.

Table 4
Dyes chemical characteristics and configuration at minimum steric energy

| | |
|---|--|
| Vat dye N°1: Generic name : Vat Red 10 Commercial name: Indanthren Red FBB Chemical formula: C ₂₉ H ₁₄ N ₂ O ₅ – Molecular weight: 470 g.mol ⁻¹ Purity: 98.5%w - Minimum steric energy: 44.94 kcal.mol ⁻¹ | |
|  |  |
| Dye N°2: Generic name : Vat Orange 11 Commercial name: Cibane Yellow 3R Chemical formula: C ₄₂ H ₁₈ N ₂ O ₆ - Molecular weight: 646 g.mol ⁻¹ Purity: 98.5%w - Minimum steric energy: 46.79 kcal.mol ⁻¹ | |
|  |  |

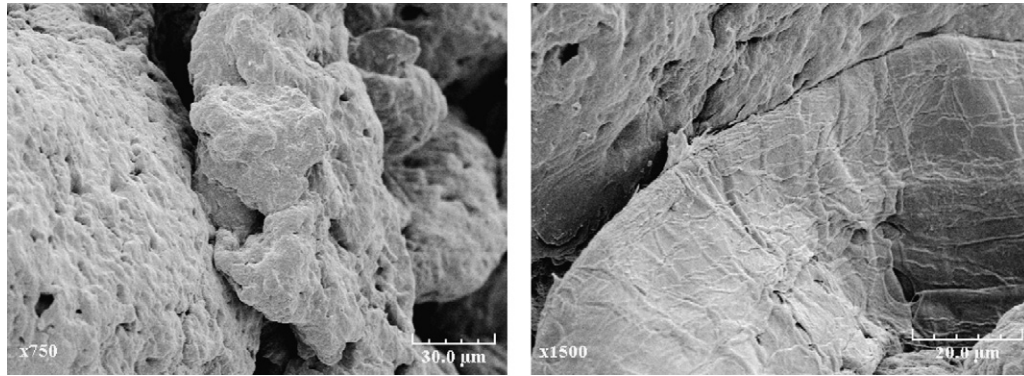


Fig. 1. Scanning electron microscopy images for the dehydrated sewage sludge sample magnified 750× and 1500×.

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 5 h. Two dyes (VAT RED 10 and VAT ORANGE 11) were used in this work. The Chemical formula and some other specific characteristics of the used dyes are summarized in Table 4. All the batch experiments are carried out at constant pH values which are about 11.7 and 12.1 for respectively the VAT RED 10 and VAT ORANGE 11 experiences where the leuco sodic form groups, R–C–O⁻, Na⁺, are predominant in dyes molecules. For both used dyes here, the re-precipitation pH is found around 8.4.

The dye concentration was determined using CECIL® UV–Visible Spectrophotometre by measuring the absorbance at different wavelength corresponding to the used dye. The used wavelengths were 520 and 410 nm respectively for the VAT RED 10 and the VAT ORANGE 11. A calibration curve obtained at each massic dye concentration with consideration to dyes purity and ranging between 0 and 100 mg L⁻¹ 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 (maximum relative centrifugal force, rcf = 3500 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. The first step is the transformation of the vat dye dispersed into a reduced form, using the hydrosulphite salt and addition of cleaning agent. The second

step is the dyeing step usually made at a temperature of 50–60 °C, and it is conducted in basic conditions using caustic soda salt, followed by 'rinse and oxidize phase' using air or H₂O₂. The last step is '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 is to study the vat dye removal using an available, abundant and cost free materiel which is crude dehydrated sewage sludge. The first step was a set of 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 some superficial macro porosity of the material and the presence of silicium, carbon and calcium minerals was revealed by the Energy Dispersive ED X-ray spectrometre (Fig. 2). No additional significant element appears with the ED X-ray analysis after the dye retention since the adsorbent elements include the dye one. The organic matter fraction of the sewage sludge is about 50 wt% (5.68% Moisture, 50.71% Volatiles and 43.61% Ash). The C, H, N elemental analysis of the adsorbent is respectively 42.66 ± 0.3%, 5.32 ± 0.3% and 8.72 ± 0.3%. The used material had an average volumetric diametre (D [4,3]) measured using a "Malvern" mastersiser of 121 μm. With the BET method, it was found that the used adsorbent offered a surface area of 3.27 m² g⁻¹. The median

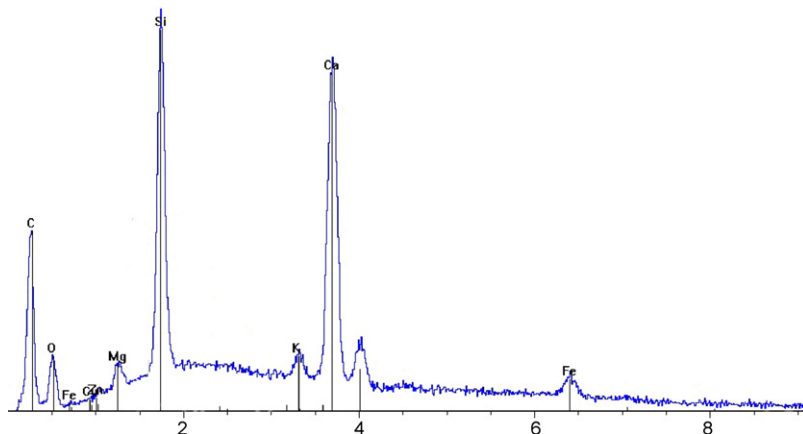


Fig. 2. Energy dispersive X-ray analysis for element composition's determination of the dehydrated sewage sludge sample.

