Studies on Removal of Acid Orange 8 from Aqueous Solution Using HDTMA-Modified Zeolite from Coal Bottom Ash

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Abstract: *Zeolite synthesized from coal bottom ash (ZBA) was modified with hexadecyltrimethylammonium bromide and was examined for the adsorption of Acid Orange 8 (AO8) from water. The ZBA and surfactant-modified ZBA (SMZBA) were characterized to obtain chemical and mineralogical composition, total and external cation-exchange capacity among other parameters. Results indicate that, while ZBA had no affinity for AO8, SMZBA showed greatly enhanced adsorption capacity. The dye adsorption equilibrium was rapidly attained after 90 min of contact time. The adsorption kinetic was discussed using the pseudo-first order and pseudo-second order. The experimental equilibrium data were tested by four widely used isotherm models namely, Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich. It was found that adsorption of AO8 on SMZBA well with the Langmuir isotherm model. The monolayer adsorption capacity was 1.15 mg g-1 with the correlation coefficient of 0.99. The negative value of the free energy change indicates the spontaneous nature of the adsorption. The experimental results suggest that SMZBA could be employed as an adsorbent in the removal of AO8 dye from aqueous solution and wastewater.*

Keywords: *Bottom ash, Modified Zeolite, Acid dye, Adsorption*

1. INTRODUCTION

Organic dyes constitute one of the larger groups of pollutants in wastewater discharged from textile and other industries. However, their discharge into water has a severe environmental impact. A textile azo dye processing plant effluent was identified as one of the sources of mutagenic activity detected in the Cristais River, a drinking water source in Brazil [1].

Acid Orange 8 (AO8) is an important commercial textile dye. As a strong electrolyte, it is completely dissociated under the acid conditions used in the dyeing process. Its principal application is in leather dyeing and paper coloration and the second principal application is in wool dyeing, which makes its waste byproducts an important economic regional issue. AO8 possesses no outstanding coloristic properties among the acid monoazo dyes, but it is distinguished by the brilliance of its shade and particularly low production cost. Anionic monoazo dyes are still used in larger quantities for cheap articles and, consequently, are abundant in wastewater [2].

AO8 belongs to the azo dye family, which are characterized by the presence of one or more azo groups (-N=N-) and represent up to 70% of the amount of dyestuffs consumed in industrial applications [3].

Conventional methods of wastewater treatment have limitations textile to remove color discarding these aqueous. Furthermore, these methods involve the production amount of sludge or use of oxidizing agents that can be harmful. In order to overcome these limitations the adsorption process with activated carbon has been used as adsorbent for color removal. However, its application is limited due to its high cost, so it is necessary to seek low-cost adsorbents.

A wide variety of low-cost adsorbents have been prepared from different materials utilizing industrial, biomass, and municipal wastes [4-7].

The production of low cost adsorbents and their application in water treatment are considered valuable components in the implementation of sustainable development policies of national and local programs, and present economic advantages [8].

The ashes are classified as fly and bottom ashes due to different temperature zones in the boiler during combustion of pulverized coal in power plants. The finely divided residue resulting from combustion is entrained by flue gas (fly ash). The material clumps falling into the bottom of the combustion chamber, called bottom ash [9].

Although an amount of fly ash has already been utilized in the construction industry as a partial cement replacement and/or mineral additive in cement production, the usage of coal bottom ash is limited due to its relatively higher unburned carbon content and different structural properties compared to fly ash [10].

Recycling of bottom ashes is a proposal for low cost, as becomes a problem of disposal in economy, cleanliness and environmental protection. In this context is that propose studies the transformation of coal bottom ash into zeolitic material, considered a value-added product.

It is known that zeolitic material modified with quaternary amines can substantially enhance the adsorption of nonionic organic solutes from aqueous solutions. One of the most commonly used surfactants for zeolite surface modification is hexadecyltrimethylammonium bromide (HDTMA-Br), because of its availability and low cost [11, 12].

