Sorption of indigo carmine by a Fe-zeolitic tuff and carbonaceous material from pyrolyzed sewage sludge

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ABSTRACT

Indigo carmine removal from aqueous solution has been evaluated using Fe-zeolitic tuff and carbonaceous material from pyrolyzed sewage sludge treated with HCl (CM). The adsorbents were characterized by scanning electron microscopy, BET surface area and X-ray diffraction. Sorption kinetics and isotherms were determined and the adsorption behaviors analyzed. Kinetic pseudo-second order and Langmuir–Freundlich models were successfully applied to the experimental results obtained with the Fe-zeolitic material, while kinetic first order and Langmuir–Freundlich models were applied to the results from the carbonaceous materials. This indicates mechanisms of chemisorption and physic sorption, respectively, on the heterogeneous materials. The results indicate that the carbonaceous material from the pyrolysis of sewage sludge (sorption capacity 92.83 mg/g) is a better adsorbent of indigo carmine than the zeolitic material (sorption capacity 32.83 mg/g).

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1. Introduction

Textile industries consume large volumes of water and chemicals and generate large volumes of wastewater. Color is one of the greatest contaminants in wastewater, as it is highly visible and undesirable. Color contamination causes considerable environmental pollution because it absorbs and reflects sunlight entering the water, which interferes with the growth of bacteria, impedes photosynthesis in aquatic plants [1], and raises the chemical oxygen demand (COD) of the effluent [2].

Although the exact amount of dye produced in the world is not known, there are estimated to be more than 100,000 commercially available dyes with over 7×10^5 tons of dye produced annually [2]. It has been reported that 2% of dyes produced annually are discharged in effluent from manufacturing operations, while 10% are discharged from textile and associated industries [3].

Vat dyes are mainly used in the textile industry, especially indigo blue (vat blue 1) and indigo carmine, which are used in the dyeing of polyester fibers and denim. Unfortunately, 30% of applied dyes remain unfixed and end up in the effluent [4]. Moreover, indigo carmine is used in food industry (typical products include milk desserts, sweets, biscuits), cosmetics industries, as a diagnostic aid (e.g., in kidney function tests) and it has also been employed as redox indicator in analytical chemistry and as a microscopic stain in biology. Indigo carmine is also used as a photometric detector [5]. However, indigo carmine is considered a highly toxic indigoid class of dye and its touch can cause skin and eye irritations to human beings. It can also cause permanent injury to cornea and conjunctiva. The consumption of the dye can also prove fatal, as it is carcinogenic in nature and can lead to reproductive, developmental, neuro and acute toxicity. It has also been established that the dye leads to tumors at the site of application [6,7]. Indigo carmine causes irritation to the gastrointestinal tract leading to nausea, vomiting and diarrhea. It may also cause irritation to the respiratory tract. Symptoms may include coughing and shortness of breath [5].

In general, dyes have complex chemical structures and are resistant to biological degradation. There are various methods available for the removal of dyes, including membrane-separation, electrochemical, flocculation–coagulation, reverse osmosis, ozone oxidation, biological treatments, sorption, etc. [1].

Roessler and Crettenand [8] investigated the electrochemical reduction of several vat dyes on graphite granules to produce leuco dyes by increasing the solubility of the dyes to promote a more efficient reduction. Bio-sludge from wastewater treatment plants that is treated with NaOH 0.1N solution has the potential to adsorb vat dyes from synthetic solutions, depending on the bio-sludge adsorption capacity and the type of dye (chemical structure) [9].

Manu [4] studied the removal of indigo blue from synthetic solutions using $FeSO_4$, alum and lime and color removals of 95%, 97% and 97%, respectively, were reported when an initial dye concentration of up to 2000 mg/L was used. While these methods are used as primary treatments, adsorption processes are a more economi-

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cally feasible, alternative method for removing low concentrations of dyes.

Indigo carmine removal from aqueous solutions has been studied using cross-linked chitosan [10]; the results indicated that increasing the chitosan mass from 100 to 300 mg decreases the adsorption of indigo carmine whereas increasing the temperature from 25 to 35 °C increases the removal capacity.

Nowadays, the search for low-cost and easily available adsorbents appears to be increasing.

Numerous studies have demonstrated the effectiveness of the minerals in the recovery of metals [11,12]. A dump bioleaching plant was designed to extract copper metal from the waste dump of a copper mine and resolve the environmental problems caused by acidic water and heavy metals [13].

Clinoptilolite is one the most abundant forms of zeolitic minerals and has the chemical formula, $(Na_2,K_2,Ca)_3Al_6Si_{30}O_{72}\cdot24H_2O$. It has been applied as an ion exchanger for the removal of heavy metals from water [14–16], while surfactant-modified clinoptilolite has been used for the removal of organic compounds and dyes from aqueous solutions. The removal of remazol yellow was studied [17] using HDTMA (hexadecyltrimethyl ammonium) modified clinoptilolite-rich tuff as the adsorbent. The regeneration of the saturated modified zeolitic tuff was accomplished using Fenton's solution, and it was observed that the regenerated clinoptilolite-rich tuff had greater sorption capacity than the original surfactant-modified zeolite. Some studies have reported the degradation of phenol in aqueous solutions using Fe-exchanged zeolite in Fenton-type catalysis [18].

Alternatively, sewage sludges are produced in considerable amounts by wastewater treatment plants, and these materials are disposed of through landfills, forestry, sea dumping, and applications to agriculture and incineration. Although there are several ways to dispose of sewage sludges, it is better still to make use of these waste materials by turning them into a resource. Farmland application of sewage sludges is no longer a viable solution because the sludges are composed largely of the substances responsible for the offensive, pathogenic and toxic characteristics of the untreated wastewater. Ocean dumping of sewage sludge is also now forbidden. As such, incineration has become the accepted method of disposal; it reduces the volume of waste, but it has gaseous emissions. Another alternative method for the disposal of sewage sludge is pyrolysis—a thermal treatment in anoxic atmosphere that can be used to obtain reusable byproducts. Previous studies have demonstrated the possibility of using pyrolyzed sewage sludges as adsorbents for organic pollutants [19] like dyes (remazol yellow) [17] and heavy metals, such as copper [20], mercury [21], cadmium and lead [22]. This adsorbent may offer both a management option for sewage sludges and also low-cost adsorbent. Therefore, the purpose of this paper was to investigate the possibility of utilizing Fe-zeolitic tuff for the adsorption of indigo carmine using batch sorption system and to compare its efficiency with carbonaceous material obtained from the pyrolysis of sewage sludge, although different sorbents have been used for the removal of dyes, Fe-zeolitic materials have not been investigated before to remove dyes from aqueous solutions.

