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Adsorption of methylene blue from aqueous solution on zeolitic material and the improvement as toxicity removal to living organisms

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ABSTRACT: *The adsorption of methylene blue (MB) from aqueous solution was carried out using zeolite. This adsorbent material was synthesized from fly ash as a low-cost adsorbent, allowing fly ash to become a recycled residue. Factors that affected adsorption were evaluated: initial dye concentration, contact time and temperature. The equilibrium of adsorption was modeled by Langmuir, Freundlich and Temkin models. The adsorption obtained data were well described by Temkin, the adsorption isotherm model. Thermodynamic calculations suggest that the adsorption of methylene blue on zeolite synthesized from fly ash is a spontaneous and exothermic reaction. Acute toxicity was determined for raw and adsorbed methylene blue solutions, as if it was a real liquid residue. Acute effects were substantially reduced after the adsorption treatment. The values of untreated solution of methylene blue were 16.58 ppm up to 18.64 ppm for Vibrio fischeri bacteria and from 0.16 ppm up to 0.43 ppm for Daphnia similis cladoreca exposed to the dye for 48 hours*.

Keywords: *methylene blue; zeolite; dye adsorption; acute toxicity; D. similis; V. fischeri*

Introduction

Synthetic dyes are used extensively by several industries including the textile dyeing and paper industry. It is estimated that at least 10% of the dyes are lost in the dye effluent during such dyeing processes. The colored wastewater damages the aesthetic nature of water and reduces the light penetration through the water's surface and the photosynthetic activity of aquatic organisms due to the presence of metals,

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chlorides and other contaminants. Many of the dyes used in these industries may also be carcinogenic and mutagenic [1-4].

Textile industries feature among the eight most important sectors of the industrial activity of Brazil, occupying first place in direct employment and in billing. The discharge of colored wastewater has increased considerably with the development of the textile industry in the Santa Catarina state (Brazil), aggravating the environmental problems [5].

Among several chemical and physical treatment methods, the adsorption has been found to be superior to other techniques for the removal of dyes from aqueous solution in terms of methodology, operational conditions and efficiency. Currently, the most common procedure involves the use of activated carbons as adsorbents due to their higher adsorption capacities. Commercially available activated carbons are usually derived from wood or coal, being considered expensive. This has led to the scientists to use lower-cost adsorbents which are cheaper efficient substitutes [6-7].

Fly ash is formed by combustion of coal in coal-fired power station as a waste product. The generation rate of coal fly ash in Brazil is approximately 4 million tons per year and is predicted to increase. Efficient disposal of coal fly ash is a worldwide issue due to its massive volume and harmful risks to the environment. As a technique for recycling coal fly ash, synthesis of zeolites from coal fly ash has attracted a great deal of attention.

Holler and Wirsching [8] and Henmi [9] were the first to report the modification of fly ash by hydrothermal treatment in alkaline solutions at elevated temperatures and pressures to produce zeolites. Since them, the synthetic approach has been modified to include microwave assisted synthesis [10] and the fusion of ash with base prior to hydrothermal treatment [11]. Zeolitic materials have been widely used as low-cost adsorbents as reviewed by Querol et al. and Rayalu et al. [12-13].

In our group we have been developing zeolites synthesized from Brazilian coal fly ashes from the Figueira power plant to remove metals ions from aqueous effluents and soil [14-16]. The efficiency of zeolitic materials from baghouse filter as adsorbent allowed investigations focused on the removal of dye [17-18].

Methylene blue (MB) is one of the most commonly used basic dyes for printing and textural dyeing for acrylic, nylon, silk, wool and medicinal purposes. Although it's not strongly hazardous, can causes permanent injury to the eyes of human and animals. On inhalation, it can give rise to short periods of difficult breathing, while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion, painful micturition, and methemoglobinemia [19]. The

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uptake of methylene blue is usually used as an index of adsorption performance for adsorbents.

Regarding to biological aspects few data is available on the efficacy of developing treatment technology on toxicity removal. The importance of ecotoxicological and mutagenic aspects for suitable developing of treatment technologies is a growing understanding. The negative effects of treated dyes and their byproducts is an important way to confirm if the treatment will really imply in a better product for the environment [20].