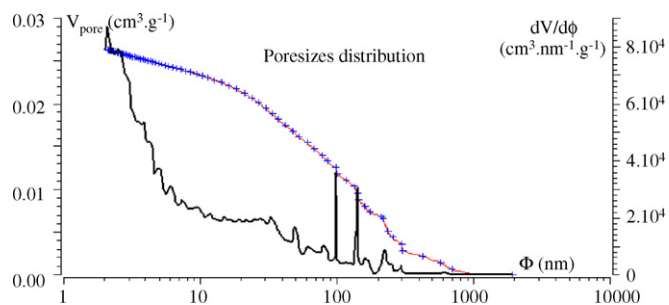


Fig. 3. Poresizes distribution of the dehydrated sewage sludge sample given with Barrett–Joyner–Halenda (BJH) method.

pore width calculated with Barrett–Joyner–Halenda (BJH) method was found to be 85.99 nm and the cumulative pore volume was about 0.0264 cm³/g (Fig. 3). Several functional groups may be present on the surface of the crude dehydrated sewage sludge

(Fig. 4). The –OH and –NH of either alcohols or phenols, and nitrogen containing surface groups; and the C=O of carbonyl groups, indicated by the peaks at the bands of 3900–3400 and 1640 cm⁻¹, respectively. For instance the intensive band near 1640 cm⁻¹ has been explained by stretching vibration of aromatic C=C bonds which are polarized by oxygen atoms bound near one of the C atoms [6,25]. These oxygenated functional groups are normally related to the acidity of the carbon. The evidence of the C=C bond of aromatic rings polarized by oxygen atoms bound near one of the C atoms is observed at the band of 1440–1430 cm⁻¹ suggesting the presence of basic oxygen-containing functionalities such as quinone or diketones groups and pyrone-like groups. One of the major bands of the sewage sludge sample spectra is observed at nearly 1060 cm⁻¹ may be assigned to either Si–O–Si or Si–O–C structures, which is associated with the silicon content in sewage sludge as revealed by the ED-X-ray spectra. Most carbons contain hydrogen, and band of C–H stretch and wagging vibrations are observed. Following the acid titration method, the point of zero charge (Figure 5) was found at

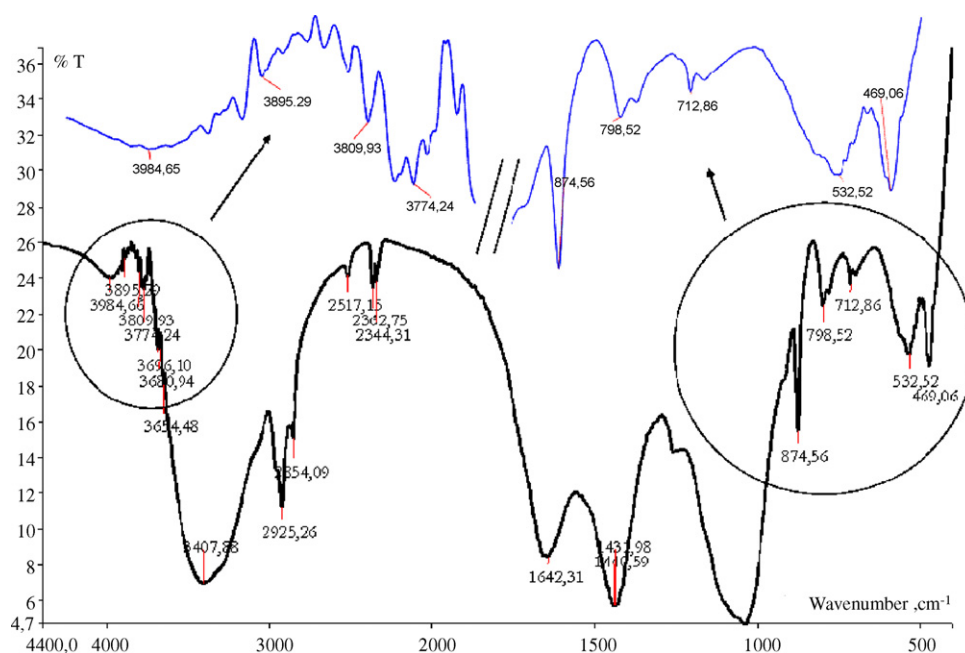


Fig. 4. Fourier transform infrared spectra of the dehydrated sewage sludge sample.

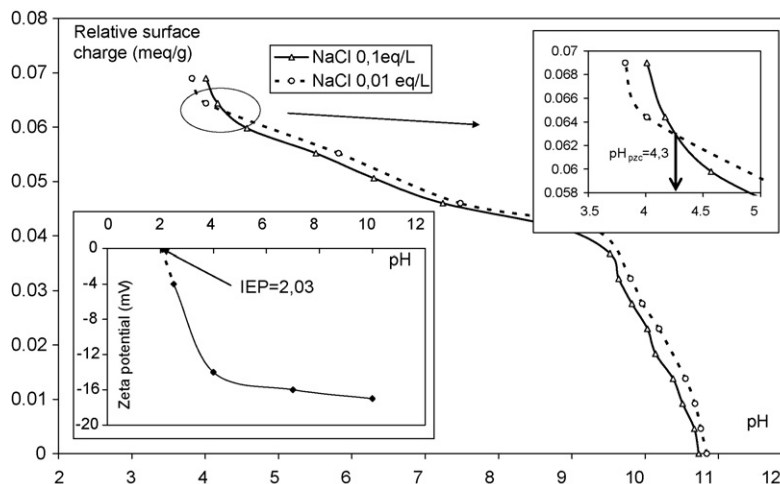


Fig. 5. Relative adsorbent surface charge and zeta potential for pH's point of zero charge and isoelectric point determination.