In this study, coal bottom ash zeolite was prepared by a hydrothermal method, and was modified by HDTMA-Br. The adsorption capacity and mechanism of Acid Orange 8 from water by HDTMA-modified zeolite were evaluated in batch experiments.

2. MATERIALS AND METHODS

All the reagents used for experimental studies were of analytical grade. The samples of coal bottom ash (CBA) were collected from the bottom ash tank of the coal-fired power plant located at Figueira State, Brazil.

The quaternary ammonium salt hexadecyltrimethylammonium bromide with molar mass 364.46 g mol-1 (HDTMA-Br, Merck) was used. The Acid Orange 8 dye (AO8; CI 15575; $C_{17}H_{13}N_2NaO_4S$; 364.35 g mol^{-1}) provided by Aldrich with a dye content of 65% and was used without further purification.

The chemical structure of AO8 is shown in Fig.1. A stock solution of AO8 was prepared in 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 1E) at 488 nm the maximum of absorption AO8.
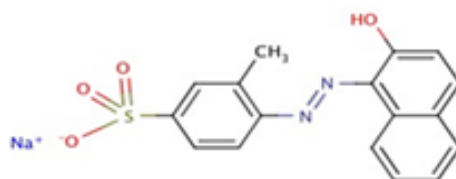

Fig 1. *Chemical structure of Acid Orange 8*

2.1. Synthesis of Zeolite from Coal Bottom Ash (ZBA)

CBA (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 °C in oven for 24 h. After finishing of the process, the suspension was filtered with 4A quantitative filter paper. ZBA was repeatedly washed with deionized water until the pH of washing water reach ~ 11 and dried at 50 °C for 12 h [13].

2.1. Synthesis of surfactant-modified zeolite from bottom ash (SMZBA)

Zeolite modified with surfactant was prepared by mixing 20 g of ZBA with 400 mL of 1.8 mmol L^{-1} HDTMA-Br. The mixtures were shaken in a mechanical shaker for 7 h at 120 rpm

and 25 °C. After this period, the solid was filtered and taken to the stove for drying at 50 °C for 12 h [14].

2.2. Adsorption studies

Adsorption experiments were carried out by using the batch technique. Aliquots of 10 mL of AO8 with initial concentrations of 10, 25 and 50 mg L^{-1} were placed in beakers with 0.2 g of SMZBA. The suspensions were shaken at 120 rpm at intervals of 30-300 min (25 ± 2 °C). The supernatant was separated by centrifugation for 30 min at 2000 rpm. An aliquot of the supernatant was analyzed using a UV spectrophotometer by measuring absorbance at $\lambda = 491$ nm and pH = 5.

Equilibrium experiments were performed by contacting 0.2 g of SMZBA with 10 mL of the dye solution in different initial concentrations (10 to 97 mg L^{-1}). The samples were stirred at 120 rpm until they reach equilibrium time under constant temperature of 25 ± 2 °C. Each experiment was duplicated under identical conditions with maximum deviation was found to be 3%. The amount of adsorption at equilibrium (q_e, mg g^{-1}) was calculated by using the following equation:

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

where q_e is the adsorbed amount of adsorbate per gram of adsorbent at any time t 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 M is the mass of the adsorbent (g).

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

$$R\,(\%) = \left(\frac{C_o - C_t}{C_o}\right) x\ 100 \quad (2)$$

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

The data of the isotherm adsorption equilibrium were fitted using the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) [15]. 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, we analyzed six error functions of nonlinear regression basin, with the lowest values will be used to further validate the applicability of isotherms tested. To estimate the best fit isotherm, the equations used (abbreviated as ARED, SSE, MPSED, HYBRID, SAE and X2) are described in Ncibi, 2008 [16].

