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Surfactant-Modified Zeolites from Coal Fly and Bottom Ashes as Adsorbents for Removal of Crystal Violet from Aqueous Solution

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Abstract: Zeolites synthesized from coal fly and bottom ashes were modified with the surfactant hexadecyltrimethylammonium bromide and were used as adsorbent to remove the dye Crystal Violet (CV) from aqueous solution. The coal fly ash and bottom ash used in the synthesis of the zeolites were collected in the largest coal burning thermoelectric complex of the Latin America - Thermoelectric Complex Jorge Lacerda, located in the Santa Catarina State, Brazil. The surfactant modified zeolites from fly ash (MZSF) and bottom ash (MZSB) were characterized to obtain chemical and mineralogical composition, and some physicochemical properties. The adsorption kinetic of CV onto adsorbents was discussed using the pseudo-first order, pseudo-second order and Elovich models, and the pseudo-second order model provided the best correlation of the experimental data. The equilibrium data was analyzed using equations linear and non-linear of the Langmuir and Freundlich models. The Freundlich model was better adjusted to the experimental data for the systems studied. The maximum adsorption capacities were 36.7 mg g^{-1} and 21.1 mg g^{-1} for CV/MZSF and CV/MZSB, respectively. The parameters of adsorption isotherms were used to predict the design of the equipment for performing adsorption discontinuous single stage.

Keywords: coal fly ash; coal bottom ash; modified zeolite; crystal violet; adsorption.

INTRODUCTION

The expansion of the industrialization process provided to the man a lot of convenience, expanding the space for consumption. This development caused detrimental impacts on the environment.

One of the major challenges for sustainable development of society is the treatment of wastewater containing dyes. Some classes of synthetic dyes and their byproducts can be carcinogenic and/or mutagenic.

A dye frequently used in industrial processes and in medicine is the crystal violet. This dye is known as Basic Violet 3, gentian violet and methyl violet 10B. The crystal violet is little metabolized by the microorganisms, it is not biodegradable and can persist in many environments, being considered as a molecule recalcitrant [1].

Conventional methods generally consisting of coagulation-flocculation, activated sludge process and chlorination are unable to perform the treatment of colored effluents. Adsorption is a technique that can be used in the final treatment processes preventing the release of water with colorants or toxic intermediates from the degradation to the environment.

The lower-cost adsorbents have been investigated for removing contaminants from wastewater. A large variety of low-cost adsorbents have been prepared from different materials utilizing industrial, biomass, and municipal wastes [2,3].

The Thermoelectric Complex Jorge Lacerda (TCJL) is located in the township of Capivari de Baixo, in the Southeast area of the state of Santa Catarina, 130 km from Florianópolis. The TCJL is the largest coal burning thermoelectric complex of Latin America, formed by seven power plants and with a total capacity of 857 MW [4].

Brazilian coal burning generates large amount of ash. The thermoelectric power stations in the southern of Brazil produce approximately 4 Mt of ashes per year, of which 65-85% is fly ash and 15-35% bottom ash [5,6]. The main uses of fly ash include pozzolanic cement, paving, and bricks. The bottom ashes are previously disaggregated and transported to the settling ponds through pumping hydraulic [7].

An alternative to reduce the environmental impact is the recycling, transforming the waste into a value-added product. The coal ashes can be converted into zeolites due to their high contents of silicon and aluminum. The synthesized zeolite can be used to remove toxic substances from contaminated waters [8-12].

The zeolite has hydrophilic nature and a net negative surface charge of zeolites. Therefore, this adsorbent has a good affinity toward inorganic pollutants, but little or no ability to remove organic pollutants. As is well known, the surface properties of zeolites may be greatly modified with cationic surfactant by simple ion-exchange reactions. One of the most commonly used surfactants for zeolite surface modification is hexadecyltrimethylammonium bromide (HDTMA-Br), because of its availability and low cost [13,14].

The surfactant-modified zeolite has been employed for removal of major categories of water contaminants [15]. Several studies reported the effective use of zeolite from fly ash for removing dye, but there are few reports in the literature for the zeolite from bottom ash.

This study presents the application of modified zeolite in treating colored wastewater. Coal fly and bottom ashes zeolites were synthesized by hydrothermal method, and were modified with cationic surfactant quaternary ammonium namely hexadecyltrimethylammonium. The removal of cationic dye Crystal Violet from aqueous solutions on the materials was evaluated. Adsorption kinetics and isotherm studies were undertaken to determine the adsorbate removal rate and the maximum adsorption capacity of the zeolites.

MATERIAL AND METHODS

The samples of coal fly (CFA) and bottom ashes (CBA) were collected in the Thermoelectric

Complex Jorge Lacerda, located in the Santa Catarina State, Brazil, the largest coal burning thermoelectric complex of Latin America. All chemicals used for experimental studies were of analytical grade. The quaternary ammonium salt hexadecyltrimethylammonium bromide with molar mass 364.46 g mol^{-1} (HDTMA-Br, Merck) was used. Crystal Violet (CV; CI 42555; $C_{25}H_{30}N_3Cl$; 408 g mol^{-1}), which was used as a model cationic dye in this work, was purchased from Proton-Research and considered as purity 100%. The chemical structure of CV is show in Figure 1. A stock solution of CV was prepared with deionized water (Millipore Milli-Q) and the solutions for adsorption tests were prepared by diluting it. Concentrations of the aqueous solutions of dye were monitored on UV/Visible spectrophotometer (Varian-Model Cary 1E) at 590 nm, the maximum of absorption peak of CV. The commercial grade zeolite 4A in the form of spheres (Bayer AG) was used in the study for comparison and was designated as ZBayer.