2. Materials and methods

2.1. Fe-zeolitic tuff (ZM)

The clinoptilolite-rich tuff from Villa de Reyes, San Luis Potosí, Mexico was milled and sieved. The grain size used in this work was between 0.8 and 1.0 mm. The zeolitic material was treated with a solution of sodium chloride and refluxed (50 g of material with 250 mL of 0.125 M NaCl). This procedure was repeated four times.
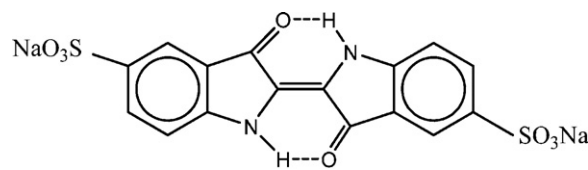

Fig. 1. Chemical structure of indigo carmine.

After, the zeolitic material was washed with distilled water until no presence of chloride ions was indicated in the washing solution using an $AgNO_3$ test. The sodium-treated zeolitic tuff was then dried at 333 K for 2 h.

Fe-zeolitic tuff was prepared by mixing 50 g of the sodium-zeolitic tuff with 250 mL of 0.08 M $FeCl_3\cdot6H_2O$ solution. This procedure was carried out twice, in the same way as above. Then, the Fe-zeolitic tuff was dried at 333 K for 2 h.

2.2. Carbonaceous material (CM)

The carbonaceous material was obtained from industrial sewage sludge. The sludge feed-stock and the pyrolysis procedure have been described elsewhere [17]. The pyrolysis of the sludge was performed at 500 °C for 60 min. Later, the samples were milled and sieved, and grains with diameters between 0.42 and 0.84 mm were selected. The carbonaceous material was then treated with 10% hydrochloric acid solution at 20 °C for 8 h. After, it was washed five times with distilled water and dried at 100 °C for 2 h.

2.3. Indigo carmine dye

In this study, indigo carmine (5,5-indigosulfonic acid, acid blue 74), was obtained as a commercial dye (denim blue) from Mariposa colorants®. As shown in Fig. 1, indigo carmine has two sulfonate groups. The general characteristics of this dye are: molar mass = 466.35 g/mol, color index number = 73015, and maximum light absorption at λ_{max} = 586.5 nm.

2.4. Characterization

2.4.1. IR spectroscopy

IR spectra in the $4000-400\,cm^{-1}$ range were recorded for the dye and the adsorbents treated with it, at room temperature using a Nicolet Magna IRTM 550 FTIR. Samples were prepared using the standard KBr pellet method.

2.4.2. Scanning electron microscopy

For scanning electron microscopy (SEM) observations, the Fe-zeolitic tuff and carbonaceous samples before and after indigo carmine sorption were mounted directly on the holders and then observed at 20 kV in a JEOL JSM-5900-LD electron microscope. The microanalysis was done with an EDS (Energy X-ray Dispersive Spectroscopy) system.

2.4.3. Surface areas, BET (S_{BET})

The BET specific surface areas were determined by standard multipoint techniques of nitrogen adsorption, using a Micromeritics Gemini 2360 instrument. The samples were heated at 373 K for 2 h before specific surface areas were measured.

2.4.4. Thermogravimetric analysis

Thermogravimetric analyses were carried out with a TGA 51 TA Instrument Thermogravimetric Analyzer (New Castle, DE, USA), which was operated in a nitrogen atmosphere with a heating rate of 10 K/min, from 293 to 1073 K.
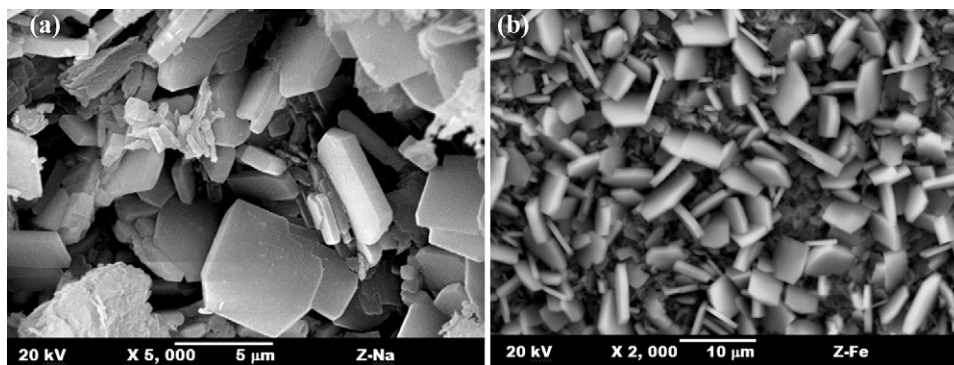
Fig. 2. Scanning electron micrograph of Na-zeolitic tuff (a) and Fe-zeolitic tuff (b).

2.5. X-ray diffraction (XRD)

Powder diffractograms of the zeolitic samples were obtained with a Siemens D500 diffractometer coupled to a copper anode X-ray tube. The conventional diffractograms were used to identify the compounds and to verify crystalline structure and were compared with clinoptilolite patron (JCPDS 039-1383) and quartz (JCPDS 33-1161).

2.6. Sorption kinetics

Kinetic removal of indigo carmine dye by the Fe-zeolitic tuff or carbonaceous material was performed as follows: 100 mg of each adsorbent and 10 mL aliquots of a 200 mg/L solution (pH 6.5) were placed in centrifuge tubes and shaken for different time periods (5, 15 and 30 min, 1, 3, 5, 7, 24, 48 and 72 h) at 120 rpm in a shaker at 30 °C. After the samples were centrifuged and decanted, the experiments were performed in duplicate. The indigo carmine dye concentrations in the solutions were determined using a UV/Vis Perking Elmer Lambda 10 ultraviolet–visible spectrophotometer analyzer, with $\lambda = 586.5$ nm. The pH of each solution was measured before and after the treatments.

2.7. Sorption isotherms

One hundred milligrams of samples of Fe-zeolitic tuff were put in contact with 10 mL each of different concentrations of indigo carmine dye solution (20, 40, 60, 80, 100, 120, 140, 160, 180 and 200 mg/L) for 40 h at 30 °C. Sorption isotherms of the carbonaceous material were carried out by mixing 100 mg of the sample with 10 mL each of dye solutions at different concentrations (100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 mg/L) the experiments were performed in duplicate. Later, the samples were centrifuged and decanted. Dye concentrations were determined in the liquid phases as described above and the pH was measured in each solution.

