

# Surfactant Modified Zeolite from Cyclone Ash as Adsorbent for Removal of Reactive Orange 16 from Aqueous Solution

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**Abstract** Zeolite synthesized from cyclone ash (ZCA) was modified with various loadings of hexadecyltrimethylammonium bromide (HDTMA-Br) and was used as adsorbent to remove Reactive Orange 16 (RO16), an azo reactive dye, from aqueous solution. The RO16 adsorption efficiencies for ZCA and surfactant-modified zeolites from cyclone ash (SMZCAs) were compared. SMZCAs presented higher RO16 adsorption efficiency than ZCA, and SMZCA with higher loading amount of HDTMA-Br exhibited higher RO16 adsorption efficiency. A series of experiments was conducted to examine the effects of contact time, solution pH, and adsorbent dosage on dye removal. The adsorption kinetic of RO16 onto adsorbents was discussed using the pseudo-first order, pseudo-second order and intra-particle diffusion models, and the pseudo-second order model provided the best correlation of the experimental data. The equilibrium adsorption data were well represented by Langmuir isotherm model with maximum adsorption capacity of 0.58 and 12.6 mg g<sup>-1</sup> for ZCA and SMZCA, respectively. The toxicity tests of dye solutions before and after the adsorption treatment were evaluated with *D. similis* and *V.fischeri*.

**Keywords:** reactive azo dye; cyclone ash, zeolite, cationic surfactant

## 1. Introduction

In Brazil, the coal used in power plants is pulverized and burned inside a boiler, producing bottom ash (15-20 wt.%) of the bulk solid combustion-by-products produced, which falls inside the boiler, and fly ash (80-85 wt.%) [1]. The fly ash is a fine-grained, powdery particulate material that is carried off in the flue gas and usually collected from the flue gas by means of electrostatic precipitators, baghouses, or mechanical collection devices such as cyclones [2].

Cyclones are low-cost, low-maintenance centrifugal collectors that are typically used to remove particulates in the size range of 10-100 microns. The cyclone fly ash is the ash fraction that has been carried through the flue gas channels into the cyclone and precipitated there. Technically speaking, cyclone ash is the ash fraction that has been trapped in the cyclone.

During combustion most of the heavy metals in the fuel are retained in the ash. The various ash fractions such as bottom ash, cyclone ash and baghouse filter ash may contain relatively high concentrations of heavy metals [3]. Combustion acts like a thermodynamic separation process for the different inorganic materials in the fuel. Elements with a low volatility will concentrate in the bottom ash, while more volatile elements will concentrate in the fly ash [4]. The consequence of this separation effect in combustion plants is that the different ash fractions have a different chemical composition. Before ash residue can be

utilized or disposed of in a landfill, its chemical as well as extraction (leaching) characteristics must be known.

Fly ash from baghouse filter produced in the Brazilian power plant is mostly recycled as cement raw material to be used in civil engineering materials. However, cyclone ash does not find at present time a commercial application; rather, it is usually stored in abandoned surface mine or dumped in landfills in the vicinity of the power plant.

The main drawback of coal-fired power plants in Brazil is the high production of ash. The synthesis of zeolites has produced an environmentally friendly and economically viable way of recycling coal fly ash. The initial findings indicate that zeolite synthesized from Brazilian fly ash used as low cost adsorbent has high adsorptive capacity for dyes from water [5,6,7].

It is known that although zeolites have little affinity toward organic pollutants, permanent negative charges in their crystal structures enable them to be modified by cationic surfactants so that they better retain organic pollutants [8,9,10].

The most commonly used surfactant for zeolite surface modification is hexadecyltrimethylammonium bromide (HDTMA-Br), in which each molecule is composed of a hydrophilic and positively charged head group, and a hydrophobic tail. HDTMA-Br may form monolayers and/or bi-layers on the zeolite surface [11,12,13,14,15].

It is proposed that cyclone ash be used as raw material for zeolite synthesis. To the best of the authors' knowledge, the preparation of surfactant-modified zeolite synthesis from cyclone ash and the removal of dyes by this adsorbent have never been reported. Cyclone ash

samples contained larger particles than fabric filter and electrostatic precipitator ash samples and showed lower cytotoxicity, very little mutagenicity and lower concentrations of trace elements [1,16].

Reactive Orange 16 (RO16) is one of the reactive azo dyes most intensively produced and used globally. High water solubility, excellent coloring properties and covalent bonding with both natural and synthetic textile fibers are the major advantages of this dye class. The reactive dyeing process is accompanied by the loss of 10-50% of the dye due to a hydrolysis reaction involving the vinyl group (dye) under alkaline dyeing conditions, giving rise to a highly colored effluent [17].

Comparative use of bacterial, algal and protozoan tests to study toxicity of various dyes was evaluated. RO16 was the only dye tested that exhibited mutagenic effects in both the presence and absence of metabolic activation, which indicated that both substitution and frameshift mutations were induced by the compound acting like a direct and indirect mutagen [18].

In a previous paper [19] it was proposed, the use of zeolite from fly ash collected in baghouse filter as an adsorbent for the removal of reactive orange 16 from aqueous solution. Continuing the application of this adsorbent, in the present work, we investigated the adsorption capacities of surfactant-modified zeolite from cyclone fly ash. This study helps to understand the adsorption properties and potential applications of unmodified and modified zeolites for dye removal from aqueous environments.