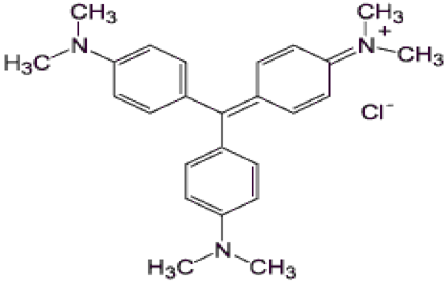

Fig. 1: Chemical structure of Crystal Violet

Synthesis of Surfactant-modified Zeolite from coal fly (ZFA) and bottom ashes (ZBA): The zeolite was synthesized by hydrothermal treatment. The coal fly or bottom ash (20 g) was mixed with 160 mL of 3.5 mol L^{-1} aqueous NaOH solution in a Teflon vessel. This mixture was heated to 100°C in oven for 24 h [16]. The zeolitic material was repeatedly washed with deionized water to remove excess sodium hydroxide until the washing water the pH~10, then it was dried at 50°C for 12 h. The modified zeolite was prepared by mixing of 10 g of ZFA or ZBA with 0.2 L of 1.8 mmol L^{-1} HDTMA-Br. The mixture of zeolite and HDTMA-Br solution was stirred for 7 h at 120 rpm and 25°C. The suspension was filtered and the solid was dried in oven at 50°C for 12h. The modified zeolites were labeled as MZSF and MZSB for zeolite prepared with fly ash and bottom ash, respectively. **Characterization of Materials:** The chemical composition of materials synthesized in this study (MZSF and MZSB) was determined by X-ray fluorescence (XRF) in a Rigaku RIX- 3000 equipment. The chemical composition and the some physicochemical properties of the coal ashes and unmodified zeolites have been described in a previous paper [17,18].

The mineralogical compositions of the modified zeolites and modified zeolites saturated with dye CV were determined by X-ray diffraction analyses (XRD) with an automated Rigaku multiflex diffractometer with Cu anode using Co K_α radiation at 40 kV and 20 mA over the range (2θ) of 5-80° with a scan time of 0.5°/min. The crystalline phases present in the materials zeolitics were identified with the help of ICDD (International Centre for Diffraction Data).

The bulk density and the specific surface area of the modified zeolites samples were determined by a helium picnometer (Micromeritcs Instrument

Corporation - Accupyc 1330) and by a BET Surface Area Analyser (Quantachrome Nova - 1200), respectively. Prior to determination of the specific surface area, the samples were heated at 423.15 K for 12 h to remove volatiles and moisture in a degasser (Nova 1000 Degasser). The BET surface areas were obtained by applying the BET equation to the nitrogen adsorption data.

The degree of hydrophobicity of the MZSF and MZSB was determined by a liquid-liquid partition (water/hexane). The procedure consisted of mixing 1 g of the adsorbent with 100 ml of water in a separation funnel. The mixture was stirred manually for 3 min. Then, 100 mL of hexane was added in the funnel and stirred for another 3 min. The resultant mixture was then let to stand for 5 min, the time required for separation of the phases. The quantity of material transferred to the organic phase was determined by filtration followed by drying and weighing. It calculated the solid mass transferred into the organic phase (m_{org}) using the equation 1:

$$m_{org}=m_0-m_{aquo} \tag{1}$$

where m_0 (g) is the initial mass of adsorbent and m_{aquo} (g) is a solid mass which was retained on the filter paper.

The values of the percent proportion used as the estimations of the degree of hydrophobicity of the adsorbents MZSF and MZSB were calculated based on the following equation:

$$\text{Degree of hydrophobicity (\%)} = \frac{m_{org}}{m_0} \tag{2}$$

For the determination of pH and conductivity, the samples of the modified zeolites (0.25 g) were placed in 25 mL of deionized water and the mixture was stirred for 24 h in a shaker at 120 rpm (Ética - Mod 430). After filtration, the pH of the solutions was measured with a pH meter (MSTecnopon - Mod MPA 210) and the conductivity was measured with a conductivimeter (BEL Engineering - Mod W12D).

The point of zero charge (pH_{PZC}) was determined as follows: the samples adsorbents (0.1 g) were treated with 50 mL of potassium nitrate solution (0.1 mol L^{-1}) and the mixtures were stirred for 24 h in the mechanical stirrer (Quimis - MOD Q-225M) at 120 rpm. The initial pH values of solutions were adjusted to the values of 2, 4, 10, 11, 12 and 13 by addition of 0.1 and 1 mol L^{-1} HCl or 3 mol L^{-1} NaOH solution. After 24 h, the mixtures were filtered and final pH values of the filtrates were measured again The difference values between the initial and final pH (pH Δ) were plotted, generating a graph in function of the initial pH. The point x where the curve intersects the y = 0 is the point of zero charge.

In cation exchange capacity (CEC) measurements, the samples MZSF and MZSB were saturated with sodium acetate solution (1 mol L^{-1}), washed with 1L of distilled water and then mixed with ammonium acetate solution (1 mol L^{-1}) [19]. The sodium ion concentration of the resulting solution was determined by optical emission spectrometry with inductively coupled plasma - ICP-OES (Spedtroflame - M120).

Adsorption studies: The adsorption studies were performed using batch process. The kinetic experiments for the adsorbents MZSF, MZSB and ZBayer with aqueous solution of CV were carried out by agitating (with a mass/volume of 0.01 mL g^{-1}) at 120 rpm for different time intervals (Table 1). All tests were performed at room temperature of 25°C ± 2°C. The collected samples were then centrifuged (3000 rpm during 60 min for MZSF and during 15 min for MZSB). The concentration in the supernatant solution was analyzed using a UV spectrophotometer (Cary 1E, Varian) by measuring absorbance at λ = 590 nm after pH adjustment to the value 5 (the pH of the dye aqueous solution) with HNO_3 0.05 mol L^{-1}.