2.8. Effect of pH

In order to check the effect of pH on indigo carmine uptake by the Fe-zeolitic tuff and the carbonaceous material, experiments were carried out with 10 mL of a 200 mg/L solution of indigo carmine and 100 mg of each sorbent. The initial pH values were adjusted by adding 0.1 M HCl or NaOH to solutions. The pH of each solution was measured periodically with a pH STAT Controller MeterLab PHM 290 pH meter and was kept constant until equilibrium was reached the experiments were performed in duplicate.

2.9. Effect on adsorbent dosage

Experiments were done with different amounts of each sorbent (10, 20, 30, 40, 60, 70, 90, 120, 150, 170 and 200 mg) and 10 mL of a dye solution (200 mg/L) at pH 6.5. The mixtures were shaken until equilibrium was reached the experiments were performed in duplicate.

3. Results

3.1. Pyrolysis

The carbonaceous material obtained from the fraction of the sewage sludge was $52 \pm 0.111\%$ and the carbon content in the sample after treatment with 10% HCl solution was $52.85 \pm 4.21\%$, which is higher than the value (43.83%), reported in the literature for carbonaceous material treated with 1% HCl solution [17]. This treatment increased the amount of carbon and, consequently, the sorption characteristics of the carbonaceous material.

3.2. Characterization

3.2.1. Infrared of indigo carmine

Indigo carmine is a soluble derivative of indigo blue dye. The IR spectrum of indigo carmine shows a number of absorption peaks in the region from 1290 to 1630 cm^{-1}; those peaks correspond to the following vibrations: C–C, C–H and N–H of the indigoid dyes. The O–H and N–H aromatic peaks are found in the 3500–3200 cm^{-1} region [23].

3.2.2. Scanning electron microscopy

3.2.2.1. Fe-zeolitic tuff. Fig. 2a shows the typical morphology of sedimentary, clinoptilolite-rich tuffs [24] with coffin and cubic-like crystals of the sodium-zeolitic tuff. Fig. 2b shows the morphology of the Fe-zeolitic tuff, the different shapes of surface crystal faces along with their imperfections are shown. The typical morphology of the crystals is better observed in the sodium-zeolitic tuff. Trgo and Perić [25] showed that the amphoteric nature of hydroxyl surface groups [=(Al/Si)–OH] can lead to the formation of sites with different energies, such that this mechanical effect increases the number of possible adsorption locations. The chemical compositions of the sodium and Fe-zeolitic tuff are presented in Table 1. The main elements, Si, Al, and O, corresponding to aluminosilicates, were identified. The Na content diminished when the material was treated with FeCl$_3$·6H$_2$O, and this behavior indicates that sodium was replaced in the material by Fe, since the content of this element was higher in the Fe-zeolitic tuff than in the sodium-zeolitic tuff. As a result, it may induce oxidation processes [26]. The external cation exchange capacity has been reported in previous research [27].

Table 1
Elemental analysis of the Na-zeolitic tuff (Na-Z), Fe-zeolitic tuff (Fe-Z), carbonaceous material (CM) and carbonaceous material treated with HCl (CM/HCl) adsorbents by EDS.

Element	Weight percent Na-Z	Weight percent Fe-Z	Element	Weight percent CM	Weight percent CM/HCl
O	46.73 ± 1.89	40.61 ± 2.42	C	41.4 ± 2.3	52.85 ± 4.21
Na	1.65 ± 0.25	0.45 ± 0.16	O	27.4 ± 1.2	21.97 ± 3.38
Al	9.24 ± 2.97	6.64 ± 0.83	Na	1.3 ± 0.2	0.26 ± 0.09
Si	37.59 ± 2.79	36.61 ± 1.22	Mg	0.6 ± 0.1	0.16 ± 0.14
Cl	–	0.66 ± 0.21	Al	2.1 ± 0.1	5.33 ± 2.62
K	3.35 ± 0.42	3.78 ± 0.51	Si	7.8 ± 0.5	11.16 ± 0.87
Ca	0.72 ± 0.05	0.67 ± 0.11	P	1.4 ± 0.1	1.84 ± 0.84
Fe	0.72 ± 0.12	10.57 ± 4.07	S	1.0 ± 0.1	0.76 ± 0.08
			Cl	0.9 ± 0.1	0.35 ± 0.02
			K	1.0 ± 0.2	0.51 ± 0.04
			Ca	12.8 ± 2.1	2.22 ± 0.41
			Ti	0.2 ± 0.1	0.26 ± 0.05
			Cr	0.3	0.22 ± 0.04
			Fe	1.1 ± 0.3	2.13 ± 0.37
			Zn	0.6 ± 0.4	–

3.2.2.2. Carbonaceous material. Fig. 3 shows the morphology of the carbonaceous material, which corresponds to the morphology reported elsewhere [20]. The elemental composition (Table 1) shows that the carbon content increased to 52.8% after the sample was treated with a 10% HCl solution. The amount of some elements (Na, Mg, K, Ca) diminished after treating the material with this solution, and this was expected since the ashes should be removed with an acid solution. Other chemical elements (such as oxygen, which contributes to the acidity of the carbon) are also present in the sample and they may be important in the sorption processes [22]. The acidic carbon has a net negative charge and promotes the adsorption between the active adsorbent sites and the dye molecules.

3.2.3. Specific surface area

The BET specific surface areas for the untreated, sodium and Fe-exchanged zeolitic samples were 21.2, 22.5 and 63.4 m^2/g, respectively. It was observed that the specific surface area increased when the sample was treated with iron chloride. This suggests the presence of non-crystalline Fe formations located in cationic positions in the mineral channels and iron complexes in extra-framework positions, which makes the material more amorphous [26]. The specific surface area of carbonaceous material was 100.0 m^2/g, which is lower than the values reported in the literature for this kind of material [17]. The particle size for both materials was 0.84 mm.