$pH_{pzc} = 4.30$. The isoelectric point (IEP) was obtained by plotting the zeta potential vs pH. Compared to the pH_{pzc} (4.30) the IEP is smaller (2.03). The pH_{pzc} would be the same as the isoelectric point (IEP) if there is no adsorption of other ions than the potential determining H^+/OH^- at the surface of the used adsorbent. At pH values above the IEP, the predominate surface species is $M-O^-$. Boehm pH titration of basic solutions, NaOH ($pH_0 = 12.12 - pH_{eq} = 11.95$), Na_2CO_3 ($pH_0 = 10.85 - pH_{eq} = 10.24$) and $NaHCO_3$ ($pH_0 = 8.03 - pH_{eq} = 7.43$) indicates that the major part of acidic functional groups are carboxylic one ($0.98 \text{ meq/g} - 299.7 \mu\text{eq/m}^2$). The lactonic functional group represents 0.057 meq/g ($17.43 \mu\text{eq/m}^2$) while the phenolic one titrates 0.069 meq/g ($21.10 \mu\text{eq/m}^2$). The total surface basicity is found to be of 2.170 meq/g ($663.6 \mu\text{eq/m}^2$) while the total acidity is 1.106 meq/g ($338.22 \mu\text{eq/m}^2$).

For the dye molecules, the steric energy calculation made using the MM2 (Molecular Mechanics) model had been performed using commercial software. The distance in Å found in Table 4 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 the VAT RED 10, the distance was observed to be about 15.74 \AA and about 20.86 \AA for the VAT ORANGE 11.

Table 5

Kinetic models estimated parameters for the two studied dyes

| Model | Dye | Parameters | |
|---------------------|---------------|--|--|
| | | Linear form | Non-linear form |
| Pseudo-first order | VAT RED 10 | $k_1 = 1.47 \times 10^{-2} \text{ min}^{-1}$ $q_{eq} = 10.85 \text{ mg/g}$ $R^2 = 89.56\%$ | $k_1 = 2.84 \times 10^{-2} \text{ min}^{-1}$ $q_{eq} = 14.58 \text{ mg/g}$ $R^2 = 96.55\%$ |
| | VAT ORANGE 11 | $k_1 = 1.54 \cdot 10^{-2} \text{ min}^{-1}$ $q_{eq} = 14.11 \text{ mg/g}$ $R^2 = 97.63\%$ | $k_1 = 2.01 \times 10^{-2} \text{ min}^{-1}$ $q_{eq} = 16.48 \text{ mg/g}$ $R^2 = 99.28\%$ |
| Pseudo-second order | VAT RED 10 | $k_2 = 3.47 \times 10^{-3} \text{ min}^{-1}$ $q_{eq} = 15.34 \text{ mg/g}$ $R^2 = 99.97\%$ | $k_2 = 3.36 \times 10^{-3} \text{ min}^{-1}$ $q_{eq} = 15.70 \text{ mg/g}$ $R^2 = 95.12\%$ |
| | VAT ORANGE 11 | $k_2 = 1.24 \times 10^{-3} \text{ min}^{-1}$ $q_{eq} = 19.57 \text{ mg/g}$ $R^2 = 99.70\%$ | $k_2 = 1.70 \times 10^{-3} \text{ min}^{-1}$ $q_{eq} = 18.01 \text{ mg/g}$ $R^2 = 95.32\%$ |

3.2. Dye retention capacity determination

In aqueous solution, vat dyes are insoluble. To obtain the soluble form, the addition of a reduction and basic agents is necessary and then the dye will be transformed to its leuco sodic soluble