## 2. Experimental

### 2.1. Materials

All the reagents used for experimental studies were of analytical grade. The samples of coal fly ash from cyclone filter (CCA) were obtained from a coal-fired power plant located at Figueira County, in Paraná State, Brazil. The quaternary ammonium salt hexadecyltrimethylammonium bromide (HDTMA-Br, Merck), with molar mass  $364.46 \text{ g mol}^{-1}$  and minimum 99% active substance, was used. Reactive Orange 16 dye (RO16; C.I. 17757;  $\text{C}_{20}\text{H}_{17}\text{N}_3\text{Na}_2\text{O}_{11}\text{S}_3$ ;  $617.54 \text{ g mol}^{-1}$ ;  $\lambda_{\text{max}} = 493 \text{ nm}$ ) was obtained from Sigma-Aldrich with a dye content of 50% and was used without further purification. A stock solution of RO16 was prepared in double distilled water 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). As shown in Figure 1, RO16 has two sulfonate groups, which have negative charges in aqueous solution.

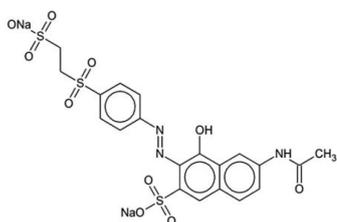


Figure 1. Chemical structure of Reactive Orange 16

### 2.2. Synthesis of Surfactant-modified Zeolite from Cyclone Fly Ash

CCA (30g) was mixed with 240mL of  $3.5 \text{ mol L}^{-1}$  aqueous NaOH solution in a 300mL Teflon vessel. This mixture was heated to  $100 \text{ }^\circ\text{C}$  in oven for 24h. After finishing of the process, the suspension was filtered with 4A quantitative filter paper. The zeolite from cyclone fly ash (ZCA) was repeatedly washed with deionized water until the pH of washing water reach  $\sim 11$  and dried at  $50 \text{ }^\circ\text{C}$  for 12h [20]. Twenty-five grams of ZCA were mixed with 0.5L of HDTMA-Br solution at varied concentrations ranged between  $0.9 \text{ mmol L}^{-1}$  and  $20 \text{ mmol L}^{-1}$ . The mixture of zeolite and HDTMA-Br solution was stirred for 7 h at 120rpm and  $25 \text{ }^\circ\text{C}$ . The suspension was filtered and the solid was dried in oven at  $50 \text{ }^\circ\text{C}$  for 12h [11]. Zeolites modified with 0.9, 1.8, 9.0, and  $20 \text{ mmol L}^{-1}$  of HDTMA-Br solutions were named as SMZCA-0.9, SMZCA-1.8 and SMZCA-20, respectively. SMZCA-20 was selected for characterizations.

### 2.3. Characterization of Materials

Instrumental neutron activation analysis (INAA) was used to determine concentrations of elements of materials. About 100mg of CCA, ZCA, SMZCA-20 and reference material were weighted in polyethylene bags. The accuracy of the results was determined using IAEA standard reference material SOIL-7. For irradiation, the samples, reference material and element standards were simultaneously submitted to a thermal neutron flux in the range of  $3.5$  to  $5.0 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$  for 8 h at the nuclear research reactor IEA-R1 of the Nuclear and Energy Research Institute, (IPEN/CNEN-SP), São Paulo, Brazil. After appropriate decay periods,  $\gamma$ -ray spectra of samples, reference material and element standards were measured using High-purity Ge (HPGe) detector Model POP-TOP (EG&G Ortec, Oak Ridge, TN, USA). This detector was coupled to an EG&G Ortec card and associated electronics. Spectrum analysis was carried out using VISPECT software, in TURBOBASIC language. The particle size of the materials was measured using a laser based particle size analyzer, namely a Malvern MSS Mastersizer 2000 Ver. 5.54.

### 2.4. Adsorption Studies

The adsorption was performed using the batch procedure. Kinetic experiments were carried out by shaking 0.1g of adsorbents ZCA and SMZCA-20 with 10mL of RO16 solutions with an initial concentration of  $25 \text{ mg L}^{-1}$  at room temperature ( $25 \pm 2 \text{ }^\circ\text{C}$ ) in a shaker operated at 120rpm for 1-150min in glass bottles. The samples were withdrawn from the shaker at different time intervals, centrifuged and the concentration in the supernatant solution was determined. For adsorption isotherms, RO16 solutions of different concentrations ranging from 25 to  $125 \text{ mg L}^{-1}$  for SMZCA-20 and 2.0 to  $14.0 \text{ mg L}^{-1}$  for ZCA were agitated till the equilibrium was achieved at room temperature ( $25 \pm 2 \text{ }^\circ\text{C}$ ). Each experiment was duplicated under identical conditions with maximum deviation was found to be 3%.