3.2.4. Thermogravimetric analyses

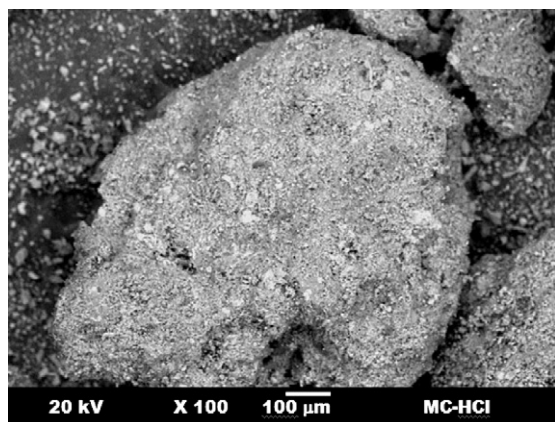The thermogravimetric analyses for indigo carmine and sorbents were performed. The TG thermogram for indigo carmine showed a weight loss of about 2% between 300 and 500 °C and it decomposed after 700 °C. In the cases of untreated, sodium and Fe-zeolitic samples, the weight loss was complete at almost 600 °C, and the maximum weight loss was 10%. After contact with indigo carmine, the Fe-zeolitic tuff showed a gradual weight loss up to 300 °C, with a maximum loss of 9.2%. The initial weight lost up to 200 °C can be attributed to weakly bound water and between 250 and 600 °C to dehydroxylation of the material [26].

On the contrary, the samples of carbonaceous material treated with 10% HCl solution before and after contact with indigo carmine showed a gradual initial weight lost up to 100 °C, attributed to the volatilization of H$_2$O and CO$_2$. Between 400 and 800 °C there was a weight loss of 25%, which was attributed to the decomposition of organic matter [20]. For this reason, the pyrolysis temperature was fixed at 500 ± 50 °C. It was observed that the weight lost for the Fe-zeolitic tuff was smaller than for the carbonaceous material.

3.2.5. X-ray diffraction (XRD)

The X-ray powder diffraction pattern of the Fe-zeolitic tuff saturated with indigo carmine is shown in Fig. 4. The diffractogram was compared with clinoptilolite (JCPDS 039-1383) and quartz (JCPDS 33-1161), which were the principal components found in the zeolitic samples. No clay minerals were observed. These results suggest there were not any notable changes in structure of clinoptilolite after it was treated with sodium chloride and iron chloride solutions.
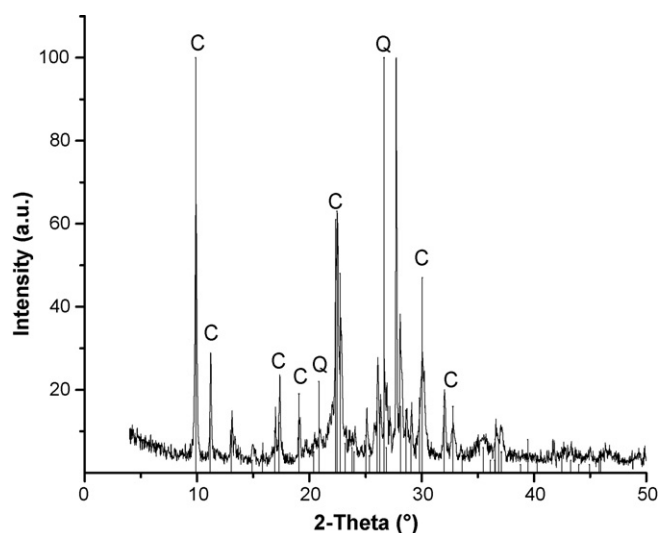

Fig. 3. Scanning electron micrograph of carbonaceous material from pyrolyzed sewage sludge.

Fig. 4. X-ray powder diffraction pattern of the Fe-clinoptilolite. C, clinoptilolite; Q, quartz.

Table 2
Kinetic parameters of indigo carmine sorption by Fe-zeolitic tuff and carbonaceous material adsorbent.

Material	Kinetic models								
	First order			Second order			Pseudo-second order		
	q_e (mg/g)	K_L (h^{-1})	r	a (mg/g)	b (mg/g)	r	q_e (mg/g)	K (g/mg h)	r
Fe-Z	13.51	0.08	0.974	13.53	0.36	0.947	18.18	0.010	0.993
CM	16.14	0.06	0.992	10.46	0.38	0.898	18.69	0.006	0.966

3.3. Sorption kinetics

The sorption kinetics, as expressed in terms of the rate of uptake of solute (which governs the residence time), is one of the important considerations for economical wastewater treatment applications [28]. Fig. 5 shows the relationship between contact time and the sorption capacities of sorbents. According to the figure, equilibrium was reached in about 40 h for both materials. It was observed as well that the adsorption rate was slightly higher for the zeolitic tuff than for the carbonaceous material. In the case of Fe-zeolitic tuff, the equilibrium pH decreased immediately to 3.2 and in the case of carbonaceous material, the pH was about 7.0 and did not change.

Several kinetic models were applied to the experimental data of the sorption of indigo carmine by Fe-zeolitic tuff and carbonaceous material. The feature constants of sorption were obtained by using a pseudo-first order model, second order model and pseudo-second order model. The sorption behavior of the dye was analyzed using both linear and non-linear regressions. The linear equations showed the highest correlation; therefore, they were chosen to describe the sorption process.

3.3.1. Pseudo-first order model (Lagergren)

In this model, which is commonly used for homogeneous sorbents and physical sorption, the sorption rate is proportional to the solute concentration. If the sorption behavior is first order, then the experimental results could be adjusted to the following equation:

$$q_t = q_e(1 - e^{K_L t})$$

with the linear form being:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_L t}{2.303}$$

where q_t and q_e are the amounts of adsorbed dye (mg/g) in the equilibrium and at time t (h), respectively, and K_L (h^{-1}) is the sorption constant of Lagergren. The linear plots of $\log(q_e - q_t)$ vs. t show the applicability of the Lagergren equation for both adsorbents [29]. K_L, q_e and their respective correlations are shown in Table 2. The
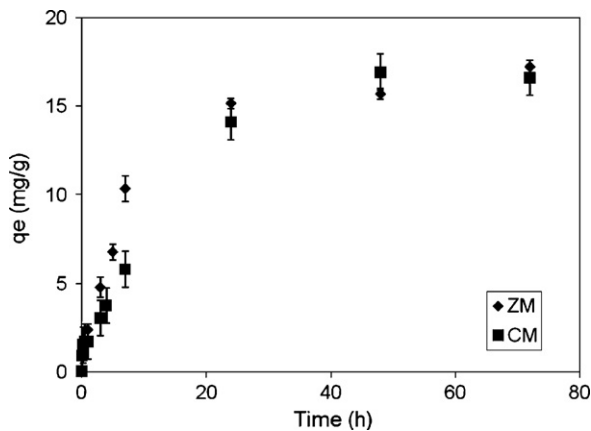

Fig. 5. Sorption kinetics of indigo carmine by Fe-zeolitic tuff and carbonaceous material adsorbents.

sorption capacity (q_e) is similar for both sorbents, while the kinetic constant (K_L) of the Fe-zeolitic tuff is higher than for carbonaceous material and the correlation coefficient for the Fe-zeolitic tuff is higher as well. This behavior could indicate that the carbonaceous material is more heterogeneous than the zeolitic samples.