Part of the study was dedicated to evaluate the capability of zeolite from fly ash for the decoloration of methylene blue and the second objective was addressed to the toxicity of dye and how the treatment will modify this property. To this end, fly ashes from cyclone filter were selected. The zeolite efficacy was evaluated for toxicity reduction using two lived organisms: the crustacean *D. similis* and luminescent bacteria *V. fischeri*. These species are significant for treatment aspects and water quality. Brazilian water monitoring plan is looking to toxicity evaluation for the same organisms and this is partially the reason why they were selected [21].

Material and Methods

Materials

Methylene blue (CI 52015) was obtained from Merck and used as received. A stock solution (3.2 g. L^{-1}) was prepared with deionized water (Millipore Milli-Q) and the solutions for adsorption tests were prepared by diluting. The samples of coal fly ash (CFA) from cyclone filter were obtained from a coal-fired power plant located at Figueira County, in Paraná State, Brazil. A Commercial zeolite 4A from Bayer was also used in the adsorption study for comparing.

Zeolite synthesis

Coal fly ash (20 g) was mixed with 160 mL of 3.5 mol L^{-1} aqueous NaOH solution in a 300 mL Teflon vessel. This mixture was heated to 100 ^{o}C in oven for 24 h. After finishing of the process, the suspension was filtered with 4A quantitative filter paper. The zeolitic material was repeatedly washed with deionized water until the pH of washing water reach ~11 and dried at 100 ^{o}C for 24 h [9]. The zeolite obtained was label as ZM.

Characterization techniques

The physico-chemical characteristics of materials were determined using standard procedures. Bulk density was determined by helium pycnometer (Micromeritics – Accupyc 1330). The surface area was determined by N_2 adsorption isotherm with relationship using NOVA 1200 (Quantachrome Corp.). Before adsorption experiments, the samples

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were degassed at 150 ^{o}C for 12 h. The specific surface area was obtained by five points at p/p^0 between 0.05 and 0.20 applying the Brunauer–Emmet–Teller equation to the adsorption data. The phases of the zeolite were determined by X-ray diffraction analyses (XRD) with an automated Rigaku multiflex diffractometer with Cu anode using Co Kα radiation at 40 kV and 20 mA over the range (2θ) of 5–80° with a scan time of 1°/min. The chemical composition of zeolite was determined by a RIX-3000 RIGAKU X-ray fluorescence spectrometer (XRF) equipped with a Rh X-ray tube (operated at 50 kV-60 mA). Scanning Electron micrograph was obtained by using XL-30 Philips scanning electron microscope (SEM). The cation exchange capacity (CEC) value was determined using ammonium solutions. The pH of zeolite was measured as follows: 0.1 g of samples were mixed with 10 ml of distilled water and shaken for 24h. After filtration, the pH of solution was determined by a pH meter.

Adsorption studies

The adsorption was performed by batch experiments. Kinetic experiments were carried out by stirring 100 mL of dye solution of known initial dye concentration with 1 g of zeolite at room temperature (25 ^{o}C) at 120 rpm in different 250 mL PE flasks. At different time intervals, samples have been drawn out and then centrifuged at 2000 rpm for 20 min. The concentration in the supernatant solution was analyzed using a UV spectrophotometer (Cary 1E – Varian) by measuring absorbance at λ_{max} = 650 nm and pH = 5. Adsorption isotherms were carried out by contacting 1 g of zeolite with 100 mL of methylene blue over the concentration ranging from 3.2 to 96 mg L^{-1}. The agitation last 10 min, which is sufficient time to reach equilibrium. The methylene blue adsorption performance of the original coal fly ash was also studied for comparison.

The amount of adsorption at equilibrium (q_e, mg g^{-1}) was calculated by using the following equation:

$$q_e = \frac{V(C_o - C_e)}{W} \quad (1)$$

where C_o and C_e (mg L^{-1}) are the liquid-phase concentrations of dye at initial and equilibrium, respectively, V is the volume of the solution (L) and W is the mass of the adsorbent (g).

Toxicity evaluation

Daphnia similis crustacean and *Vibrio fischeri* luminescent bacteria were the tested-organisms for the evaluation of methylene blue acute toxicity. While the first assay evidences the immobility of the organisms due to the exposure, the second is

based on the light emission reduction caused by the toxicant. Three acute toxicity experiments were performed for MB solutions before and after zeolite adsorption.