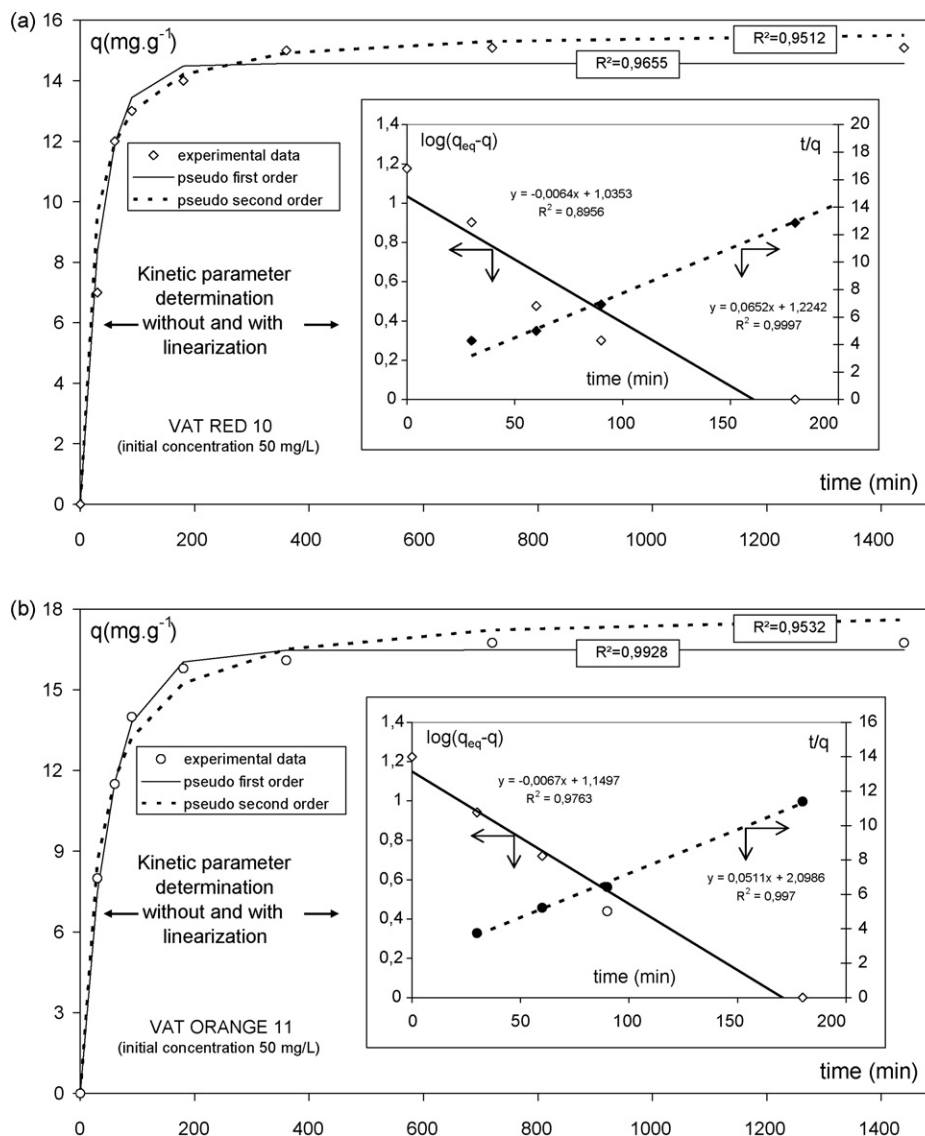


Fig. 6. Kinetic parameter determination with and without linearization for (a) "VAT RED 10" and (b) "VAT ORANGE 11" experimental data.

form $R-C-O^-$, Na^+ . 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 VAT RED 10 and the VAT ORANGE 11 by the difference in the chemical structure 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 86 nm. At minimum steric energy, the maximum molecular distance for the two used dyes ranges between 15 and 20 Å. This means that all the adsorbent pores are accessible to the dyes 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 sites could be occupied. In another hand, the adsorption of organic compounds such as vat dyes on dehydrated sewage sludge particles may be attributed to mineral and organic carbon fraction. The mineral fraction in sludge plays a great part in the adsorption of organic compounds by dipole-cation interactions and coordination bonds between exchangeable cations involved in mineral and organic cations [5]. Much research indicates that the contribution of organic carbon to the sorption of organic chemicals comes mainly from possible binding mechanisms such as the ion exchange of cationic molecules, hydrogen bonds, charge transfers, and London-van der Waals dispersion forces or the hydrophobic effect of hydrophobic molecules. In spite of its reduced specific area ($3.27 \text{ m}^2 \text{ g}^{-1}$) compared to the activated carbon (may reach $1300 \text{ m}^2 \text{ g}^{-1}$) and the relative high steric clogging of the studied dyes, the used adsorbent shows interesting retention capacities. The effectiveness of the observed chemisorption may be attributed to the adsorbent surface state. The acid base titration showed a more pronounced basic state of the adsorbent surface than the acidic sites which, according to the Boehm titration, are mainly carboxylic functional groups. The FT-IR spectra qualitatively confirm this result and it may be concluded that the solvated vat dye as they are schematically represented in Table 4 may establish bond with the negatively charged carboxylic functional groups. The dye/adsorbent interaction is for sure maximum at the external Connolly surface as indicated by the surface charge distribution of the two solvated vat dye molecules. The zeta potential variation vs pH shows that for dye solution with pH value greater than the pH_{pzc} or the IEP the adsorbent surface is negatively charged which is expedient for the establishment of chemisorption bonds. This shows the importance of the adsorbent surface state on the sorption processes.

For the dye retention capacity determination, the Langmuir monolayer model does not fit in an acceptable way the experimental data with both used dyes (R^2 about 0.65). This means that the monolayer coverage adsorption model can not be applied for the used vat dyes with the crude dehydrated sewage sludge adsorbent used here. However, all the other used equilibrium models fit in a satisfactory way the experimental observations. For the used dyes, the best fitting is obtained with Freundlich model (R^2 about 0.98 for the VAT RED 10 and about 0.92 for the VAT ORANGE 11). Multi layer coverage equilibrium model seems to meet the retention mechanism taking place at the adsorbent surface. The Langmuir Freundlich monolayer retention capacity is about 73.1 mg/g for the VAT RED 10 and about 58.7 mg/g for the VAT ORANGE 11. Those retention capacities are comparable to nearly all non-conventional materials with respect to their specific surface area (kudzu, soy meal hull, peat, palm kernel fibre, raw fresh water alga, etc.) and sludge based activated carbons found in many published papers as summarized in Table 7.