Table 1: Concentration of CV and time interval in the adsorption kinetics study

Adsorbent	Initial concentration	Time of agitation (min)
MZSF	185	1 - 12
MZSB	185	2 - 20
ZBayer	63	1 - 20

The adsorption capacity (mg g^{-1}) of adsorbents was calculated using equation 3:

$$q = \frac{V(C_0 - C_f)}{M} \tag{3}$$

where q is the adsorbed amount of dye per gram of adsorbent, C_0 and C_f the concentrations of the dye in the initial solution and equilibrium, respectively (mg L^{-1}); V the volume of the dye solution added (L) and M the amount of the adsorbent used (g).

The efficiency of adsorption (or removal) was calculated using the equation:

$$R = 100 \times \frac{(C_0 - C_f)}{C_0} \tag{4}$$

where R is the efficiency of adsorption (%), C_o is the initial concentration of dye (mg L^{-1}), C_f is the equilibrium concentration of dye at time t (mg L^{-1}).

For the adsorption isotherms study, the modified zeolites and commercial zeolite with aqueous solution of CV were carried out by agitating of (with a mass/volume of 0.01 mL g^{-1}) over the concentration ranging from 23.4 a 579 mg L^{-1} for MZSF and MZSB and 24.4 a 236 mg L^{-1} for ZBayer till the equilibrium was achieved. The equilibrium time was determined from kinetic studies. The adsorption capacity (mg g^{-1}) of adsorbents was calculated according to equation 3.

Kinetic and Equilibrium Models: In order to investigate the adsorption processes of CV onto adsorbents, characteristic constants were determined using the linearized form of pseudo-first order (equation 5) and pseudo-second order (equation 6) and Elovich (equation 7) kinetic models with equations as follows:

$$\log_{10}(q_e - q) = \log_{10} q_e - k_1 t / 2.303 \tag{5}$$

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

where q_e is the amount of dye adsorbed at equilibrium (mg g^{-1}), q_t is the amount of dye adsorbed at time t (mg g^{-1}), $k_1$is the rate constant of the pseudo-first-order adsorption (min^{-1}), and k_2 is the rate constant of the pseudo-second-order kinetics (g mg^{-1} min^{-1}) [20, 21, 22]. The values of k_1 and q_e were obtained from the slope and intercept respectively of plot of *log* $(q_e - q_t)$ versus t for pseudo-first order model. The values of q_e and k_2 can be determined from the slope and intercept of a plot of t/q_t versus t, respectively for pseudo-second-order model.

The initial adsorption rate, h (mg g^{-1} min^{-1}), as t→0 can be defined as (equation 7):

$$h = k_2 q_e^2 \tag{7}$$

where k_2 is the rate constant of the pseudo-second order kinetics (g mg^{-1} min^{-1}) and q_e is the maximum adsorption capacity (mg g^{-1}). The Elovich model is satisfied in chemical adsorption processes and is suitable for systems with heterogeneous adsorbing surfaces [23]. The equation is given as follows [24,25]:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \qquad (8)$$

where α is the initial sorption rate (mg $g^{-1}min^{-1}$) and β is the desorption constant (mg g^{-1}). Thus, the constants can be obtained from the slope and intercept of a straight line plot of q_t versus *ln t*. The linearization of the equation giving the rate of reaction obtained the initial sorption rate, α from the intercept of a straight line plot of q_t versus ln *t*.

The equilibrium data obtained in the present study were analyzed using two different isotherm models, Langmuir (equation 9) and Freundlich (equation 10). The adsorption parameters were evaluated by using the linear and nonlinear regression methods of analysis.

$$q_e = \frac{(Q_0 \cdot b_L \cdot C_e)}{(1 + b_L \cdot C_e)} \quad \text{or} \quad \frac{C_e}{q_e} = \frac{1}{Q_0 b_L} + \frac{C_e}{Q_0} \qquad (9)$$

$$q_e = kf \cdot (C_e)^{1/n} \quad \text{or} \quad \log(q_e) = \log(kf) + \frac{1}{n}\log(C_e) \qquad (10)$$

where C_e is the equilibrium concentration (mg L^{-1}), q_e the amount adsorbed at equilibrium (mg g^{-1}), Q_0 is the maximum amount of adsorbate per unit weight of adsorbent to form a complete monolayer on the surface (mg g^{-1}); *b* is the Langmuir isotherm constant (L mg^{-1}), related to the affinity of the adsorption sites; k_f [(mg g^{-1}) (L m $g^{-1})^{1/n}$] and *n* are the Freundlich constants related to adsorption capacity and adsorption intensity of adsorbents, respectively.

In assessing the fit using linear analysis, the correlation coefficients are compared. The model that best fits the experimental data present value of R higher and closer to one. Besides the value of R, the Chi-square (χ^2) test was employed, the lowest values will be used to further validate the applicability of isotherms tested. This statistical analysis is based on the sum of the squares of the differences between the experimental and model calculated data, of which each squared difference was divided by the corresponding data obtained by calculating from models [26]. The Chi-square (χ^2) can be represented by:

$$\chi 2 = \sum \frac{(q_{e\,exp} - q_{ecal})^2}{q_{ecal}} \qquad (11)$$

where q_{eexp} is the equilibrium capacity of the adsorbent obtained from experiment (mg g^{-1}), and q_{ecalc} is the equilibrium capacity obtained by calculating from the model (mg g^{-1}).

RESULTS AND DISCUSSION

Characterization of the zeolitic materials: The chemical composition of the modified zeolites determined by X-ray fluorescence (XFR) is shown in Table 2. The chemical composition of the fly and bottom ashes and unmodified zeolites has been described in detail in previous paper [17, 18].