3.3.2. Second order model (Elovich)

This model has been used suitably in chemisorptions on highly heterogeneous materials [30] and is represented by the following equation:

$$q_t = \frac{1}{b}(1 - abt)$$

with the linear form being:

$$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}t$$

where q_t is the amount of adsorbed dye at time t, a is the sorption constant of the dye (mg/g) and b is the desorption constant (mg/g). Thus, the constant can be obtained from the slope and intercept of the linear plot of q_t vs. $\ln(t)$. Table 2 shows the kinetic constants obtained for this model. The sorption constant (a) of carbonaceous material was higher than the sorption constant of Fe-zeolitic tuff and the obtained desorption constant (b) was similar for both sorbents.

3.3.3. Pseudo-second order model

The pseudo-second order model proposed by Ho and McKay [31] is based on the assumption that the rate-limiting step may be chemisorption, involving valence forces through the sharing or exchange of electrons between adsorbent and adsorbate. This model can be represented in the following form:

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

with linear form being:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t$$

where q_t and q_e are the amount adsorbed at time t and at equilibrium (mg/g), respectively, and k is the pseudo-second order rate constant for the sorption process (g/mg h). Thus, a plot of t/q_t vs. t should give a linear relationship with a slope of $1/q_e$ and an intercept $1/kq_e^2$. Fig. 6 shows the adjustment of the experimental data to this model, and the calculated k and q_e parameters are reported in Table 2. It was found that the adsorption system was best described by the pseudo-second order model. Also, it was shown that the pseudo-second order constant for the Fe-zeolitic tuff was higher than that for the carbonaceous material.

In general, the sorption behaviors for Fe-zeolitic tuff and carbonaceous material were of the same order of magnitude. The experimental data were best adjusted to the linear form of the pseudo-second order model. The first order model correlation coefficient was the highest for the carbonaceous materials, which may indicate that the sorption process is physical sorption.

Table 3
Sorption isotherm parameters of indigo carmine by Fe-zeolitic tuff and carbonaceous material adsorbent.

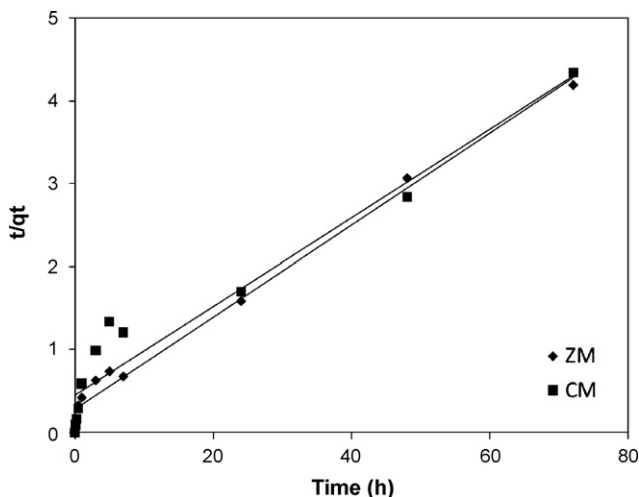| Material	Sorption isotherms									
	Langmuir			Freundlich			Langmuir–Freundlich			
	q_o (mg/g)	b	r	K_f	$1/n$	r	K	a	$1/n$	r
Fe–Z	32.83	0.020	0.992	1.25	0.66	0.984	0.10	0.010	1.78	0.997
CM	92.83	0.022	0.986	11.36	0.36	0.981	4.05	0.037	0.79	0.987

Fig. 6. Kinetic pseudo-second order model applied to the indigo carmine dye sorption from aqueous solution by Fe-zeolitic tuff and carbonaceous material adsorbents.

3.4. Sorption isotherms

The maximum sorption capacities of sorbents were obtained from the sorption isotherms to optimize the use of these kinds of materials. The experimental results were analyzed by non-linear Langmuir, Freundlich and Langmuir–Freundlich sorption models. The experimental data were analyzed using STATISTICA version 6.0 software.

3.4.1. Langmuir model
This model considers that maximum sorption corresponds to a monolayer saturated with dye molecules on the sorbent surface [19]. The Langmuir isotherm is represented by the following equation:

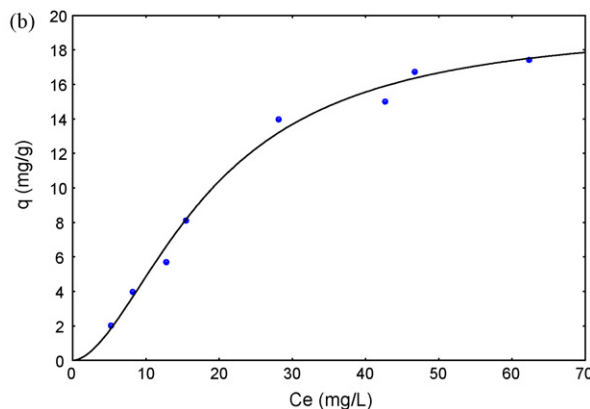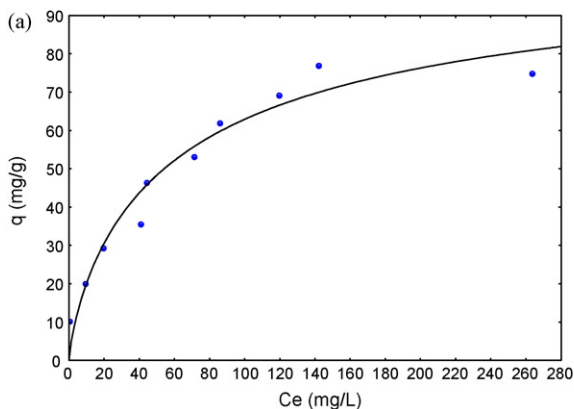$$q_e = \frac{q_o b C_e}{1 + b C_e}$$

where q_o is the amount of dye adsorbed per unit weigh of adsorbent in forming a complete monolayer on the surface (mg/g), q_e is amount of dye adsorbed (mg/g), C_e is the concentration of the dye in the solution at equilibrium (mg/L) and b is the constant related to the energy or net enthalpy of sorption. Table 3 shows the parameters obtained by applying this model to the experimental results; although the correlation was good, it was not the best using this model. It was found that the sorption capacity of the carbonaceous material for indigo carmine is three times higher than the capacity found for the Fe-zeolitic tuff. The parameter b was of the same order of magnitude for both materials.