The effect of the adsorbent dosage was tested by mixing 0.02-0.2g SMZCA-20 with 10mL of RO16 solution at  $50 \text{ mg L}^{-1}$  for 60min. The effect of pH on

adsorption of dye onto SMZCA-20 was determined over the pH range of 2 to 10.5 at an initial RO16 concentration of 50mg L<sup>-1</sup> and the pH was adjusted by adding 0.1 or 0.01mol L<sup>-1</sup> of HNO<sub>3</sub> or NaOH.

The amount of the dye uptake and percentage of dye removal by the adsorbent were calculated by applying Eqs. (1) and (2), respectively:

$$q_t = \frac{(C_0 - C_t)V}{M} \quad (1)$$

$$R(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

where  $q_t$  is the adsorbed amount of adsorbate per gram of adsorbent at any time  $t$  (mg g<sup>-1</sup>),  $C_0$  and  $C_t$  the concentrations of the adsorbate in the initial solution and at any time  $t$ , respectively (mg L<sup>-1</sup>);  $V$  the volume of the adsorbate solution added (L) and  $M$  the amount of the adsorbent used (g).

#### 2.4.1. Kinetic and Equilibrium Models

In order to investigate the mechanism of adsorption, characteristic constants were determined using the linearized form of pseudo-first order (Eq. 3) and pseudo-second order (Eq. 4) kinetic models with equations as follows:

$$\log(q_e - qt) = \log q_e - \frac{k_1 t}{2.303} \quad (3)$$

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} - \frac{1}{q_e} t \quad (4)$$

where  $q_e$  is the amount of dye adsorbed at equilibrium (mg g<sup>-1</sup>),  $qt$  is the amount of dye adsorbed at time  $t$  (mg g<sup>-1</sup>),  $k_1$  is the rate constant of the pseudo-first-order adsorption (min<sup>-1</sup>), and  $k_2$  is the rate constant of the pseudo-second-order kinetics (g mg<sup>-1</sup> min<sup>-1</sup>) [21,22,23]. The values of  $k_1$  and  $q_e$  were obtained from the slope and intercept respectively of plot of  $\log(q_e - qt)$  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  $t/qt$  versus  $t$ , respectively for pseudo-second-order model.

The initial adsorption rate,  $h$  (mg g<sup>-1</sup> min<sup>-1</sup>), as  $t \rightarrow 0$  can be defined as (equation 5):

$$h = k_2 q_e^2 \quad (5)$$

where  $k_2$  is the rate constant of the pseudo-second order kinetics (g mg<sup>-1</sup> min<sup>-1</sup>) and  $q_e$  is the maximum adsorption capacity (mg g<sup>-1</sup>).

The kinetic results were analyzed by the intraparticle diffusion model to elucidate the diffusion mechanism, which model is expressed as [24]:

$$qt = k_{id} t^{0.5} + C \quad (6)$$

where  $k_{id}$  is the intraparticle diffusion rate constant (mg g<sup>-1</sup> min<sup>-0.5</sup>). According to Eq. (6), a plot of  $qt$  versus  $t^{0.5}$  should be a straight line with a slope  $k_{id}$  and intercept  $C$  when adsorption mechanism follows the intraparticle diffusion process.

The equilibrium data obtained in the present study were analyzed using the linear forms of the expressions of

Langmuir (Eq (7)) and Freundlich (Eq (8)) isotherm models:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (7)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (8)$$

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

The non-linear regression Chi-square ( $\chi^2$ ) test, represented by Eq. (9), was employed as a criterion for the fitting quality due to the inherent bias resulting from linearization of isotherm models [25].

$$\chi^2 = \sum \frac{(q_e \text{ exp} - q_e \text{ calc})^2}{q_e \text{ calc}} \quad (9)$$

where  $q_e \text{ exp}$  is the equilibrium capacity of the adsorbent obtained from experiment (mg g<sup>-1</sup>), and  $q_e \text{ calc}$  is the equilibrium capacity obtained by calculating from the model (mg g<sup>-1</sup>). A low value of  $\chi^2$  indicates that experimental data fit better to the value from the model.

## 2.5. Toxicity Assessments

Young individuals of *Daphnia similis* were exposed to different concentration of dye (from 6.25mg L<sup>-1</sup> to 100.0mg L<sup>-1</sup>), during 48h. The concentrations that could lead to the immobilization of 50% of the organisms (EC<sub>50</sub>) were calculated from the number of immobile organisms per sample concentration and by applying statistical tests with the program Trimmed Spearman Karber [26]. The experiment with the bioluminescent bacteria *Vibrio fischeri* was performed with the Microtox System, model M-500 from Microbics, exposing the samples to concentrations between 10.23mg L<sup>-1</sup> and 81.90mg L<sup>-1</sup> during 15min. The statistical analysis was carried out with proper statistics program by Microbics (version 7.82), that calculates the values of EC<sub>50</sub> based on the reduction of the 50% of light emitted by the microorganism after exposure [27].