Table 1: Chemical composition of the modified zeolites

ELEMENTS	MZSF	MZSB
SiO_2	36	33
Al_2O_3	37	38
Fe_2O_3	8.5	13
Na_2O	8.7	8.0
CaO	3.4	2.7
TiO_2	2.7	2.0
MgO	1.6	1.4
SO_3	1.0	0.24
K_2O	0.8	0.7
Br	0.06	0.05
ZnO	0.09	0.02
ZrO_2	0.06	0.04
SiO_2/ Al_2O_3	0.97	0.87

The main constituents found for MZSF and MZSB are silica (SiO_2), alumina (Al_2O_3) and iron oxide (Fe_2O_3) (Table 2), similar to raw zeolitic material used as the starting material for the surface modification experiments. MZSF and MZSB exhibited also a significant amount of Na element when compared with fly and bottom ash due to hydrothermal treatment with NaOH solution. The bromide detected in the modified zeolites is the counterion present in the cation HDTMA adsorbed on the zeolite surface.

The SiO_2/Al_2O_3 ratio for zeolites is associated to the cation exchange capacity. MZSF and MZSB showed low values of the SiO_2/Al_2O_3 ratio (lower than 1.00) indicating materials with high cation exchange capacity [17].

The X-ray diffractograms of unmodified zeolite, modified zeolite and modified zeolite saturated with dye are shown in Figures 2 and 3, respectively.

The crystalline phases in all zeolitic materials were hydroxysodalite (JCPDS 31-1271) and NaX (JCPDS 38-0237) with peaks of quartz (JCPDS 85-0796) and mullite (JCPDS 74-4143) of ash that remained after the treatment. The mineralogical composition of ash used as raw material for the synthesis of zeolites depends on the geological factors related to the formation and deposition of coal and its combustion conditions.

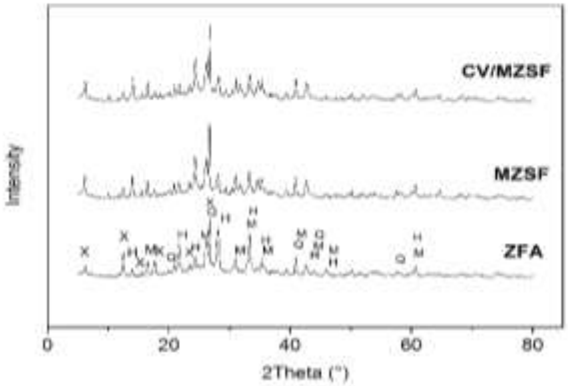

Fig. 2: The X-ray diffraction patterns of the unmodified zeolite from fly ash; modified zeolite from fly ash before and after CV adsorption (Q = Quartz; M = Mulitte; H = Hydroxysodalite zeolite, X = NaX zeolite)

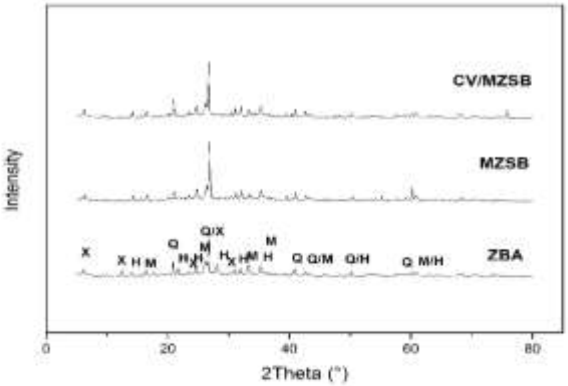

Fig. 3: The X-ray diffraction patterns of the unmodified zeolite from bottom ash, modified zeolite from bottom ash before and after CV adsorption (Q = Quartz; M = Mulitte; H = Hydroxysodalite zeolite, X = NaX zeolite)

The crystalline nature of the zeolitic materials remained intact after modification with HDTMA-Br as evidenced by structural parameters of MZSF and MZSB. It is also evident from the Figures 2-3 that there is no appreciable change in the spectra of adsorbents after CV molecules adsorption. The result suggests that when modified zeolitic materials get loaded by dye molecules the lattice structural not changed [27]. Some peaks for saturated zeolite have lower relative intensity than that for zeolite, which results from the adsorption of dye onto zeolite.

Some physicochemical properties of modified zeolites are given in Table 3. The same physicochemical properties for ZFA and ZBA are presented in previous paper [18].

Table 3: Physicochemical properties of the of zeolitic materials

PHYSICOCHEMICAL PROPERTIES	MZSF	MZSB
Bulk density (g cm^{-3})	2.38	2.49
BET surface área (m^2 g^{-1})	64	62
pH in water	8.3	8.5
pH$_{PZC}$^{a}	6.3	6.1
CEC (meq g^{-1})^b	1.61	1.49
Degree of hydrophobicity (%)	86	98

(a) point of zero charge; (b) cation exchange capacity

The bulk density values found for MZSF and MZSB were 2.38 and 2.49 g cm^{-3}, respectively. These values are very close to the value found for the unmodified zeolites in the previous study. The specific surface area values of ZFA and ZBA were 2 and 1.4 times greater than those MZSF and MZSB, respectively. This indicates that the surface of the zeolite was covered by the molecules of the HDTMA [27].

The CEC values obtained for the modified zeolites were very similar with the values of the ZFA (1.27 meq g^{-1}) and ZBA (1.19 meq g^{-1}). The CEC values of the zeolitic materials from fly ash were higher than bottom ash samples because CEC increase as the particle size of material becomes finer.

The values of the point zero charge (pH$_{PZC}$) of zeolites MZSF and MZSB (Table 3) were lower than pH in water indicating that the presented negative charge in aqueous solution (pH> pH$_{PZC}$) for both adsorbents. Variations in the pH$_{PZC}$ values of adsorbents may be attributed to factors such as Si/Al ratio, the nature of crystallinity, impurity content, temperature, adsorption efficiency of electrolytes, degree of adsorption of H$^+$ and OH$^-$ [28]. Among the factors that influence the pH$_{PZC}$ is also the concentration of surfactant used in surface modification. The change in relation to the pH$_{PZC}$ is related to the formations of monolayer or bilayer structure on the zeolite surface [29]. The negative charge of MZSF and MZSB indicated incomplete formation of bilayer of surfactant on the surface of zeolites.