Acute toxicity for crustacean assays were performed with *D. similis* exposure for 24 h and 48 h at 20 ^{o}C $\pm$0.5 [22]. The water hardness was adjusted and fixed to 46 mg L^{-1} CaCO$_3$ for the toxicity tests and for the culture of this lived organism. At least five MB solution concentrations were analyzed and MB was diluted at the same water used for the maintenance of test-organisms. The results were expressed as EC$_{50}$ (%, 48 h). Once this parameter is inversely proportional, the values were transformed into Toxic Units (TU = 100 / EC$_{50}$) to allow an easier comparison.

Acute toxicity for luminescent bacteria was carried out with Microtox® System – model 500 (Azur Environment, USA). The bacterial luminescence was measured after 15 min exposition and the lost sign (luminescence) was related to the effect according to the dye concentration. The assay results were expressed as EC$_{50}$, which is the effective concentration that causes 50% of light inhibition after 15 min exposure. The assay considered the suitable color correction when required due to hard blue color of the untreated samples. These assays were performed according to ABNT and ISO methods [23]. After obtaining Toxic Units the efficacy of zeolites adsorption was calculated as removal percentage.

The contaminants of *dye-saturated zeolite* were analyzed by means of leaching and solubilization tests [24-26].

Results and Discussion

Characterization of materials

The morphology of the starting material CFA and synthesized product ZM were examined using SEM (Fig. 1). Fig. 1a confirms that CFA particles had the predominance of spherical shapes of different size ranges and smooth surfaces. By contrast, the surface of ZM is rough, indicating that zeolite crystals were deposited on the surface of underlying fly ash particles during the hydrothermal treatment (Fig. 1b).

Table 1 shows some properties of fly ash and zeolitic material. XFR measurement indicates that the original fly ash is a ready source of Al and Si for forming zeolites. According to the American Society for Testing Materials (ASTM C618) [27], fly ashes are defined as Class F produced from the burning of higher rank coals. Vitrinite reflectance analyses indicated a high volatile B/C bituminous coal at the Figueira Power Plant [28]. The chemical composition of zeolitic material synthesized from fly ash is mainly silica, alumina, iron oxide and sodium oxide. A significant amount of Na element is incorporated in the final product due the hydrothermal treatment with NaOH solution. Table 1 also includes data on the specific surface areas of materials and the value of zeolitic product

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has increased 5-fold. This surface area increase is related to the crystallization of the many zeolite crystals on the originally smooth ash spheres. The CEC rose from 1.55 meq 100 g^{-1} for the unmodified ash to 137.6 meq 100 g^{-1} for the modified product due to crystal formation of the material-type zeolite.
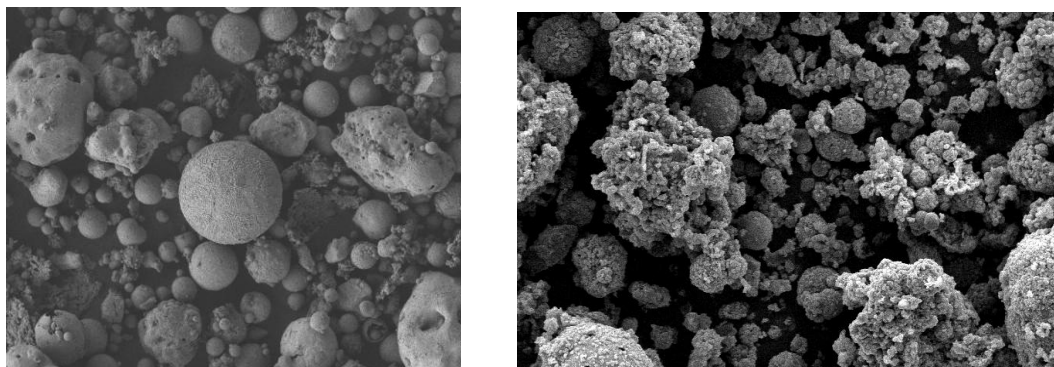

Figure 1. SEM images of (a) CFA (b) ZM.