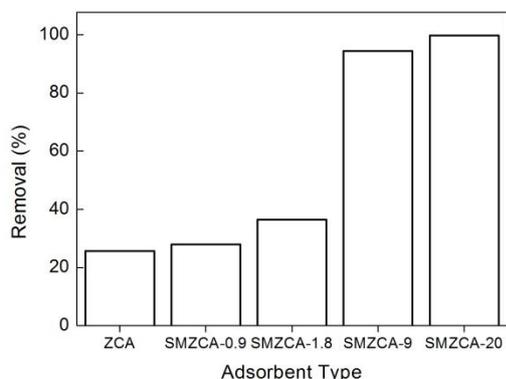
## 3. Results and Discussion

### 3.1. Effect of Initial Surfactant on Dye Adsorption

In order to investigate the effect of HDTMA concentration on removal of RO16 HDTMA concentration was used as 0.9, 1.8, 9.0 and 20mmol L<sup>-1</sup> while initial RO16 concentration was 10 mg L<sup>-1</sup>. As it can be seen from Table 1 and Figure 2, with augmentation of HDTMA, removal efficiency of RO16 enhanced and maximum dye removal was observed at 20mmol L<sup>-1</sup> surfactant concentration.

**Table 1. Effect of surfactant loading on fly ash based zeolites on percentage removal of RO16**

Adsorbent Type	[HDTMA-Br] (mmol L <sup>-1</sup> )	Removal (%)
ZCA	0	25.6
SMZCA-0.9	0.9	27.9
SMZCA-1.8	1.8	36.4
SMZCA-9	9.0	94.4
SMZCA-20	20	99.8

**Figure 2.** RO16 percentage removal by different adsorbents Chemical structure of Reactive Orange 16

Thus treatment of zeolite with initial concentration of 20mmol L<sup>-1</sup> of surfactant appears to be the optimal loading for RO16 removal and was selected to be used in remaining experiments. The theoretical critical micelle concentration (CMC) of HDTMA-Br is about 0.9mmol L<sup>-1</sup> [10] and this initial concentration exceeds the critical micelle concentration of the surfactant. It is therefore envisaged that these micelles attach as such to the external surface and then rearrange to form a patchy mono-layer and/or bi-layers that tends to impart anionic exchange and hydrophobic characteristics to the adsorbent [11].

### 3.2. Characterization of the Materials

The characterizations of ZCA and SMZCA-20 have been described in detail in previous paper [11]. Some important physicochemical characteristics of ZCA and SMZCA-20 materials with respect to this study are shown in Table 2.

The XRD analyses of two zeolitic materials showed that hydroxysodalite (ICDD 00-011-0401) was the major zeolitic phase with peaks of quartz (ICDD001-0649) and mullite (ICDD002-0430) of fly ash that remained after the alkaline hydrothermal treatment. The structural parameters of SMZCA-20 are very close to that of corresponding parent zeolite which indicate that the crystalline nature of the zeolite material remained intact after required chemical treatment with HDTMA molecules and heating treatment for drying [11].

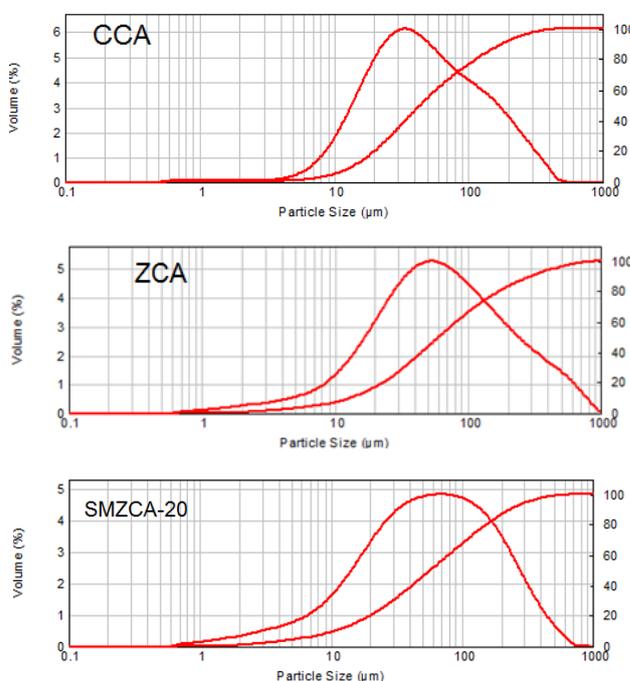
Laser granulometric analysis results for CCA, ZCA and SMZCA-20 samples are reported both as absolute and cumulative volumetric distributions (Figure 3). The particle size distributions of materials are given in Table 3. These distributions specify that the majority of particles (90%) lie below 174.8, 291.8 and 230.0 $\mu$ m in case of CCA, ZCA and SMZCA-20, respectively. The Sauter mean diameter ( $D_{[3,2]}$ ) was 24.3  $\mu$ m for CCA, 23.9  $\mu$ m for ZCA and 20.7  $\mu$ m for SMZCA-20. The  $D_{[3,2]}$  values are indicative of the active surface area of the materials, therefore based on these results it would seem appropriate to consider SMZCA-20 as having better adsorption

potential than others materials. The particle size of the modified zeolite is as a function of the amount and the molecular size of surfactant added.