Table 6
Isotherm models estimated parameters for the two studied dyes

| Isotherm model | Parameter | VAT RED 10 | VAT ORANGE 11 |
|-------------------------------|--|-----------------------|------------------------|
| Langmuir | q_{\max} (mg/g) | 77.65 | 59.55 |
| | K_L (mg/L) $^{-1}$ | 6.21×10^{-3} | 8.99×10^{-3} |
| | R^2 (%) | 63.40 | 67.64 |
| Freundlich | K_F (mg/g) \times (mg/L) $^{-n}$ | 2.89×10^{-3} | 1.99×10^{-2} |
| | n | 2.68 | 1.92 |
| | R^2 (%) | 98.07 | 92.24 |
| Redlich–Peterson | K_{RP} (mg/g) \times (mg/L) $^{n-1}$ | 1.8×10^{-3} | 109.78 |
| | α_{RP} | -0.98 | 6.32×10^{-5} |
| | n | 6.1×10^{-3} | 2.28 |
| | R^2 (%) | 97.88 | 91.99 |
| Höll-Kirch | q_{\max} (mg/g) | 73.12 | 58.73 |
| | K_{HK} (mg/L) $^{-n}$ | 1.89×10^{-5} | 6.45×10^{-4} |
| | n | 2.97 | 1.79 |
| | R^2 (%) | 97.65 | 85.68 |
| Toth | q_{\max} (mg/g) | 22.00 | 19.83 |
| | α_T | -1.36 | -0.86 |
| | n | -0.26 | -0.17 |
| | R^2 (%) | 98.06 | 91.83 |
| Langmuir–Freundlich two sites | q_{\max} (mg/g) | 154.90 | 135.74 |
| | K_{LF} (mg/L) $^{-n}$ | 5.58×10^{-5} | -5.39×10^{-3} |
| | n | 2.44 | 3.69×10^{-3} |
| | K_p (mg/L) $^{-1}$ | -0.14 | 0.72 |
| | R^2 (%) | 97.44 | 81.36 |

3.3. Modelisation study of the dye adsorption mechanism

The kinetic parameters involved in the pseudo-first and second order model were estimated using both linear and non-linear form. The results of the modelization work are summarized in the Table 5. The Fig. 6a and b gather in the same graph the experimental kinetic data fitted with the two models solved using the linear and non-linear form, and this was done for the two studied vat dyes. Assuming the non-linear form, the obtained outcomes indicate that the retention mechanism is diffusion controlled. The surface sorption step seems to be relatively rapid and not rate controlling in the whole retention process.

The experimental isotherms modelization is made using the most common mathematical adsorption models (Langmuir, Freundlich, Redlich–Peterson, Höll-Kirch, Toth and Langmuir Freundlich two sites). All the models equations are solved in their original form in order to get the most reliable model parameter values. The transformation of non-linear to linear expression distorts the experimental error and also the normality assumptions of the least squares method. A further linear method does not test whether the experimental data are linear. It assumes the experimental data were linear and predicts the slope and intercept that makes a straight line that predicts the best-fit of experimental equilibrium data. The non-linear method, based on a trial and error procedure, was used to determine the isotherm parameters by minimizing the R^2 coefficient of correlation between experimental data and isotherms. The obtained results are summarized in Table 6. Fig. 7a and b 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 and Höll-Kirch models gave approximately the same curves. The best fit was obtained using the Freundlich model. The retention mechanism seems to meet a multilayer coverage one. The structure of the used adsorbent is dead cells-based, and the surface in contact with dye solutions is negatively charged. This structure is complex, and the different analysis proceeded in this work revealed the presence of minerals, acidic/basic sites and a variety of organic functional

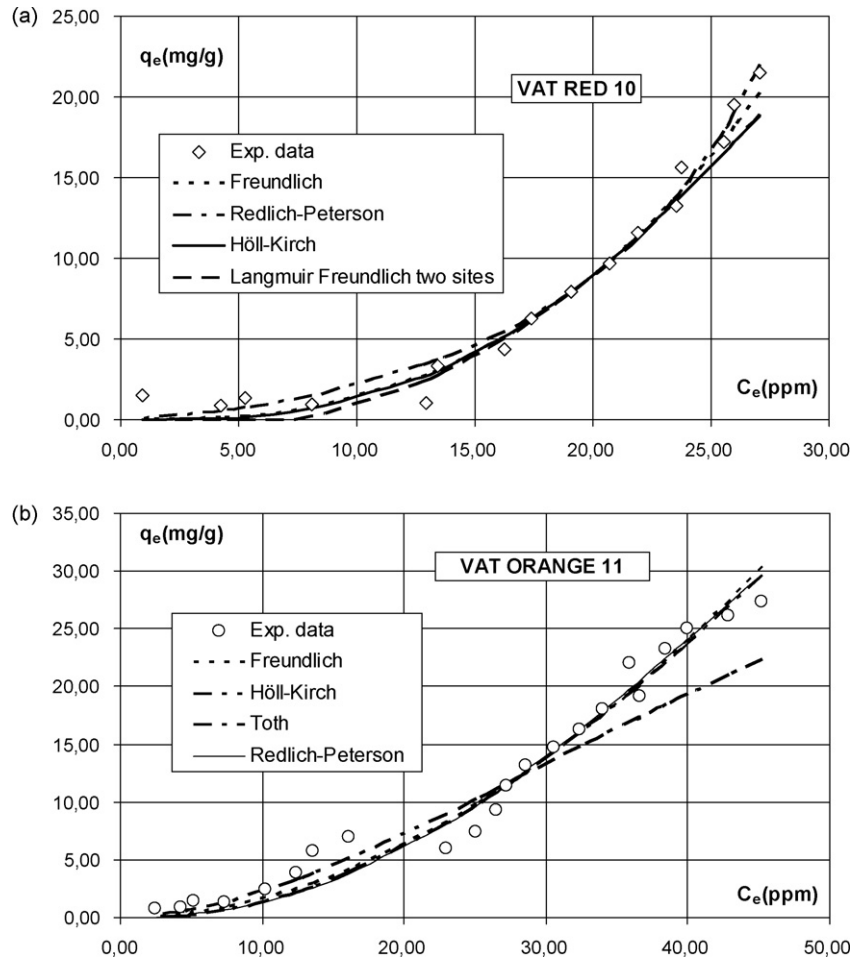


Fig. 7. Applied adsorption models for (a) "VAT RED 10" and (b) "VAT ORANGE 11" experimental isotherm.