The degree of hydrophobicity of the zeolite before and after the modification was estimated according to its partition between the water phase and a non-polar phase (hexane). The evaluation of this property is important since the interactions between the dye and water and the adsorbent are determining the adsorption rate. However, it is worth noting that the hydrophobicity estimate is a fast and easy test to verify the change of polarity of the material, and not had the objective quantify the degree of modification [30].

After the hydrophobicity pattern with the unmodified zeolites, 100% of the mass used was in the aqueous phase as expected. The high degree of hydrophobicity to the modified zeolites (Table 3) confirms that the surfactant is effectively adsorbed onto zeolite surface and MZSF and MZSB materials have, preferably, a greater interaction with organic compound that with water. This phenomenon was similar to those reported in [31], in the study of hydrophobic interaction between oil palm leaves modified and crude oil, and in [32], in the evaluation of the adsorption efficiency of an anionic surfactant (sodium dodecyl benzene sulfonate) on a natural zeolite modified.

Adsorption Studies: The effect of the contact time in the adsorption of the CV on MZSF, MZSB and ZBayer was investigated. Representative concentration-time profiles for the adsorption of CV dye on zeolitic materials are shown in Figure 4. The efficiency of dye removal was increased as the agitation time increased until equilibrium.

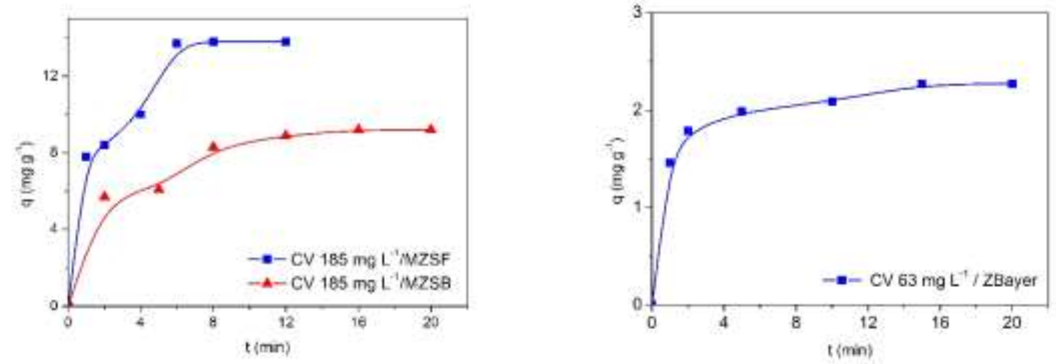

Fig. 4: Effect of contact time on the adsorption of CV onto MZSF, MZSB and ZBayer

Table 4 presents the kinetic data obtained at modified zeolites and commercial zeolite. The rapid removal of the dye and reach equilibrium in a short period of time is one of the indications that the adsorbent is efficiently and also allows the effluent treatment is more economical. As shown in Table 4, dye adsorption onto all the materials was very fast and the equilibrium was 6 min for MZSF, 16 min for MZSB, and 15 min for ZBayer. The organozeolites from coal ash presented better CV removal efficiency than the commercial zeolite. The adsorption studies of the ZFA and ZBA with CV have been described in detail in previous paper [18].

Table 4: Kinetics results for the adsorption of CV onto adsorbents

Adsorbent	Initial concentration of CV (mg L^{-1})	Equilibrium time (min)	Removal (%)
MZSF	185	6	77
MZSB	185	16	52
ZBayer	63	15	37

The result of better performance of the CV on the MZSF was expected because this material will have particles sizes smaller than the zeolite from coal bottom ash due granulometric characteristics of the ash sample that served as raw material. This also was observed in the study of unmodified zeolites. Thus, when the particle size of a material decreases, it increases the external surface area, meaning an increase in the number of active sites available for adsorption of adsorbate [33].

Kinetic models: The kinetics of adsorption of an adsorbate by any adsorbent is required for selecting optimum operating conditions for the full-scale batch process. Aiming at evaluating the adsorption kinetics of CV onto zeolites, the pseudo-first order, pseudo-second order and Elovich kinetic models were used to fit the experimental data, according to the kinetic model equations (3) to (6). The calculated constants of the three kinetics equations along with correlation coefficients, R values, are given in Table 5.

The comparison of the three selected kinetic models showed that pseudo-second order model with the highest correlation coefficient values best describe the adsorption process for all system studied. Moreover, the generated experimental (qe_{exp}) values of adsorption capacity were much closer to the theoretical values (qe_{calc}).

Table 5 presents also the kinetic parameters obtained from the Elovich model fitted to experimental data. Elovich model is used to describe second-order kinetic by assuming that the adsorbent surface is energetically heterogeneous. It was possible to observe that the initial adsorption rate (α) followed the order MZSF > MZSB, indicating that adsorption on modified zeolite from fly ash was faster than modified zeolite from bottom ash. The parameter β is related to the extent of surface coverage; the values found in this study for both modified zeolites are on the same order of magnitude.