3.4.2. Freundlich model
The Freundlich model, which has been applied to adsorbents with heterogeneous surfaces and considers multilayer sorption [17], is given by the following formula:

$$q_e = K_f C_e^{1/n}$$

where q_e is the amount of dye adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of the dye in the solution (mg/L), K_f is the equilibrium constant indicative of adsorption capacity and n is the adsorption equilibrium constant whose reciprocal is indicative of the heterogeneity of surface sorbent. K_f, $1/n$ and q_e parameters are reported in Table 3. According to the characteristics of the sorbents, it is better to apply this model to the results than the Langmuir model because they are heterogeneous materials. The equilibrium constant, K_f, was much higher for the carbonaceous material than for the Fe-zeolitic tuff, which indicates that the sorption capacity is higher for the carbonaceous material than for the Fe-zeolitic tuff. The values of $1/n$ are similar and less than unity, implying a heterogeneous surface structure with minimum interaction between adsorbed atoms [32].

3.4.3. Langmuir–Freundlich model
The Langmuir–Freundlich model is a combination of Langmuir and Freundlich models [17], and can be represented by the following

Fig. 7. Langmuir–Freundlich isotherms applied to the indigo carmine dye sorption from aqueous solution by Fe-zeolitic tuff (a) and carbonaceous material (b).

Table 4
Comparison of sorption capacities for indigo carmine for some adsorbents. aq., aqueous solution, ww, wastewater.

Adsorbent	q	Reference
Crude dehydrated sewage sludge	8 mg/g (ww)	Dhaouadi and M'Henni [33]
Pyrolyzed sewage sludge	30.82 mg/g (aq.)	Otero et al. [19]
Sewage sludge for chemical activation with H_2SO_4 + pyrolysis	54.38 mg/g (aq.)	Otero et al. [19]
Carbonaceous material	92 mg/g (aq.)	This work
Fe-zeolitic tuff	32 mg/g (aq.)	This work

equation:

$$q_e = \frac{KC_e^{1/n}}{1 + bC_e^{1/n}}$$

where q_e is the amount of dye adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of dye in solution, and K and b are empirical constants.

Although, all the correlation coefficients were greater than 0.96 for the previous methods, the data correlated best with the Langmuir–Freundlich, which had the highest correlation coefficients, as seen in Table 3 and Fig. 7. Similar results were found by Dhaouadi and M'Henni [33] using crude dehydrated sewage sludge.

Considering that the kinetic results obtained with the Fe-zeolitic tuff, were best fitted to the pseudo-second order model and the isotherms to the Langmuir–Freundlich model, it can be suggested that the sorption mechanism of the dye is chemisorption on heterogeneous materials. The experimental data obtained with the carbonaceous material were best adjusted to the kinetic first order and isotherm Langmuir–Freundlich models, which indicates physical sorption on a heterogeneous material.

Table 4 shows the sorption capacities of different sewage sludge derivative materials for indigoid dyes. Dhaouadi and M'Henni [33] reported the sorption of indigo blue using a real textile mill effluent and crude dehydrated sewage sludge (not pyrolyzed), and the equilibrium sorption capacity and sorption constants were 8 mg/g and 9.2×10^{-2} L/mg, respectively. In this work, the parameters were 92 mg/g and 2.2×10^{-2} L/mg, respectively, for the carbonaceous material, which shows that pyrolysis and the treatment of the carbonaceous material with HCl solution improves the sorption characteristics of the material. On the other hand, the sorption capacity obtained in this study is of the same order of magnitude as the values found by Otero et al. [19]. Using pyrolyzed sewage sludge, they obtained values of 30.82 mg/g and 3.0×10^{-2} L/mg, respectively, while using sewage sludge treated with H_2SO_4 followed by pyrolysis, they obtained values of 54.38 mg/g and 6.0×10^{-2} L/mg. Therefore, the treatment and origin of the sewage sludge seem to be important parameters that govern the sorption behavior of these kinds of materials.

3.5. Effect of pH

pH is an important parameter in sorption procedures, due the ionization of surface functional groups and the composition of solutions. Fig. 8 shows the variation of dye sorption capacities at various pH values for both carbonaceous material and Fe-zeolitic tuff.

The species of indigo carmine dye in acidic and basic conditions are shown in Fig. 9. This correlation indicates a redox process
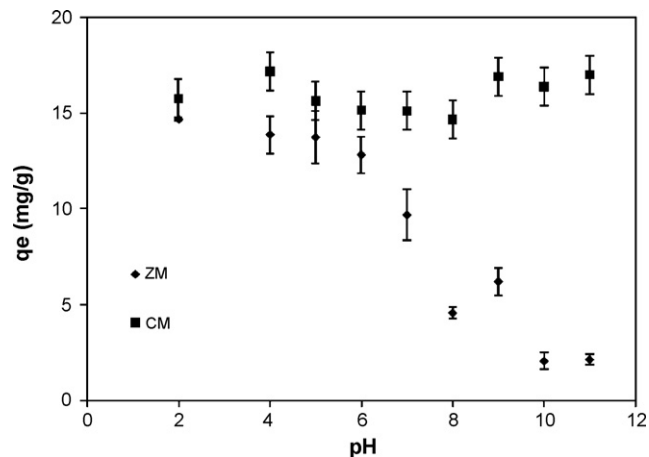

Fig. 8. Effect of pH on indigo carmine by Fe-zeolitic tuff and carbonaceous material adsorbents.

involving the uptake of one proton per electron transferred or two protons per two electrons transferred. Transfer of the second electron results in formation of the hydroquinone; this reduction mechanism is similar to the reduction of indigo dye by the bacterium *Clostridium isatidis*, which can reduce indigo to leuco-indigo, the soluble intermediate in the indigo dyeing process [34].