groups. The heterogeneity of the adsorbent surface's active sites is in accordance with the adsorption model, Freundlich, which is the most suitable to describe adsorption process over heterogeneous surface. Physical adsorption and chemisorption may be indistinguishable in certain situations, and in some cases a degree of both types of bonding can be present, as with covalent bonds between two atoms having some degree of ionic character and vice versa. Although dyes are considered to be organic compounds, vat dyes ionize in solution to leuco acid/sodic form. The removal of vat dye in its leuco acid form may be also due to the formation of Si, Ca or Na⁺ chelate with the -OH groups present on the dye molecule [4]. A quick survey of the best fitting adsorption models when non-conventional adsorbents are used shows that mostly Freundlich model is used (Table 7) or models that do not follow ideal monolayer adsorption.

For the modelling work, the MODEST[®] software was used to fit the model parameters to the isotherm data. The first cri-

teria retained for the fitting job was that the fitted maximum adsorbate concentration should not be smaller than the maximum value derived from experiments. The second one was the sum of residual squares. The most common methods according to which the parameters are estimated are the average relative error deviation (ARED), the sum of the squares of the errors (SSE), the Marquardt's percent standard deviation (MPSD), etc. In this work, a hybrid method combining ARED and SSE function is used. The main advantage of this error function is the minimization of the fractional error distribution across the entire studied concentration range. The fit appreciation is assessed by the coefficient of determination R^2 which is given by the expression:

$$R^2 = 100 \left(1 - \frac{\|q_{\text{exp}} - q_{\text{mod}}\|^2}{\|q_{\text{exp}} - q_{\text{avr}}\|^2} \right)$$

Table 7
Surface area and retention capacity of some low cost adsorbents

| Adsorbent | Surface area (m ² g ⁻¹) | Dye type | Best fitting model | Retention capacity (mg/g) | Reference |
|---|--|-------------|-------------------------------|---------------------------|-----------|
| Kudzu | 10 | Basic | Not specified | 150–210 | [29] |
| Soy meal hull | 0.7623 | Direct/acid | Freundlich (for acid red 14) | 100–180 | [30] |
| Peat | 32 | Basic | Redlich–Peterson | 200–600 | [31] |
| <i>Chlorella vulgaris</i> (green algae) | Not specified | Reactive | Koble–Corrigan and Freundlich | 420 | [32] |
| Crude dehydrated sewage sludge | 3.27 | Vat | Freundlich | 60–75 | This work |
| Dried sewage sludge | Not specified | Basic | Langmuir and Freundlich | 115 | [9] |
| Activated sewage sludge | Not specified | Basic | Freundlich | 25 | [9] |

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

3.4. Sensitivity analysis

For the non-linear form isotherm models used in this work a sensitivity analysis based on the contour plots methods was performed. The visualization is provided right after the calculation using MATLAB® software. A FORTRAN program is used which links

MODEST sensitivity calculations and the contour plots as it can be seen in Fig. 8. The two dimensional contour plots appear when two parameters are simultaneously changed, the others being kept at their optimum value. The sensitivity analysis allows the identification of the most critical parameter in each used model and where the most improvement has to be focused for its determination. This sensitivity analysis was performed for the Redlich–Peterson model parameters. By plotting the contour lines with varying parameters intervals for the R^2 values of the fit, it was found that no crucial intercorrelations exist. Therefore, the identifiability of the three Redlich–Peterson parameters proved to be good and precise. However it is apparent at a glance that the most influential parameter is α_{RP} and its determination being precise. Redlich–Peterson equilibrium model is more sensible to α_{RP} variation than n parameter which is in turn very much more influential than K_{RP} parameter. The same analysis using the contour curves was performed for the entire used model parameters fitted with the VAT RED 10 experimental data. For all the other used models, no crucial intercorrelation exists and also the parameters identifiability presented to be good. For Langmuir model, q_{max} parameter is more influential than K_L and its determination has to be as precise as possible. For Freundlich model n parameter is much more influential than K_F . For Höll–Kirch, Toth and Langmuir–Freundlich two sites models, n parameter is by far the most influential parameter, whereas for respectively K_{HK} , q_{max} and K_p the models have practically no sensitivity to their variations around the found optimum values.