2.3. Characterization of Materials

Chemical composition of materials was determined by X-ray fluorescence (XRF) in a Rigaku RIX-3000 equipment. X-ray diffraction (XRD) with an automated Rigaku MiniFlex II diffractometer using CuKα radiation (λ=1.5405 Å) was used to identify the main crystalline compounds. The crystalline phases present in the samples were identified with the help of ICDD (International Centre for Diffraction Data). The cation exchange capacity (CEC) and external cation exchange capacity (ECEC) were determined by adopting literature techniques [11, 17]. The pH of zeolite was measured as follows: 0.1 g of samples were mixed with 10 ml of distilled water and shaken for 24 h. After filtration, the pH of solution was determined by a pH meter. The point of zero charge (pH$_{PZC}$) was estimated by using batch equilibrium techniques. For this, 0.1 g of each adsorbent was treated with 50 mL 0.1 mol L^{-1} NaNO$_3$ solution which was used as an inert electrolyte. The initial pH values were adjusted in the range 2 to 13 by adding minimum amounts of 0.01 mol L^{-1} NaOH or 0.01 mol L^{-1} HNO$_3$. The suspensions were allowed to equilibrate for 24 h in a shaker fixed at 120 rpm. After completion of the equilibration time, the admixtures were filtered and final pH values of the filtrates were measured again. A plot of the final pH as a function of the initial pH provides pHpzc of the adsorbent by the plateau of constant pH to the ordinate.

3. RESULTS AND DISCUSSION

3.1. Characterization of Materials

The chemical constituents (as their stable oxides form) of adsorbents (CBA, ZBA, and SMZBA) were determined using X-ray fluorescence (XRF) method, as shown in Table 1. The main components of coal bottom ash are the oxides of Si and Al, which are known to be the main components of zeolite; 41% and 21%, respectively. The high amount of silica of CBA was further decreased in ZBA and SMZBA due to dissolution of SiO_2 by the hydrothermal treatment. An increase in Na amount in zeolitic materials is attributed to entrapment of sodium ions to neutralize the negative charge on aluminosilicate gel during the hydrothermal treatment with NaOH solution [18]. The presence of bromide in the SMZBA was detected.

Table 1. *Chemical composition (wt. %) of the coal bottom ash and synthesized zeolites*

Oxides	CBA	ZBA	SMZBA
SiO_2	41	31	31
Al_2O_3	21	23	23
Fe_2O_3	12	11	12
Na_2O	0.8	14	11
SO_3	6.1	10	10
CaO	5.6	5.6	6.2
TiO_2	2.3	0.9	2.4
MgO	1.6	2.6	2.3
K_2O	6.1	1.1	1.1
ZnO	0.15	0.07	0.08
U_3O_8	0.06	0.08	0.08
PbO	0.06	0.15	0.13
SrO	0.03	0.02	0.03
ZrO_2	0.05	0.06	0.07
MnO	0.10	0.09	0.02
P_2O_5	☐0.02	☐0.02	0.06
As_2O_3	0.07	☐0.02	☐0.02
Cr_2O_3	0.05	0.06	0.07
NiO	0.03	0.04	0.04
Y_2O_3	0.02	0.18	0.02
CuO	0.02	0.03	0.03
Br	☐0.02	☐0.02	0.15
Cl	☐0.02	☐0.02	☐0.02
SiO_2/Al_2O_3	1.95	1.34	1.34

The SiO_2/Al_2O_3 ratio is related to the cation exchange capacity of the material and the values obtained with the synthetic zeolites were lower than that of raw bottom ash, indicating that the hydrothermal treatment contributed to the increase in the cation exchange capacity of the material. As shown in Table 1, the ratios SiO_2/Al_2O_3 in SMZBA are the same with the corresponding unmodified zeolite which imply that the framework of Al atoms are not delaminated into solution upon modification with surfactant.