**Table 2. Physicochemical properties of zeolite from cyclone ash and modified-zeolite**

	ZCA	SMZCA-20
SiO <sub>2</sub> (wt. %)	39.5	26
Al <sub>2</sub> O <sub>3</sub> (wt. %)	25	11.6
Fe <sub>2</sub> O <sub>3</sub> (wt. %)	16.6	45
CaO (wt. %)	2.68	5
Br (wt. %)	n.a	4.2
TiO <sub>2</sub> (wt. %)	1.17	2.9
SO <sub>3</sub> (wt. %)	1.05	1
Na <sub>2</sub> O (wt. %)	11.8	0.78
Others (wt. %)	1.8	1.76
pH in water	9.23	8.87
pH <sub>PZC</sub>	9.04	8.44
Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	39	14.6
CEC (meq 100 g <sup>-1</sup> )	137.6	-
ECEC (meq 100 g <sup>-1</sup> )	39.7	-

n.a.= data not available; pH<sub>PZC</sub> = point of zero charge; CEC = cation exchange capacity; ECEC = external cation exchange capacity

**Figure 3.** Particle size distribution of CCA, ZCA and SMZCA-20**Table 3. Particle size distributions of materials**

Sample	D <sub>10</sub> ( $\mu$ m)	D <sub>50</sub> ( $\mu$ m)	D <sub>90</sub> ( $\mu$ m)
CCA	13.579	43.624	174.833
ZCA	12.965	59.928	291.832
SMZCA-20	10.449	57.092	230.022

Fly ash has a broad size distribution with diameters spanning more than three orders of magnitude. The median diameters of ash samples from six representative coals collected in cyclones and baghouses of american coal fired power plants were between 1.2-3.4  $\mu$ m and 0.4-1.2  $\mu$ m, respectively [28].

The grain size distribution of fly ash sample from a Brazilian power plant (Presidente Medici Power Plant or UTPM-446 MW) collected from electrostatic precipitator was determined. The continuous interval of particle sizes was between 0.5 and 600  $\mu$ m, and the average diameter was 49.30  $\mu$ m. Ninety percent of the particles have diameters smaller than 232  $\mu$ m, while the finest particles

(< 5  $\mu\text{m}$ ) correspond to  $\sim 1\%$  of the total mass of the sample [29].

Table 4 presents the trace elemental concentration in CCA, ZCA and SMZCA-20 samples obtained by instrumental neutron activation analyses. A considerable reduction in the elements contents was attained in the fly ash zeolitization for arsenic and zinc that decreased between 86-90% and 16-25%, respectively. A significant amount of Na element is incorporated in the zeolitic products after hydrothermal treatment with NaOH solution due to entrapment of sodium ions to neutralize the negative charge on aluminosilicate gel [30]. The presence of bromide in the modified zeolitic material was detected. The positive charge of cation HDTMA adsorbed on the surface of the zeolite is counterbalanced by anions bromide. The other elements are present in approximately the same amount in the three samples.

**Table 4. Chemical elements in CCA, ZCA and SMZCA-20 samples analyzed by INAA**

Element	Concentration ( $\mu\text{g g}^{-1}$ )		
	CCA	ZCA	SMZCA-20
As	632 $\pm$ 95	64 $\pm$ 7	86 $\pm$ 3
Br	< dl	4.0 $\pm$ 1.2	5060 $\pm$ 1320
Co	24.0 $\pm$ 0.1	26.4 $\pm$ 0.8	24.7 $\pm$ 0.5
Cr	93 $\pm$ 6	103 $\pm$ 6	79 $\pm$ 23
Eu	4.1 $\pm$ 0.1	4.6 $\pm$ 0.1	4.3 $\pm$ 0.1
Fe	95100 $\pm$ 4076	100973 $\pm$ 4538	88549 $\pm$ 13299
La*	121 $\pm$ 4	147 $\pm$ 147	145 $\pm$ 4
Na	8293 $\pm$ 50	76884 $\pm$ 530	63435 $\pm$ 270
Sb	8.3 $\pm$ 0.4	2.5 $\pm$ 0.5	2.2 $\pm$ 0.6
Sc	25.8 $\pm$ 0.6	27.5 $\pm$ 0.7	25 $\pm$ 3
Sm	19 $\pm$ 1	19.3 $\pm$ 0.3	24 $\pm$ 1
Th	23.9 $\pm$ 1.1	26.5 $\pm$ 0.7	20 $\pm$ 3
U	227 $\pm$ 11	256 $\pm$ 29	266 $\pm$ 9
Zn	822 $\pm$ 82	689 $\pm$ 1	620 $\pm$ 1

(1) Mean and standard deviation of two determinations; (\*) element that can be fission products; dl = detection limit

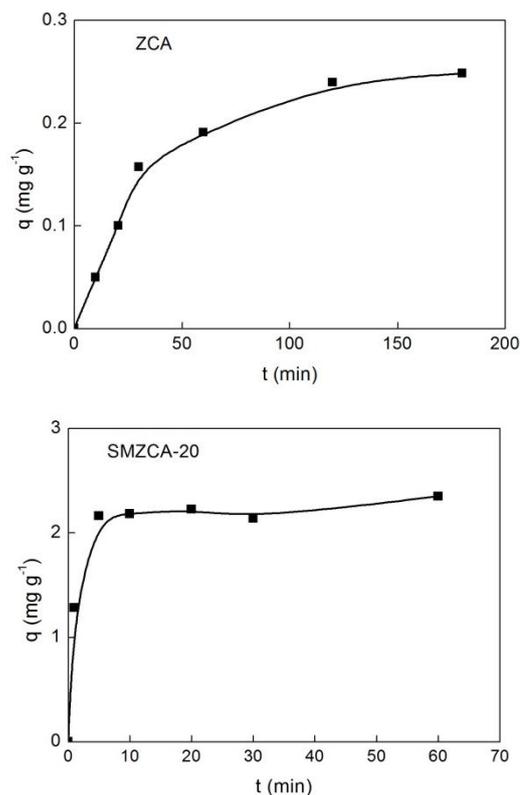
The high concentrations of As, Fe and Zn are due to the high content of pyrite of the feed coal. Concentrations of U are relatively high because the area near Figueira coal-fired power plant is rich in uranium, with an average of 0.148%  $\text{U}_3\text{O}_8$  in calcitic sandstone above the coal seam [1,31].