4. Conclusion

Investigating the sorption properties of vat dyes using a crude material has been one of the main objectives of the present work. The decolorization of two synthetic textile wastewater using crude dehydrated sewage sludge as an adsorbent is studied in batch system. It was found that the used material has good dye retention capacity. This retention capacity varies from 60 to 75 mg/g according to the used equilibrium model and its affinity to retain the vat dyes seems to be good. The negatively surface charge distribution measured with zeta potential and the presence of charged acidic carboxylic groups seems to promote the vat dye chemisorption over the adsorbent surface. It may be concluded that the crude dehydrated sewage sludge, in fact waste of waste, and in spite of its low specific surface area, has undoubtedly a real potential to remove and retain large amounts of different vat dyes. This process could be adopted as an efficient approach for industrial effluent decolorization and it may be an alternative to more costly materials such as activated carbons. This work indicates that the locally available and abundant dehydrated sewage sludge could be employed as a low-cost, natural and plentiful source for the removal of many vat dyes from textile mill effluents. Several equilibrium non-linear models have been applied to fit the experimental data within the studied dye concentration range. With the exception of Langmuir model, all the other models acceptably fitted the experimental data. It has also been found that the retention kinetic is better described by the pseudo-second order linear model suggesting that chemisorption might be the rate-limiting step that controls the adsorption process. Further works should be carried out to investigate the level of pollutants desorbed from the used material. The effect of salt presence and binary retention tests should also be carried out to highlight the competition effects.

References

- [1] R.W. Martin Jr., C.R. Baillod, J.R. Mihelcic, Low-temperature inhibition of the activated sludge process by an industrial discharge containing the azo dye acid black 1, Water Research 39 (2005) 17–28.

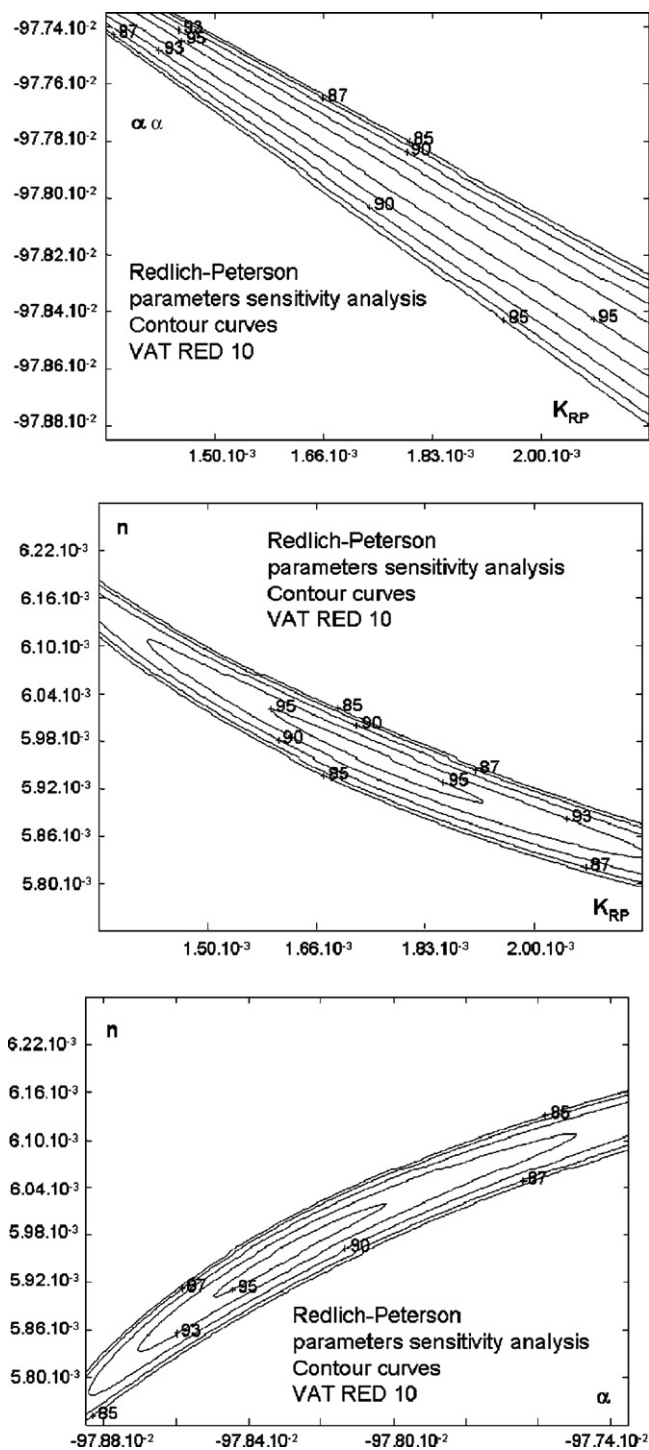


Fig. 8. Contour curves sensitivity analysis of Redlich–Peterson adsorption model (VAT RED 10).