The physicochemical properties of adsorbents are summarized in Table 2. Point of zero charge (pH_{PZC}) for a given mineral surface is the pH at which surface has net neutral charge. A given mineral surface will have positive charge at solution pH values less than the point of zero charge. On the other hand, the mineral surface will have negative charge at solution pH values greater than the point of zero charge. The zeolite from bottom ash has a point of zero charge of 6 and is negatively charged. After modification by 1.8 mmol L^{-1} HDTMA-Br, the pH_{PZC} moved to 7.0 and the particle surface was still negative. SMZBA has negative charge probably due to the formation of a patchy mono-layer and/or bi-layers form on the external zeolite surface [14, 19-22]. The ECEC value of ZBA is far lower than the CEC value, which represents the main negative charges locate in the internal pore. The external surface was used to load HDTMA because the pore size of zeolite is too small for the HDTMA cation to enter.

Table 2. *Physicochemical properties of zeolitic materials*

Characteristics	ZBA	SMZBA
pH in water	9.2	9.1
pH_{PZC}[a]	6.0	7.0
CEC (meq g^{-1})[b]	1.19	1.00
ECEC (meq g^{-1})[c]	0.243	-

(a) Point of zero charge; (b) cation exchange capacity;(c) external cation exchange capacity

Previous studies have shown that toxic elements are leached from bottom ash and are transported to natural water sources [23-25]. The physicochemical characterization of bottom ash generated in the Santa Catarina power station (Jorge Lacerda - Brazil) indicated the presence of iron oxide nanocrystals mixed with silicate glass particles. The results suggest that there is a health risk associated with inhalation of nanoparticle from coal bottom ash [26]. The mobility of hazardous elements contained in coal during combustion and the environmental impact potential of ashes were also evaluated [27].

Figure 2 shows the XRD patterns of the coal bottom ash (CBA), unmodified zeolite (ZBA) and HDTMA-modified zeolite from bottom ash (SMZBA). The majority crystalline phases in the CBA were quartz (SiO_2, ICDD/JCPDS 001-0649), mullite (Al_2O_3 ICDD/JCPDS 002-043), Fe-material (Magnetite, ICDD/JCPDS 89-0691; Hematite, ICDD/JCPDS 89-0598) and Calcite ($CaCO_3$, ICDD/JCPDS 01-071-3699). The amorphous halo between 10 and 32 in the 2θ angular zone corresponds to the vitreous component of CBA.

The ZBA contains part of quartz and more mullite contents because mullite is quite stable in alkaline solution, both of them are present in the bottom ash as major content. This significantly demonstrates that under the given experimental conditions, these phases have not been digested completely. Hydroxysodalite (JCPDS 31-1271) with traces of Na-X (JCPDS 38-0237) were the main zeolitic products obtained after activation of CBA in NaOH solution.

To monitor the effect of surfactant modification on structure stability, the powder XRD analysis of unmodified zeolite and modified zeolite was compared (Fig. 2). The structural parameters of the HDTMA-modified zeolite are very close to that of corresponding parent zeolite, which indicate that the crystalline nature of the zeolite remained intact after chemical treatment with HDTMA-Br molecules.

In the XRD pattern of the SMZBA (Fig. 2) it was also noticed that the relative intensity of the hydroxysodalite increased when the zeolite was modified with surfactant. In contrast, the zeolite NaX characteristic peaks disappeared, revealing that cation exchange reaction took place mainly in the zeolite X when they were treated by HDTMA solution [28].
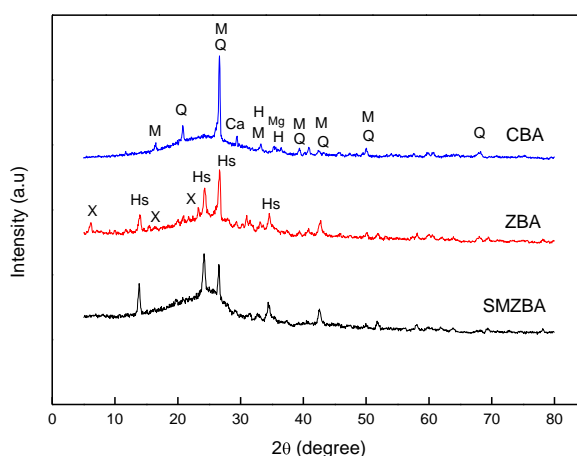