Table 1. Physicochemical properties of fly ash and zeolitic material

| Property	CFA	ZM
SiO_2 (wt%)	40.4	39.5
Al_2O_3 (wt%)	15.2	25.0
Fe_2O_3 (wt%)	10.6	16.6
Na_2O (wt%)	0.988	11.8
CaO (wt%)	1.65	2.68
K_2O (wt%)	2.23	0.480
TiO_2 (wt%)	0.781	1.17
SO_3 (wt%)	0.914	1.05
MgO (wt%)	0.348	1.04
ZnO (wt%)	0.101	0.120
ZrO_2	0.0851	0.16
CEC (meq/100 g)	1.55	137.6
Specific surface area (m^2/g)	7.55	40.0
Bulk density (g/cm^3)	2.40	2.65
pH	8.18	9.23

Figure 2 illustrates the XRD profiles of the original coal fly ash (CFA) and zeolitic product (ZM). The mineralogical composition of fly ash depends on the geological factors related to the formation and deposition of coal and its combustion conditions. XRD profile of CFA is composed mainly of peaks of quartz (JCPDS 001-0649) and mullite (JCPDS 002-0495). Mullite and quartz are produced during the decomposition of clay minerals such as kaolinite [29]. Intensities of these peaks decrease and peaks caused by generation of zeolite increase with treatment of zeolite production. The major phase in zeolitic material was hydroxysodalite (JCPDS-ICDD 00-011-0401) with peaks of quartz and mullite of fly ash that remained after the treatment. The modification process leaded to reductions in the amount of mullite and quartz as indicated by the decrease in the peaks at 26.65. Hydroxysodalite is a condensed phase, and thermodynamically it is the most stable phase formed from the $Na_2O-Al_2O_3-SiO_2-H_2O$ quaternary system [30].

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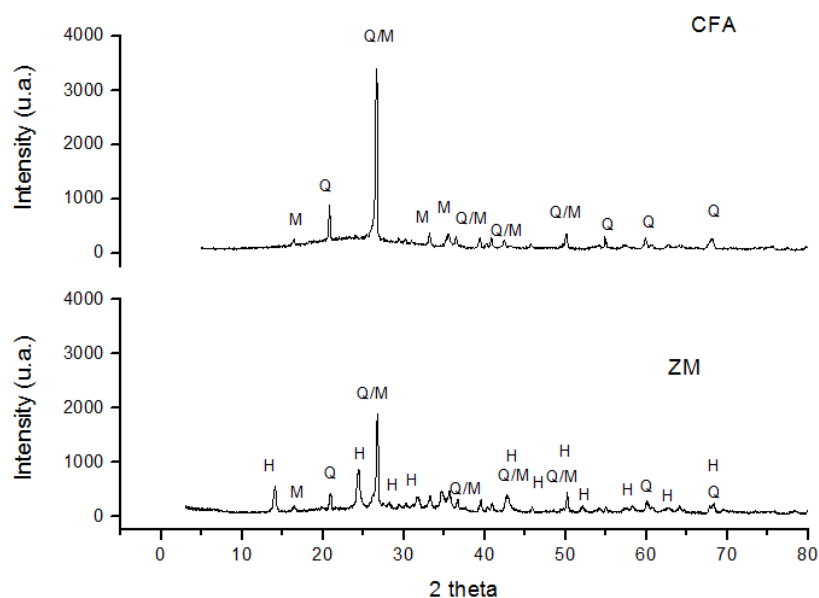
Figure 2. X-ray diffractograms for (a) CFA; (b) ZM. M = mulitte; Q = quartz; H = hydroxysodalite.