For the Fe-zeolitic tuff, removal of the dye was the highest between the pH values 2 and 6; the sorption decreases down to 2.15 mg/g at pH 11. When the pH of the solution increases up to 7, the number of positively charged sorbent sites decreased and the number of –OH groups increased [35]. Therefore, the positive sites of the sorbent are likely responsible for low sorption as well as the species of indigo carmine present in solution. The –OH groups in the dye are likely responsible for the sorption process.

For the carbonaceous material, it was found that sorption capacities were not affected by pH variation. This may imply that neither the chemical species present in solution nor the effects of pH on the carbonaceous material are important parameters for the sorption processes.

According to Fig. 9, the chemical species of the dye has an important effect on the sorption of indigo carmine on the Fe-zeolitic tuff. These results may indicate that the species present in acid medium interacts with the iron of Fe-zeolitic tuff and the species present in basic medium does not because the sorption decrease as the pH increases. Another possible interaction mechanism of the dye with the zeolitic material is catalytic degradation; recently, Kasiri et al. [36] used Fe-ZSM5 zeolite as a heterogeneous photo-Fenton catalyst for the degradation of acid blue 74.
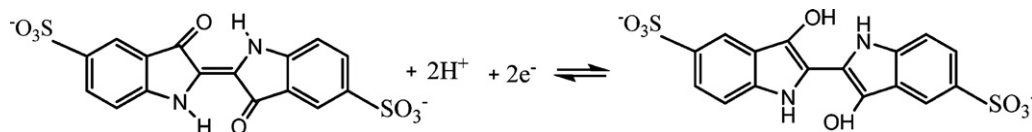

Fig. 9. A probable degradation mechanism of indigo carmine in the presence of Fe-zeolitic tuff.
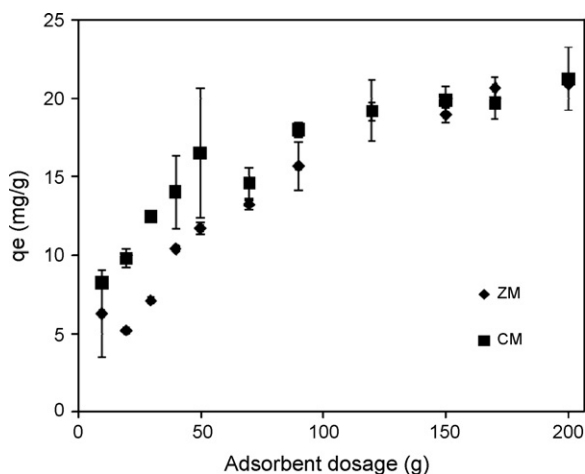
Fig. 10. Effect of adsorbent dosage on indigo carmine by Fe-zeolitic tuff and carbonaceous material adsorbents.

3.6. Effect on adsorbent dosage

The sorption capacities for indigo carmine increased with the increment of adsorbent dosage, from 10 to 200 mg for both carbonaceous material and Fe-zeolitic tuff. Fig. 10 illustrates indigo carmine sorption capacity versus adsorbent dosage. Although the amount of adsorbed dye increased as the quantity of sorbents increased, the adsorption was not proportional to the increment of adsorbent dosage. The maximum was found with 200 mg of adsorbent for both cases, but the adsorption quantity of dye was not very different between 100 and 200 mg of adsorbent. Therefore, 100 mg was the amount used in all experiments. A similar finding was reported for the sorption of methyl red on sulfuric acid-treated *Sugarcane bagasse* and powdered activated carbon (PAC). It was found that the percentage of dye removal increased with the increment of adsorbance dosage and the authors concluded that this behavior could be attributed to the increase in surface area and availability of adsorption sites [37].

4. Conclusions

Fe-zeolitic tuff and carbonaceous material are suitable sorbents for the removal of dyes like indigo carmine from aqueous solutions. Carbonaceous material treated with 10% HCl was found to be more efficient in terms of sorption than Fe-zeolitic tuff.

A pseudo-second order model and the Langmuir–Freundlich model were successfully applied to the experimental data obtained with the Fe-zeolitic tuff, which may indicate that the sorption mechanism of the dye on this material is one of chemisorption on heterogeneous materials. The experimental data obtained with the carbonaceous material were best adjusted to the kinetic first order and isotherm Langmuir–Freundlich models, which indicates physical sorption on a heterogeneous material.

Indigo carmine sorption capacity on Fe-zeolitic tuff was observed to decrease with a pH above 7, while the sorption capacity for carbonaceous material was not affected by pH.