Fig 2. *The X-ray diffraction patterns of CBA, ZBA and SMSZBA (M = Mulitte; Q = Quartz; Ca=Calcite; Mg= Magnetite; H = Hematite, Hs = Hydroxysodalite; X = NaX)*

Synthesis of zeolites from coal bottom ash was studied with different hydrothermal reaction parameters such as temperatures, molarity of caustic reagents, reaction time, etc. The products obtained were zeolites NaP1 and hydroxysodalite, and tobermorite [29-30].

3.2. Effect of Contact Time and Initial Dye Concentration

The effect of the initial concentration of acid orange 8 dye solutions on the adsorption rate onto SMZBA was investigated at various concentrations from 10 mg L^{-1} to 50 mg L^{-1} (Fig. 3). The removal increases with increasing contact time and attains equilibrium at about 30-90 min. It is further noted that the adsorption capacity of dye was increased from 0.350 mg g^{-1} to 1.05 mg g^{-1} when the initial concentration of dye increased from 10 mg L^{-1} to 50 mg L^{-1}. It is because of the fact that at lower concentration, the ratio of the initial number of dye molecules to the available surface area is low subsequently the fractional adsorption becomes independent of initial concentration. However, at higher concentration the available sites of adsorption becomes fewer and hence the percentage removal of dye is dependent upon initial concentration.

As expected, the non-modified zeolite from bottom had little affinity for AO8 in aqueous solution. The removal efficiency was in the range of 23-28% with initial dye concentration of 10-25 mg L^{-1}. Results of zeta potential indicated that HDTMA-modified zeolite from bottom ash had negative charge (Table 2). Thus, hydrogen bonding and partitioning process are suggested to be predominant mechanisms in AO8 adsorption by SMZBA.
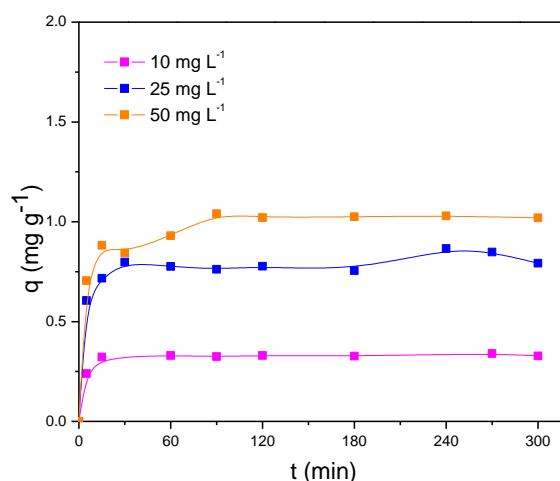

Fig 3. *Effect of time and initial concentration on removal of AO8 by SMZBA*

In order to investigate the removal of AO8 using HDTMA-modified zeolite from bottom ash, pseudo-first-order and pseudo-second-order kinetic models were used [31-32]. The parameters of the kinetics models with their correspondent coefficients of determination are calculated from the slopes and intercepts of the linear plot of these models as shown in Fig. 4 and they are summarized in Table 3.
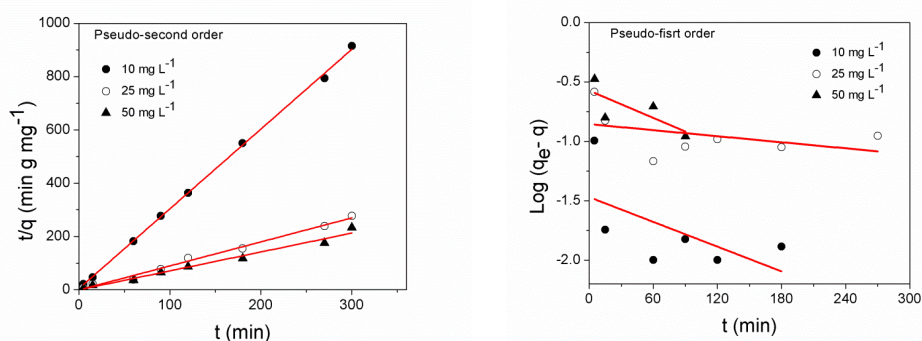