Effect of contact time

The effect of contact time on adsorption process was investigated at various initial dye concentrations. It can be seen from Fig. 2 that the adsorption of methylene blue on zeolite occurred very quickly within the first 10 min. after which a maximum value of adsorption capacity was attained. This rapid uptake can be attributed to the concentration gradient created at the start of the adsorption process between solute concentration in solution and that at the zeolite surface. Another factor that contributes to the rapid adsorption rate is that there are only adsorbate and adsorbent interactions with negligible interference from solute– solute interactions [31]. The equilibrium of the adsorption process was attained so fast that the kinetic data could not be modeled.
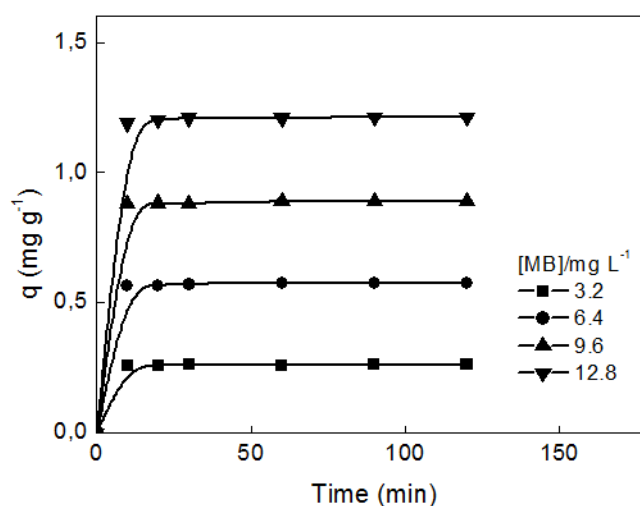
Figure 2. Adsorption kinetics for methylene blue onto zeolite.

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Adsorption isotherms

Equilibrium isotherm is described by an adsorption isotherm, characterized by certain constants whose values express the surface properties and affinity of the adsorbent. The adsorption equilibrium is established when the concentration of adsorbate in the bulk solution is in dynamic balance with that at the adsorbent interface.

In order to quantify the affinity of zeolite for the basic dye studied, three widely used isotherm models (Langmuir, Freundlich and Temkin isotherm models) were used to analyze the data obtained from the adsorption process.

The linear form of the Langmuir expression may be written as:

$$C_e/q_e = 1/bK_L + C_e/K_L \quad (2)$$

where q_e is solid-phase adsorbate concentration at equilibrium (mg g^{-1}), C_e is aqueous-phase adsorbate concentration at equilibrium (mg L^{-1}), K_L (mg g^{-1}) is the maximum amount of adsorbate per unit weight of adsorbent to form a complete monolayer on the surface, and b is the Langmuir isotherm constant (L mg^{-1}), related to the affinity of the adsorption sites. A plot of C_e/q_e versus C_e gives a straight line of slope $1/K_L$ and intercept $1/K_L b$.

The linear form of Freundlich equation is expressed as:

$$\text{Log } q_e = \log K_F + 1/n \, (\log C_e) \quad (3)$$

where K_F (mg/g(L/mg)$^{1/n}$) and n are Freundlich constants related to adsorption capacity and adsorption intensity of adsorbents. The Freundlich constant K_F and n can be calculated from the intercept and slope of plot between log q_e and logC_e.

The linear form of the Temkin isotherm model is:

$$q_e = B_T \ln K_T + B_T \ln C_e \quad (4)$$

where B_T = RT/b, *b* is the Temkin constant related to heat of sorption (J mol^{-1}); K_T is is the equilibrium binding constant (L g^{-1}) corresponding to the maximum binding energy, *R* the gas constant (8.314 J/mol K) and *T* the absolute temperature (K). A plot of q_e *versus* ln C_e enables the determination of the isotherm constants B_T and K_T from the slope and the intercept, respectively.

Equilibrium data of methylene blue onto zeolite synthesized from fly ash are shown in Fig. 3. The isotherm shapes are largely determined by the adsorption mechanism and can therefore be used to diagnose the nature of the adsorption [32]. The equilibrium isotherm has the shape of L3 type curve and indicates that the second layer of dye can form readily.

The parameters obtained from the isotherms are given in Table 2. Langmuir

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constants are not given in Table 2 due this poor fit to experimental data. Negative values for the Langmuir isotherm constants imply that this model is not suitable to explain the adsorption process, since these constants are indicative of the surface binding energy and monolayer coverage. This suggests that some heterogeneity in the surface or pores of the zeolite synthesized from fly ash will play a role in dye adsorption.
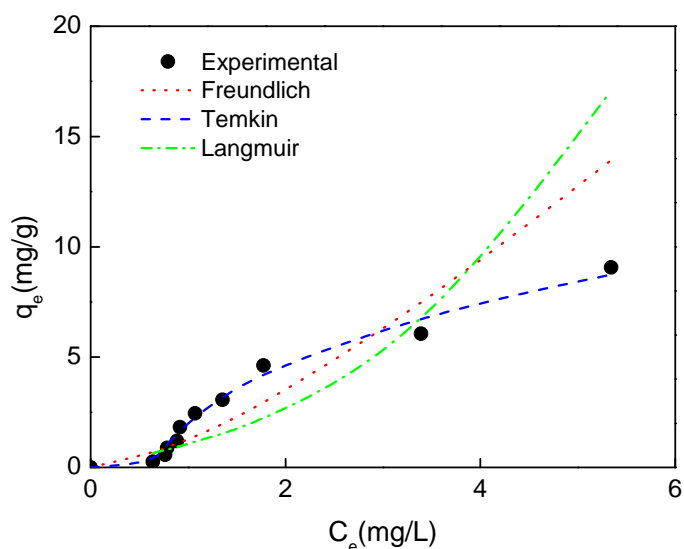
Figure 3. Adsorption isotherm of methylene blue onto zeolite.