### 3.3. dsorption Knetics

To determine the equilibration concentration and time, the adsorption of the RO16 onto zeolites was studied as a function of contact time. These experiments were performed against time (range 10-80min for ZCA and 1-60min for SMZCA-20) and the effect of equilibrium time on the adsorption of RO16 onto the unmodified and modified zeolites is presented in Figure 4.

It should be pointed out that apparent equilibrium was reached after 120min for ZCA. The adsorption of RO16 onto modified zeolite was almost instantaneous and an apparent equilibrium was reached within the first 5min. The adsorption capacities of unmodified zeolite are low and when zeolite was modified with HDTMA-Br, the

adsorption capacities were increased remarkably. The degree of removal of RO16 was 100% for concentrations < 25.0mg  $\text{L}^{-1}$  using SMZCA-20.



**Figure 4.** Influence of equilibrium time on the adsorption of RO16 on ZCA and SMZCA-20

It is important to be able to predict the rate at which contamination is removed from aqueous solutions in order to design an adsorption treatment plant. Aiming at evaluating the adsorption kinetics of RO16 onto zeolites, the pseudo-first order, pseudo-second order and intraparticle diffusion kinetic models were used to fit the experimental data, according to the kinetic model equations (3) to (6). The values of kinetic constants for RO16 adsorption onto unmodified zeolite and surfactant-modified zeolite are presented in Table 5.

**Table 5. Kinetic parameters for the removal of RO16 by zeolite from cyclone ash and surfactant-modified zeolite**

	ZCA	SMZCA-20
Pseudo- first order		
$K_1$ ( $\text{min}^{-1}$ )	$2.66 \times 10^{-2}$	$2.36 \times 10^{-2}$
$q_{\text{calc}}$ ( $\text{mg g}^{-1}$ )	0.232	0.0339
$q_{\text{exp}}$ ( $\text{mg g}^{-1}$ )	0.229	2.35
$R_1$	0.989	0.579
Pseudo- second order		
$K_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	$13.2 \times 10^{-2}$	$39.4 \times 10^{-2}$
$h$ ( $\text{mg g}^{-1} \text{min}^{-1}$ )	0.0109	2.18
$q_{\text{calc}}$ ( $\text{mg g}^{-1}$ )	0.286	2.36
$q_{\text{exp}}$ ( $\text{mg g}^{-1}$ )	0.229	2.35
$R_2$	0.999	0.999
Intraparticle diffusion		
$C$ ( $\text{mg g}^{-1}$ )	0.0965	0.955
$K_i$ ( $\text{mg g}^{-1} \text{min}^{-0.5}$ )	$1.198 \times 10^{-2}$	$4.73 \times 10^{-2}$
$R_i$	0.978	0.747

It is obvious from Table 5 that the correlation coefficients  $R_2$  for the linear plots of the pseudo-second

order model is 0.999 which is higher than the correlation coefficients  $R_1$  for the pseudo-first order and the calculated  $q_e$  values are in agreement with experimental  $q_e$  values. This indicates that the adsorption kinetic is better represented by the pseudo-second order model.

The intraparticle rate constants were obtained from the plot of  $q$  versus  $t^{0.5}$  and the results are given in Table 5. The  $C$  values indicate that the line did not pass through the origin. It has been reported by various researchers that when the plots do not pass through the origin, this is indicative of some degree of boundary layer control and further shows that the intraparticle diffusion is not only the rate controlling step, but some other processes may also control the rate of adsorption.

### 3.4. Adsorption Isotherm

Langmuir and Freundlich models were applied to describe equilibrium adsorption isotherms for RO16 onto the ZCA and SMZCA-20 samples at 25 °C, and the fits of the theoretical models to the experimental values are shown in Figure. 5. The isotherm constants, their correlation coefficients and value of Chi-square test calculated from Eq. (7)-(9) are given in Table 6. For analysis of data using linear regression, the fitness of the model is often evaluated based on the value of the correlation coefficients ( $R^2$ ). Both Langmuir and Freundlich isotherms give similar  $R^2$  values for ZCA and SMZCA-20. Despite this, the  $\chi^2$  values for Freundlich were very large, mainly for ZCA, suggesting that the isotherm constants of Freundlich obtained from the linear regression do not describe well the equilibrium data.