Adsorption Isotherm: The adsorption isotherms of the CV on MZSF, MZSB, and ZBayer are shown in Figures 5 and 6. The experimental values and curves achieved from the values estimated by the Langmuir and Freundlich models from regressions linear and non-linear are presented

Table 5: Kinetic parameters for CV removal onto MZSF, MZSB and ZBayer

Adsorbents	CV ($mg\ L^{-1}$)	**Pseudo- first order**				
		k_1 $(min)^{-1}$	qe_{calc} ($mg\ g^{-1}$)	qe_{exp} ($mg\ g^{-1}$)	R_1	
MZSF	185	7.78×10^{-1}	23.5	13.8	0.878	
MZSB	185	2.63×10^{-1}	7.71	9.2	0.969	
ZBayer	63	1.53×10^{-1}	0.745	2.27	0.947	
		Pseudo- second order				
		k_2 ($g\ mg^{-1}min^{-1}$)	h ($mg\ g^{-1}min^{-1}$)	qe_{calc} ($mg\ g^{-1}$)	qe_{exp} ($mg\ g^{-1}$)	R_2
MZSF	185	4.37×10^{-2}	10.8	15.7	13.8	0.991
MZSB	185	4.25×10^{-2}	4.56	10.4	9.20	0.995
ZBayer	63	5.77×10^{-1}	3.19	2.35	2.27	0.999
		Elovich				
		α($mg\ g^{-1}\ min^{-1}$)	β ($g\ mg^{-1}$)	R_E		
MZSF	185	34.5	3.45×10^{-1}	0.938		
MZSB	185	18.9	5.67×10^{-1}	0.946		
ZBayer	63	95.0	3.85	0.982		

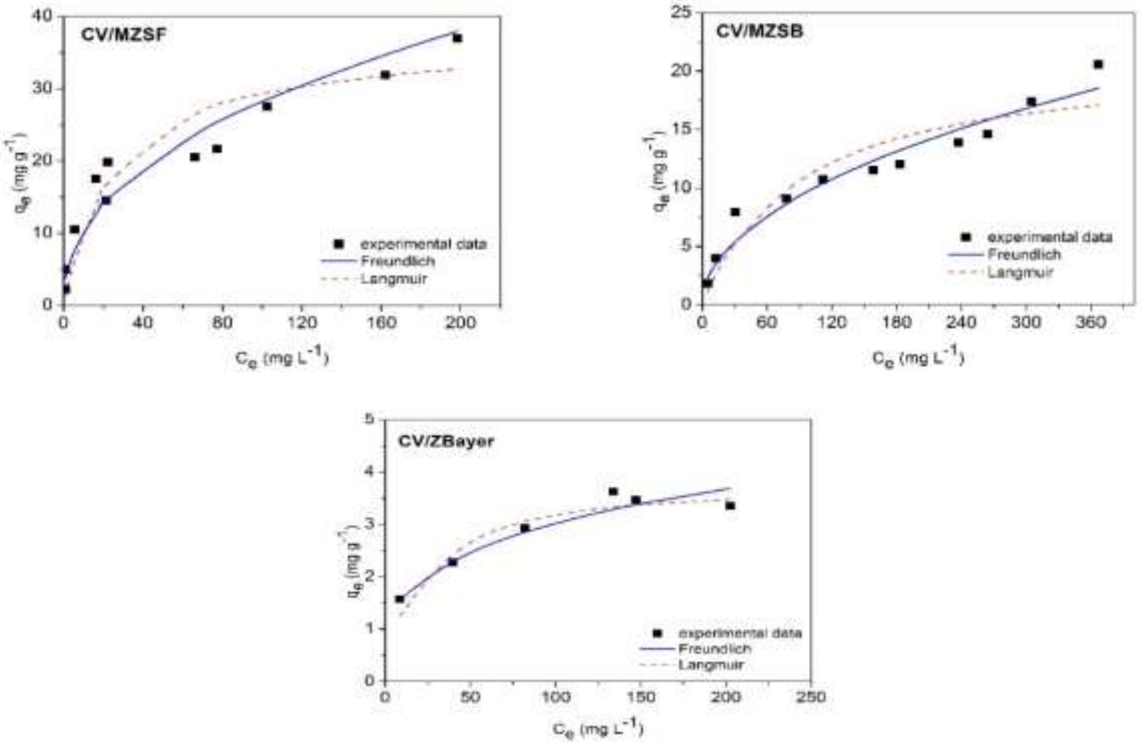

Fig. 5: Adsorption isotherm of CV onto the adsorbents (T = 25 ± 2°C) from the linear regression