Table 2. Equilibrium isotherm constants for methylene blue onto zeolite from fly ash

Adsorbent	Freundlich			Temkin		
	K_F *	n	R^2	K_T (L g^{-1})	B_t	R^2
Zeolite	1.28	0.701	0.890	1.61	4.02	0.992
Fly ash **	0.158	1.05	0.966	1.09	0.422	0.940
Zeolite 4A	1.28	1.01	0.765	1.99	2.79	0.876

(*) [(mg g^{-1}) (L mg^{-1})$^{1/n}$]; (**) [AM] = 3.2 – 12.8 mg L^{-1}; t_{equil} = 2 h

The adsorption isotherm can be fitted using Temkin model with correlation coefficient >0.99. A comparison was also made between isotherms plotted in Fig. 3, which shows the experimental data points and the two theoretical isotherms plotted on the same graph. The parameters obtained from the isotherm of methylene blue onto original coal fly ash and onto commercial zeolite type 4A were presented in Table 2 for comparison. The coal fly ash presented lower adsorption capacity for methylene blue than the zeolite. Samples using zeolite required shorter agitation before reaching equilibrium and were able to remove more methylene blue from aqueous solution than

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the fly ash. The adsorption capacity can be correlated with the variation of surface area and porosity of the adsorbent. Higher surface area will generally result in higher adsorption capacity. The surface area value in zeolite increased about 80% compared to raw ash. In addition, conversion of fly ash to zeolite changes the surface properties of solid adsorbents by increasing the cation exchange capacity, which also favours the adsorption of methylene blue on treated fly ashes. It can be seen from Table 2 that adsorption capacity values of commercial zeolite and zeolite from fly ash were the same.

Thermodynamics parameters

To understand better the effect of temperature on the adsorption, it is important to study the thermodynamic parameters such as standard Gibbs free energy change (ΔG^o), standard enthalpy (ΔH^o) and standard entropy (ΔS^o). The Gibbs free energy of adsorption by using equilibrium constant (K_c) is calculated from the following equation:

$$\Delta G^o = - 2.0303 \, RT \log K_C \quad (5)$$

Standard enthalpy, (ΔH^o), and standard entropy, (ΔS^o), of adsorption can be estimated from van't Hoff equation given in

$$\text{Log Kc} = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \quad (6)$$

where R is the gas constant, K_c is adsorption equilibrium constant. The K_c value is calculated from the equation [7]

$$K_C = \frac{C_{Ae}}{C_{Se}} \quad (7)$$

where C_{Ae} is the equilibrium concentration of the dye ions on adsorbent (mg L^{-1}) and C_{Se} is the equilibrium concentration of the dye ions in the solution (mg L^{-1}).

The plot of log K_c against $1/T$ (in Kelvin) should be linear. The slope of the van't Hoff plot is equal to $-\Delta H^o/2.303 \, R$, and its intercept is equal to $\Delta S^o/2.303 \, R$. The van't Hoff plot for the adsorption of MB onto zeolite synthesized from fly ash is given in Fig. 4. Thermodynamic parameters obtained are given in Table 3.

As shown in Table 3, the negative values of ΔG^o at different temperatures indicate the spontaneous nature of the adsorption process. Positive ΔH^o reveals endothermic adsorption. The positive value of ΔS^o suggests the increased randomness at the solid/solution interface during the adsorption of the dye onto zeolite synthesized from fly ash. A similar trend has been reported for the adsorption of methylene blue onto synthetic zeolite MCM-22 [33].