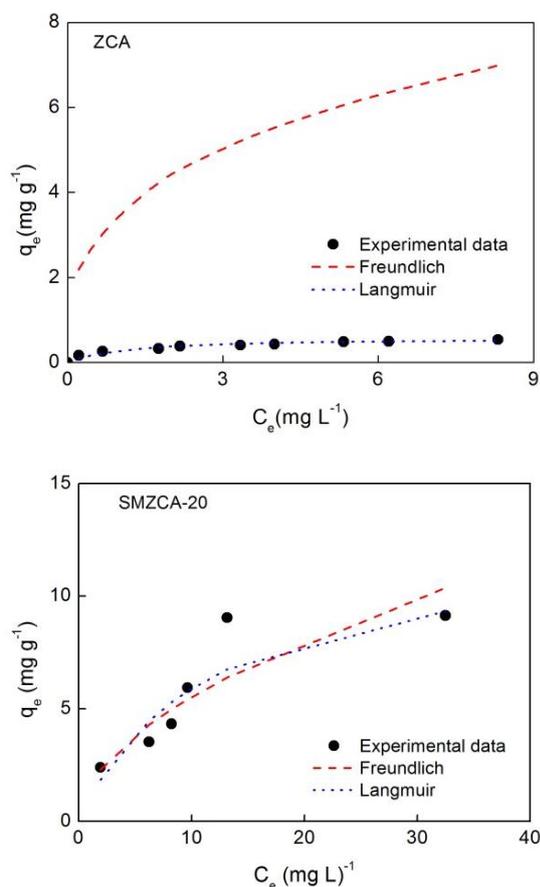


Figure 5. Equilibrium isotherms for the removal of RO16 by ZCA and SMZCA-20

The RO16 maximum adsorption capacity ( $Q_0$ ) of the ZCA sample is  $0.580 \text{ mg g}^{-1}$ . After surface modification with HDTMA, dye ion removal is greatly enhanced to  $12.6 \text{ mg g}^{-1}$ . Adsorption by zeolite is negligible presumably because of the strong dipole interaction between zeolite and water, which excludes organic solutes from this portion of the zeolite.

The measurements of  $\text{pH}_{\text{PZC}}$  revealed that surfactant-modified zeolite sample surface acquires a negative charge in water at natural pH (Table 2). The negative charge of SMZCA-20 is probably due to the formation of a patchy bilayer on the number of exchangeable active sites on the external zeolite surface [11].

Table 6. Comparison of equilibrium isotherm models

Isotherm	Adsorbents	
	ZCA	SMZCA-20
Langmuir		
$Q_0$ ( $\text{mg g}^{-1}$ )	0.58	12.6
$b$ ( $\text{L mg}^{-1}$ )	0.966	0.0878
$R^2$	0.993	0.93
$\chi^2$	0.0533	1.32
Freundlich		
$K_f$ [ $(\text{mg g}^{-1})(\text{L mg}^{-1})^{1/n}$ ]	3.56	1.61
$n$	3.14	1.87
$R^2$	0.994	0.926
$\chi^2$	37.6	1.52

The adsorption of RO16 onto SMZCA-20 with patchy bilayer coverage is attributed to multiple mechanisms, such as, electrostatic interaction, hydrogen bonding, hydrophobic interaction and ion exchange. Hydrophobic interaction and hydrogen bonding are suggested to be the predominant mechanisms. Hydrophobic interaction involves the hydrophobic tails of HDTMA and the hydrophobic functional groups of RO16 molecules, and this mechanism is of London-Van der Waals type [32].

A large number of hydrogen bonds between C or N of HDTMA and alkyl, aromatic and sulphonic groups of RO16 also is responsible for the effective adsorption. The aromatic and sulfonate groups of organic compounds and their planar shape and delocalized  $\pi$ -bonds interact strongly with ammonium centers of HDTMA [33,34,35].

A comparison of the adsorption maxima of RO16 on zeolite from cyclone fly ash (ZCA) and surfactant modified zeolite from cyclone ash (SMZCA-20) with those of some low cost adsorbents reported in the literature is given in Table 7. As seen in Table 7, the SMZCA-20 had comparable adsorption performances with chitosan cross-linked beads. Although activated carbon from waste materials [36,37,38] and various types of sludge [39] presents high efficiency in the removal of RO16, the obtaining of these adsorbents requires optimization of the preparation process involving several steps and use of relatively expensive chemical reagents [40].

Adsorption capacity for unmodified zeolites increased with decreasing adsorbent particle size. Zeolites from baghouse ash have smaller particle size than zeolites from cyclone ash. The increase in adsorption capacity with decreasing adsorbent particle size is attributable to molecules adsorbing principally in the exterior region close to the external particle surface [44]. The specific external surface area (surface area per unit mass) available for adsorption would be greater for smaller adsorbent

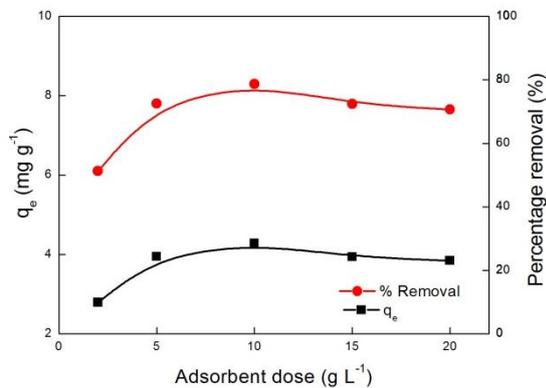
particles. The values of BET surface area were 69.3 and 39.0m<sup>2</sup> g<sup>-1</sup> for zeolite from baghouse fly ash and zeolite from cyclone ash, respectively.