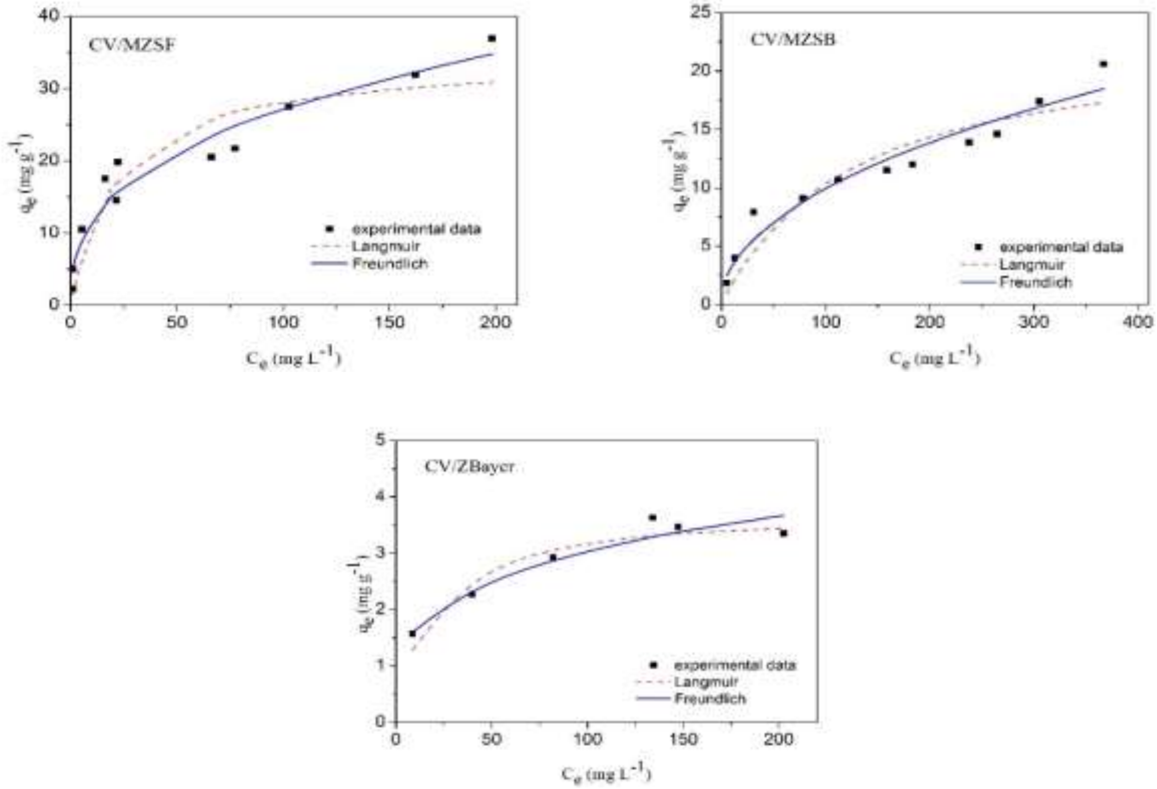

Fig. 6: Adsorption isotherm of CV onto the adsorbents (T = 25 ± 2°C) from the non-linear regression

The adsorption isotherm for solution may be classified into four main classes relating to their shapes termed S, L, H and C and subgroups 1, 2, 3, 4 or max. The curve presented in system CV/ZBayer have adapted to the class type L2, indicating the formation of a saturated monolayer of solute molecules on the surface of the adsorbent and adsorption affinity increases with increasing the concentration of the adsorbate to saturation. The equilibrium isotherms for the systems CV/MZSF and CV/MZSB showed curves corresponding to the class type L3, indicating a quick formation of a second adsorption layer [34].

The linear regressive method of least squares is used for finding the parameters of the isotherms. The relative parameters were obtained according to the intercept and slope from the linear plots. The non-linear regressive method of least sum squares of difference between calculated data and experimental data was used to determine the isotherm parameters with OriginPro 8.0. The isotherm parameters from linear method and non-linear method were all listed in Table 6, respectively.

Table 6: Langmuir and Freundlich isotherm parameters for CV adsorption on the adsorbents - comparison of linear and non-linear methods

Adsorbent	**Parameters**			
	Langmuir		**Freundlich**	
	Q_0 (mg g^{-1})	**b**	**k_f (mg g^{-1})(Lm g^{-1})$^{1/n}$**	**n**
Linear method				
MZSF	36.7	0.0413	4.03	2.36
MZSB	21.1	0.0116	1.07	2.07
ZBayer	3.77	0.0574	0.873	3.69
Non-linear method				
MZSF	34.1	0.0479	5.29	2.81
MZSB	22.9	0.00842	1.14	2.12
ZBayer	3.72	0.0614	0.911	3.81

It was observed (Table 6) that the maximum adsorption capacity (Q_0) of the CV/MZSF system was greater than the CV/MZSB system. This can be attributed to higher loading amount of surfactant molecules on the external surface of zeolite from fly ash than zeolite from bottom ash due their smaller particle size, as mentioned above.

The adsorption capacity of modified zeolites MZSF and MZSB was 9 and 6 times higher than the pure commercial zeolite, respectively. The observed difference was considered to be due mainly to the surfactant surface modification of zeolites from coal ash and the form of the commercial zeolite.

The adsorption capacities obtained for ZFA and ZBA in the previous study was 19.6 and 17.6, respectively [18]. Thus, the modified zeolites synthesized in this study were more efficient in CV adsorption. This is due to the partition mechanism, which will be described later.

After treatment with the modified zeolite, the effluent should not be discarded directly into water bodies, but can be used as non-potable water reuse. In Brazil, Resolution 54 of 2005 CNRH (Conselho Nacional de Recursos Hídricos) down rules, guidelines and criteria for the practice of water reuse for non-potable purposes. This reuse and / or recycling reduce the demand on water supplies due to the replacement of drinking water by less noble quality water. The non-potable reuse for industrial purposes can be applied to: processes, activities and industrial operations, dust abatement and cleaning in general.

The Table 7 shows the values obtained of the test Chi-square (χ^2) and the correlation coefficients for each isotherm of dye systems/adsorbent obtained from linear and non-linear methods. When the two models are compared, from the linear regression, is observed the largest correlation coefficient value (R) and the lowest values for χ^2. For comparison of the models from the non-linear regression are considered the lowest values of deviation estimate (test Chi-square (χ^2)).

Although the Langmuir model has provided correlation coefficient values near to unit, lower values for χ^2 were observed in Freundlich equilibrium model both linear fit, as in the nonlinear adjustment. Thus, it was confirmed statistically that the Freundlich model was the best fit to the experimental data to describe the adsorption process of CV onto zeolitic materials under study.

Table 7: Isotherm error deviation data related to the adsorption of CV onto the adsorbents

Adsorbent	**Models**			
	Langmuir		**Freundlich**	
	R	**χ^2**	**R**	**χ^2**
Linear method				
MZSF	0.969	16.9	0.954	5.89
MZSB	0.946	4.06	0.976	1.72
ZBayer	0.982	0.174	0.950	0.0716
Non-linear method				
MZSF	-	14.5	-	4.41
MZSB	-	5.96	-	1.64
ZBayer	-	0.160	-	0.0722

Adsorption mechanisms proposed: It is proposed that multiple mechanisms are involved in the adsorption of the CV on MZSF and MZSB due to the wide variety of functional groups that its molecules have and surface properties of the adsorbents material.

The zeolitic materials have negative charge in water as demonstrated by determining the pH_{PZC} (Table 3). Unmodified zeolites have a net permanent negative charge resulting from isomorphic substitution of Si^{4+} by Al^{3+} in their crystal structures. Modified zeolite has a negative charge due the formation of incomplete of bilayer of surfactant on the surface.