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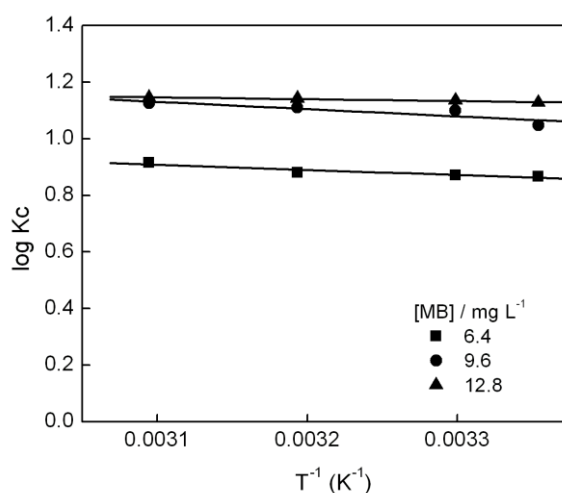
Figure 4. Van´t Hoff plot of methylene blue adsorption onto zeolite.

Table 3. Thermodynamic parameters for the adsorption of MB onto zeolite

[AM] (mg L^{-1})	ΔH^o (kJ mol^{-1})	ΔS^o (J mol^{-1})	ΔG^o (kJ mol^{-1})			
			298.15 K	303.15 K	313.15 K	323.15 K
6.40	9.27	46.43	- 4.37	- 5.05	- 5.28	- 5.67
9.61	4.89	36.79	- 5.98	- 6.39	- 6.65	- 6.96
12.8	1.25	25.82	- 6.44	- 6.59	- 6.83	- 7.08
Average	5.14	36.35	- 5.61	- 6.01	- 6.26	- 6.57

Toxicity assessment

Toxicity evaluation results were summarized at Table 4. *V. fischeri* MB acute toxicity varied from 15.55 mg L^{-1} up to 18.64 mg L^{-1}, values that increased to 29.67 mg L^{-1} and 43.90 mg L^{-1} after zeolites adsorption, meaning a 2.35 times less toxic solution, after treatment.

The MB EC_{50} (%, 48 h) values obtained for *D. similis* were 0.16 mg L^{-1} up to 0.43 mg L^{-1}. After zeolites adsorption treatment these values were 26.10 mg L^{-1} up to 47.80 mg L^{-1}. The efficacies for acute toxicity removal for bacteria and for Daphnis were on average 55.42 % and 99.18 %, respectively. Although *D. similis* response was very sensitive to methylene blue, after the zeolite adsorption the solution reduced substantially its harmful effects.

Results from solid waste classification tests showed that dye-saturated zeolite was considered neither corrosive nor reagent, according to ABNT norms. It was classified as non-inert waste, based on NBR 10004/2004 (Class II A, non-dangerous/non-inert) due to the presence of presence of heavy metals exceeding the maximum limit allowed [24].

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The residual fly ash fraction of zeolitic material contains an amount of readily leachable material deposited during cooling after combustion.

Table 4. Efficacy of zeolite adsorption for MB acute toxicity removal

EC$_{50}$ Untreated (15 min, % v/v)	EC$_{50}$ adsorved (15 min, % v/v)	TU Untreated	TU adsorved	Removal (%)
17.23 (*)	34.74	5.80	2.87	50.51
18.64 (*)	43.90	5.36	2.27	57.65
16.58 (*)	39.50	6.03	2.51	58.37
0.190 (**)	26.10	526	3.83	99.27
0.160(**)	47.80	625	2.09	99.66
0.430 (**)	31.47	233	3.17	98.63

(*) 15 min - *V. fischeri*; (**) 48h - *D.similis*

Conclusion

The present study showed that zeolite synthesized from fly ash can be used as an effective adsorbent for the removal of methylene blue dye from aqueous solution. It is observed from the experiments that about 80-94% removal is possible. The equilibrium data followed Temkin isotherm. The coal fly ash based adsorbent may be an alternative to more costly adsorbents for the treatment of aqueous waste containing methylene blue. Both lived-organisms evidenced that the proposed treatment resulted in a less toxic liquid residue. Yet, most importantly the results of this investigation demonstrated the great significance of toxicological assays associated with decolorization experiments.

Acknowledgements

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