**Table 7. Comparison of the maximum monolayer adsorption capacities of RO16 on various adsorbents**

Adsorbent	Maximum Adsorption Capacity (mg g <sup>-1</sup> )	Reference
Com cob	22.0-26.1	41
Chitosan cross-linked (beads)	5.6-30	42
Quaternized Sugar Cane Bagasse	34.48	43
Zeolite from baghouse fly ash-iron oxide	1.06	44
Zeolite from baghouse fly ash	1.14	19
Zeolite from cyclone fly ash	0.58	This study
Surfactant modified zeolite from cyclone ash	12.6	This study

### 3.5. Effect of Adsorbent Dosage

The influence of SMZCA-20 dosage on RO16 removal was studied and the results are presented in Figure. 6. As the adsorbent dosage increased, a greater surface area and a greater number of binding sites should be available for the constant amount of RO16, which results in the percentage removal of RO16 increasing with increasing SMZCA-20 dose. The highest amount of dye removal was attained for adsorbent dose of 10g L<sup>-1</sup>. For adsorbent dosages higher than this value, the percentage of the dye removal and the amount of dye uptake per gram of adsorbent (q<sub>e</sub>) remained almost constant.



**Figure 6.** Effect of adsorbent dose on the adsorption of RO16 onto SMZCA-20 (contact time: 60 min; initial dye concentration: 50 mg L<sup>-1</sup>)

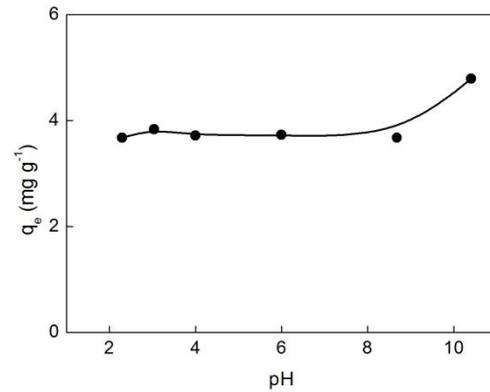
### 3.6. Effect of Initial pH

The effect of pH on the RO16 anions uptake by SMZCA-20 is shown in Figure 7. The amount adsorbed remained constant in the pH interval between 2 to 9 and increased with the medium pH 10. The hydrophobic interactions between RO16 and HDTMA chains appears to be the most important mechanism involved in anionic dye adsorption in the case where the pH does not play any role on adsorption process. The increase in RO16 removal in pH 10 may be due to strong basic nature of the loaded HDTMA on ZCA.

### 3.7. Acute Toxicity Test

The dye toxicity was evaluated for dye solutions before and after the adsorption processes with *D. similis* and *V. fischeri*. In the present study, toxicity was evaluated at

RO16 concentrations of 6.25-100mg L<sup>-1</sup> and 10.23-81.90mg L<sup>-1</sup> for to determine EC<sub>50</sub> ranges for *D. similis* and *V. fischeri*, respectively.



**Figure 7.** Effect of pH on the adsorption of RO16 onto SMZCA-20 (contact time: 60 min; initial dye concentration: 50 mg L<sup>-1</sup>)

The results indicate that the EC<sub>50</sub> of RO16 were 16.72 and 92.10mg L<sup>-1</sup> for *V. fischeri* and *D. similis*, respectively. This means that the concentration values of the dye used are considered toxic to the aquatic environment and that color removal is required. After treatment of RO16 by SMZCA-20, EC<sub>50</sub> value was 0.32mg L<sup>-1</sup> for *D. similis* and 1.32 for mg L<sup>-1</sup> *V. fischeri*. One possible reason for this increase in toxicity after treatment could be due to the presence of residual surfactant in the effluent. This hypothesis was confirmed by toxicity tests carried out with dyes solutions after adsorption process using unmodified zeolite from fly ash. It was observed that acute effects were substantially reduced or was eliminated after the adsorption treatment [6,46,47].

## Conclusion

This study investigated the equilibrium and the dynamics the adsorption of an anionic dye, which is namely Reactive Orange 16 dye, RO16, onto unmodified zeolite (ZCA) and surfactant-modified zeolite (SMZCA) that were synthesized from cyclone ash. The best conditions were established with respect to contact time, adsorbent dose and pH to saturate the available sites located on the SMZCA surface. The pseudo-second order kinetic model agrees very well with the dynamic behavior for the adsorption of RO16 onto adsorbents. The experimental data fitted well to the Langmuir adsorption isotherm. The ecotoxicity studies showed the wastewater contaminated with dyes after treatment with modified-surfactant zeolite should not be discarded directly into water bodies, but can be used as non-potable water reuse. Although zeolite synthesized from cyclone ash showed little adsorption for RO16, surface modified zeolite material proved to be an effective adsorbent for the adsorption of anionic azodye compound from wastewater.

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