- [2] S. Sirianuntapiboon, K. Chairattananwan, S. Jungphungsukpanich, Some properties of a sequencing batch reactor system for removal of vat dyes, *Bioresource Technology* 97 (10) (2006) 1243–1252.
- [3] F. Rozada, M. Otero, A.I. Garcia, A. Moran, Application in fixed-bed systems of adsorbents obtained from sewage sludge and discarded tyres, *Dyes and Pigments* 72 (2007) 47–56.
- [4] A. Mishra, M. Bajpai, The flocculation performance of *Tamarindus mucilage* in relation to removal of vat and direct dyes, *Bioresource Technology* 97 (8) (2006) 1055–1059.
- [5] R. Liu, X. Liu, H. Tang, Y. Su, Sorption Behavior of dye compounds onto natural sediment of Qinghe River, *Journal of Colloid and Interface Science* 239 (2) (2001) 475–482.
- [6] C. Jindarom, V. Meeyoo, B. Kitiyanan, T. Rirksomboon, P. Rangsunvigit, Surface characterization and dye adsorptive capacities of char obtained from pyrolysis/gasification of sewage sludge, *Chemical Engineering Journal* 133 (2007) 239–246.
- [7] M.J. Martin, A. Artola, M.D. Balaguer, M. Rigola, Activated carbons developed from surplus sewage sludge for the removal of dyes from dilute aqueous solutions, *Chemical Engineering Journal* 94 (2003) 231–239.
- [8] F. Rozada, L.F. Calvo, A.I. Garcia, J. Martin-Villacorta, M. Otero, Dye adsorption by sewage sludge-based activated carbons in batch and fixed-bed systems, *Bioresource Technology* 87 (2003) 221–230.
- [9] M. Otero, F. Rozada, L.F. Calvo, A.I. Garcia, A. Moran, Kinetic and equilibrium modelling of the methylene blue removal from solution by adsorbent materials produced from sewage sludges, *Biochemical Engineering Journal* 15 (2003) 59–68.
- [10] X. Fan, X. Zhang, Adsorption properties of activated carbon from sewage sludge to alkaline-black, *Materials Letters* 62 (2008) 1704–1706.
- [11] V. Golob, A. Ojstrsek, Removal of vat and disperse dyes from residual pad liquors, *Dyes and Pigments* 64 (1) (2005) 57–61.
- [12] B. Manu, S. Chaudhari, Decolorization of indigo and azo dyes in semicontinuous reactors with long hydraulic retention time, *Process Biochemistry* 38 (8) (2003) 1213–1221.
- [13] D.S.L. Balan, R.T.R. Monteiro, Decolorization of textile indigo dye by ligninolytic fungi, *Journal of Biotechnology* 89 (2–3) (2001) 141–145.
- [14] X.R. Xu, H.B. Li, W.H. Wang, J.D. Gu, Degradation of dyes in aqueous solutions by the Fenton process, *Chemosphere* 57 (7) (2004) 595–600.
- [15] R. Liu, H.M. Chiu, C.S. Shiau, R.Y.L. Yeh, Y.T. Hung, Degradation and sludge production of textile dyes by Fenton and photo-Fenton processes, *Dyes and Pigments* 73 (1) (2007) 1–6.
- [16] C.T.M.J. Frijters, R.H. Vos, G. Scheffer, R. Mulder, Decolorizing and detoxifying textile wastewater, containing both soluble and insoluble dyes, in a full scale combined anaerobic/aerobic system, *Water Research* 40 (6) (2006) 1249–1257.
- [17] K. Vasanth Kumar, Linear and non-linear regression analysis for the sorption kinetics of methylene blue onto activated carbon, *Journal of Hazardous Materials B137* (2006) 1538–1544.
- [18] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, *Process Biochemistry* 34 (1999) 451–465.
- [19] K. Vasanth Kumar, Pseudo-second order models for the adsorption of safranin onto activated carbon: Comparison of linear and non-linear regression methods, *Journal of Hazardous Materials* 142 (2007) 564–567.
- [20] K. Vasanth Kumar, S. Sivanesan, Pseudo second order kinetics and pseudo isotherms for malachite green onto activated carbon: Comparison of linear and non-linear regression methods, *Journal of Hazardous Materials B136* (2006) 721–726.
- [21] K. Vasanth Kumar, K. Porkodi, F. Rocha, Isotherms and thermodynamics by linear and non-linear regression analysis for the sorption of methylene blue onto activated carbon: comparison of various error functions, *Journal of Hazardous Materials* 151 (2008) 794–804.
- [22] K. Vasanth Kumar, S. Sivanesan, Isotherm parameters for basic dyes onto activated carbon: Comparison of linear and non-linear method, *Journal of Hazardous Materials B129* (2006) 147–150.
- [23] K. Vasanth Kumar, K. Porkodi, F. Rocha, Comparison of various error functions in predicting the optimum isotherm by linear and non-linear regression analysis for the sorption of basic red 9 by activated carbon, *Journal of Hazardous Materials* 150 (2008) 158–165.
- [24] K. Vasanth Kumar, S. Sivanesan, Comparison of linear and non-linear method in estimating the sorption isotherm parameters for safranin onto activated carbon, *Journal of Hazardous Materials B123* (2005) 288–292.
- [25] H.P. Boehm, Surface oxides on carbon and their analysis: a critical assessment, *Carbon* 40 (2002) 145–149.
- [26] A. Contescu, C. Contescu, K. Putyra, J.A. Schwarz, Surface acidity of carbons characterized by their continuous pK distribution and Boehm titration, *Carbon* 35 (1997) 83–94.
- [27] H.P. Boehm, Some aspects of the surface chemistry of carbon blacks and other carbons, *Carbon* 32 (1994) 759–769.
- [28] K. Laszlo, K. Josepovits, E. Tombacz, Analysis of active sites on synthetic carbon surfaces by various methods, *Analytical Sciences* 17 (2001) 1741–1744.
- [29] S.J. Allen, Q. Gan, R. Matthews, P.A. Johnson, Kinetic modeling of the adsorption of basic dyes by kudzu, *Journal of Colloid and Interface Science* 286 (2005) 101–109.
- [30] M. Arami, N.Y. Limaee, N.M. Mahmoodi, N.S. Tabrizi, Equilibrium and kinetics studies for the adsorption of direct and acid dyes from aqueous solution by soy meal hull, *Journal of Hazardous Materials* 135 (2006) 171–179.
- [31] S.J. Allen, G. McKay, J.F. Porter, Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems, *Journal of Colloid and Interface Science* 280 (2004) 322–333.
- [32] Z. Aksu, S. Tezer, Biosorption of reactive dyes on the green alga *Chlorella vulgaris*, *Process Biochemistry* 40 (2005) 1347–1361.