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References

[1] R. Sanghi, B. Bhattacharya, Review on decolorisation of aqueous dye solutions by low cost adsorbents, Color. Technol. 118 (2002) 256–269.
[2] J.-W. Lee, S.-P. Choi, R. Thiruvrnkatachari, W.-G. Shim, H. Moon, Evaluation of the performance of adsorption and coagulation processes for the maximum removal of reactive dyes, Dyes Pigments 69 (2006) 196–203.
[3] S.J. Allen, B. Koumanova, Decolourisation of water/wastewater using adsorption, J. Univ. Chem. Technol. Met. 40 (2005) 175–192 (Review).
[4] B. Manu, Physico-chemical treatment of indigo dye wastewater, Color. Technol. 123 (2007) 197–202.
[5] U.R. Lakshmi, V.C. Srivastava, I.D. Mall, D.H. Lataye, Rice husk ash as an effective adsorbent: evaluation of adsorptive characteristics for Indigo Carmine dye, J. Environ. Manage. 90 (2009) 710–720.
[6] A. Mittal, J. Mittal, L. Kurup, Batch and bulk removal of hazardous dye, indigo carmine from wastewater through adsorption, J. Hazard. Mater. B137 (2006) 591–602.
[7] N. Barka, A. Assabbane, A. Nounah, Y. Aît Ichou, Photocatalytic degradation of indigo carmine in aqueous solution by TiO_2-coated non-woven fibres, J. Hazard. Mater. 152 (2008) 1054–1059.
[8] A. Roessler, D. Crettenand, Direct electrochemical reduction of vat dyes in affixed bed of graphite granules, Dyes Pigments 63 (2004) 29–31.
[9] S. Sirianuntapiboon, K. Chairattanawan, S. Jungphungsukpanich, Some properties of a sequencing batch reactor system for removal of vat dyes, Bioresour. Technol. 97 (2005) 1243–1252.
[10] A. Cestari, E. Vieira, A. Tavares, R. Bruns, The removal of the indigo carmine dye from aqueous solutions using cross-linked chitosan—evaluation of adsorption thermodynamics using a full factorial design, J. Hazard. Mater. 153 (2008) 566–574.
[11] A.X. Wu, S.H. Yin, B.H. Yang, J. Wang, G.Z. Qiu, Study on preferential flow in dump leaching of low-grade ores, Hydrometallurgy 87 (2007) 124–132.
[12] A.X. Wu, S.H. Yin, W.Q. Qin, J.S. Liu, G.Z. Qiu, The effect of preferential flow on extraction and surface morphology of copper sulphides during heap leaching, Hydrometallurgy 95 (2009) 76–81.
[13] A.X. Wu, S.H. Yin, H. Wang, W.Q. Qin, G.Z. Qiu, Technological assessment of a mining-waste dump at the Dexing copper mine, China, for possible conversion to an in situ bioleaching operation, Bioresour. Technol. 100 (2009) 1931–1936.
[14] M.S. Berber-Mendoza, R. Leyva-Ramos, P. Alonso-Davila, L. Fuentes-Rubio, R.M. Guerrero-Coronado, Comparison of isotherms for the ion exchange of Pb(II) from aqueous solution onto homoionic clinoptilolite, J. Colloid Interface Sci. 301 (2006) 40–45.
[15] A. Günay, E. Arslankaya, I. Tosun, Lead removal from aqueous solution by natural and pretreated clinoptilolite: adsorption equilibrium and kinetics, J. Hazard. Mater. 146 (2007) 362–371.
[16] M. Sprynskyy, B. Buszewski, A. Terzyk, J. Namieśnik, Study of the selection mechanism of heavy metal (Pb^{2+}, Cu^{2+}, Ni^{2+} and Cd^{2+}) adsorption on clinoptilolite, J. Colloid Interface Sci. 304 (2006) 21–28.
[17] J. Torres-Pérez, M. Solache-Ríos, A. Colín-Cruz, Sorption and desorption of dye Remazol yellow onto a Mexican surfactant-modified clinoptilolite-rich tuff and a carbonaceous material from pyrolysis of sewage sludge, Water Air Soil Pollut. 187 (2008) 303–313.
[18] H. Kušić, N. Koprivanac, I. Selanec, Fe-exchanged zeolite as the effective heterogeneous Fenton-type catalyst for the organic pollutant minimization: UV irradiation assistance, Chemosphere 65 (2006) 65–73.
[19] M. Otero, F. Rozada, L.F. Calvo, A.I. García, A. Morán, Elimination of organic water pollutants using adsorbents obtained from sewage sludge, Dyes Pigments 57 (2003) 55–65.
[20] S. Rio, C. Faur-Brasquet, L. Le Coq, P. Le Cloirec, Structure characterization and adsorption properties of pyrolyzed sewage sludge, Environ. Sci. Technol. 39 (2005) 4249–4257.
[21] F.-S. Zhang, J. Nriagu, H. Itoh, Mercury removal from water using activated carbons derivated from sewage sludge, Water Res. 39 (2005) 389–395.
[22] E. Gutiérrez-Segura, A. Colín-Cruz, C. Fall, M. Solache-Ríos, P. Balderas-Hernández, Comparison of Cd–Pb adsorption on commercial activated carbon and carbonaceous material from pyrolyzed sewage sludge in column system, Environ. Technol. 30 (2009) 455–461.
[23] B. Smith, Infrared Spectral Interpretation: A Systematic Approach, CRC Press, USA, 1999.
[24] F.A. Mumpton, W.C. Orsmy, Morphology of zeolites in sedimentary rocks by scanning electron microscopy, Clay Clay Mineral 24 (1976) 1–23.
[25] M. Trgo, J. Perić, Interaction of the zeolitic tuff with Zn-containing simulated pollutant solutions, J. Colloid Interface Sci. 260 (2003) 166–175.
[26] M. Doula, Synthesis of a clinoptilolite-Fe system with high Cu sorption capacity, Chemosphere 67 (2006) 731–740.
[27] J. Torres-Pérez, M. Solache-Rios, M.T. Olguin, Sorption of azo dyes onto a Mexican surfactant-modified clinoptilolite-rich tuff, Sep. Sci. Technol. 42 (2007) 299–318.
[28] X.-S. Wang, J. Wang, Ch. Sun, Removal of copper (II) ions from aqueous solutions using natural kaolinite, Adsorpt. Sci. Technol. 23 (2005) 517–530.
[29] Y.-S. Ho, W.-T. Chiu, C.-S. Hsu, C.-T. Huang, Sorption of lead ions from aqueous solution using tree fern as a sorbent, Hydrometallurgy 73 (2004) 55–61.
[30] R. Cortés, V. Martínez, M. Solache, Evaluation of natural and surfactant-modified zeolites in the removal of cadmium from aqueous solutions, Sep. Sci. Technol. 39 (2004) 2711–2730.
[31] Y.-S. Ho, G. McKay, Application of kinetic models to the sorption of copper (II) on to peat, Adsorpt. Sci. Technol. 20 (2002) 797–813.

[32] M.M. Abou-Mesalam, Applications of inorganic ion exchangers: II. Adsorption of some heavy metal ions from their aqueous waste solution using synthetic iron III titanate, Adsorption 10 (2004) 87–92.

[33] H. Dhaouadi, F. M'Henni, Textile mill effluent decolorization using crude dehydrated sewage sludge, Chem. Eng. J. 138 (2008) 111–119.

[34] R.G. Compton, S.J. Perkin, D.P. Gamblin, J. Davis, F. Marken, A.N. Padden, P. John, *Clostridium isatidis* colonised carbon electrodes: voltammetric evidence for direct solid state redox processes, New J. Chem. 24 (2000) 179–181.

[35] S.W. Won, S.B. Choi, B.W. Chung, D. Park, Y.S. Yun, Biosorptive decolorization of reactive orange 16 using waste biomass of *Corynebacterium glutamicum*, Ind. Eng. Chem. Res. 43 (2004) 7865–7869.

[36] M.B. Kasiri, H. Aleboyeh, A. Aleboyeh, Degradation of Acid Blue 74 using Fe-ZSM5 zeolite as a heterogeneous photo-Fenton catalyst, Appl. Catal. B 84 (2008) 9–15.

[37] S. Saiful Azhar, A. Ghaniey Liew, D. Suhardy, H. Farizul Hafitz, M.D. Irfan Hatim, Dye removal from aqueous solution by using adsorption on *treated surgarcane bagasse*, Am. J. Appl. Sci. 2 (2005) 1499–1503.