The partition of the cationic CV dye within the group "tail" hydrophobic of the surfactant molecule on the modified zeolites is a mechanism involved in adsorption.

Addition to the hydrophobic interaction, the electrostatic interaction between the cationic dye (due to the presence of (-N + (CH3) 2)group) and negatively charged surface, the cation exchange, and the complexation with species of Si and Al of the zeolite hey are also acting in the adsorption mechanism on MZSF and MZSB [35].

Designing batch adsorption from equilibrium data: The adsorption isotherms can be used to predict the design of single stage batch adsorption systems [36, 37]. The schematic diagram is shown in Figure 7.

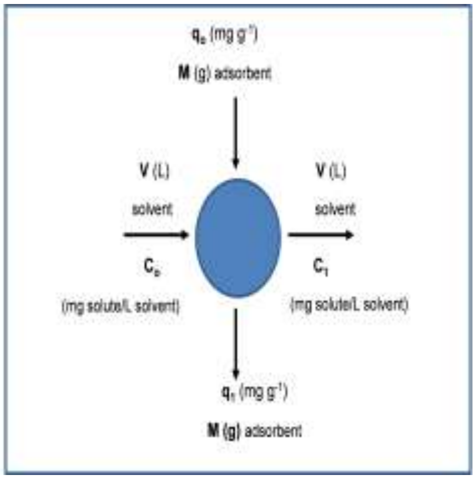

Fig. 7: Schematic representation of the single stage batch adsorber system

The design objective is to reduce the initial concentration C_o (mg L^{-1}) of the dye solution volume V (L) to the concentration C_1 (mg L^{-1}). The amount of adsorbent is M (g) and the solute loading changes from q_0 to q_1 (mg g^{-1}) adsorbent. At initial time (t = 0), $q_o = 0$ and as time passes, the mass balance equates the dye removed from the liquid to that picked up by the solid. The mass balance equation of the adsorption system can be written as:

$$V(C_0 - C_1) = M(q_0 - q_1) = Mq_1 \qquad (12)$$

If the system is allowed to come to equilibrium, then,

$C_1 \rightarrow C_e$ and $q_1 \rightarrow q_e$

Equation (12) can be rearranged as:

$$\frac{M}{V} = \frac{(C_0 - C_e)}{q_1} = \frac{C_0 - C_e}{q_e} = \frac{C_0 - C_e}{\frac{q_0 k_L C_e}{1 + k_L C_e}} \qquad (13)$$

where *q* can be obtained by the equation of the isotherm that fit best to experimental data. In the example, is the Langmuir equation.

In this study, the isotherm model Freundlich gives the best fit to experimental data. Therefore, the equation (10) can be applied for the calculation of *q*. A series of graphs for adsorption CV on the adsorbents synthesized in this work are shown in Figure 8. The initial concentration of CV of 100 mg L^{-1} was arbitrarily chosen for the purposes of the calculation of the quantities necessary of adsorbent to reduce the color (80, 85, 90 and 95% dye removal) in various volumes of effluents.

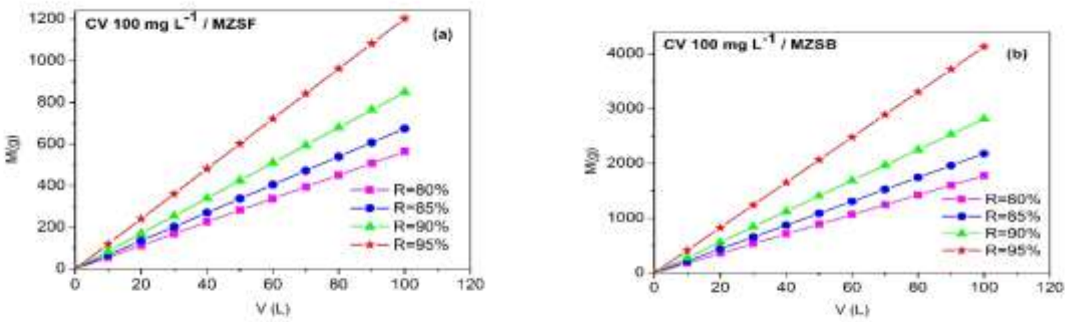

Fig. 8: Adsorbent mass ratio with the volume of the treated solution; (a) CV/MZSF; (b) CV/MZSB

The amount of adsorbent required increased with the volume of solution to be treated. According illustrate the Figure 8 (a), one can conclude that to remove 90% of the CV the amount of MZSF required will be 425, 509, 594, 679 g for volumes of 50, 60, 70, and 80 liters, respectively, for example. For the MZSB (Figure 8 (b)), the amount required to remove 90% of CV will be with 1406, 1688, 1969, 2250 g for volumes of 50, 60, 70, and 80 liters, respectively.

The procedure is outlined in the adsorption system batch process of a single stage and may be modeled for other initial concentrations of the dyes, removal rates and volumes of effluent.

CONCLUSION

In the present work, it was found that the modified zeolites synthesized from coal fly (MZSF) and bottom ash (MZSB) showed high adsorption capacities for Crystal Violet (CV), a cationic dye, from aqueous solutions. Mathematical models were developed for the adsorption of CV onto modified zeolites using kinetic data obtained experimentally via batch processes. The pseudo-second order kinetic model agrees very well with the dynamic behavior for the adsorption of CV onto adsorbents. Linear and non-linear regressions were compared in this study to determine the preferred adsorption model. The Freundlich model was the most appropriate for fit of the equilibrium experimental data. The data from single-stage optimization models suggest that it will be useful for the design of adsorption plant for large-scale adsorption of Crystal Violet by MZSF and bottom ash MZSB from wastewater. Compared to commercial grade zeolite 4A, the modified zeolites from coal ash prepared adsorbents could be alternative materials for the treatment of wastewater.

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