Fig 4. *Pseudo-first order and pseudo-second order kinetic plot for the removal of AO8 by SMZBA*

Table3. *Kinetic parameters for the removal of AO8 by HDTMA-surfactant-modified zeolite from bottom ash*

[AL8] mg L^{-1}	Pseudo-first order				
	K$_1$ (g mg^{-1} min^{-1})	q$_e$ calc (mg g^{-1})	q$_e$ exp (mg g^{-1})	R$_1$	
10	7.99x10^{-3}	0.0346	0.325	0.607	
25	868x10^{-3}	0.137	0.762	0.377	
50	16.3x10^{-3}	0.288	1.04	0.839	
Pseudo-second order					
	K$_2$ (g mg^{-1} min^{-1})	h (mg g^{-1} min^{-1})	q$_e$ calc (mg g^{-1})	q$_e$ exp (mg g^{-1})	R$_2$
10	1.99	2.29x10^{-1}	0.334	0.325	0.999
25	2.89x10^{-1}	2.00x10^{-1}	0.833	0.762	0.997
50	2.28x10^{-1}	2.52x10^{-1}	1.05	1.04	0.999

As seen in Table 3, the coefficient of determination, R$_2$ for the pseudo-second-order adsorption model has a high value (> 0.99), and its calculated equilibrium adsorption capacity (q$_e$ calc) is consistent with experimental data (q$_e$ exp). Therefore, the pseudo-second-order adsorption mechanism is predominant in AO8 adsorption on SMZBA. The pseudo-second order model suggests that the adsorption depends on the adsorbate as well as the adsorbent [28]. The intraparticle diffusion has no role in the mass transfer of this process. The AO8 molecule presents large dimension hence it is unable to diffuse through the porous network of the modified-zeolite used in the present investigation.

3.3. Adsorption Isotherms

The experimental equilibrium data of AO8 on SMZBA were compared with the theoretical equilibrium data obtained from the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherm models (Fig. 5). The shape of an isotherm not only provides information on the adsorption affinity of dye molecules, but also reflects thermodynamic data, providing relevant information about adsorption spontaneity and the stability of the adsorbent−adsorbate interactions [33-34]. According to the classification of Giles et al. (1960), the isotherm seems to be of the L2 type, indicating that the dye molecules have such a high affinity for the modified zeolite surface [35].
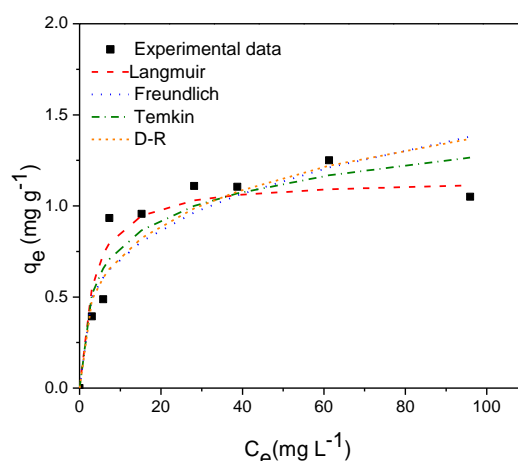

Fig 5. *Comparison of equilibrium isotherms between the experimental data and theoretical data for AO8 onto SMZBA (Experimental conditions: adsorbent dose: 0.2 g/10 mL, agitation speed: 120 rpm, pH: 5.0, contact time: 90 min, temperature: 298 K)*

The isotherm constants were calculated by evaluating the linearized form of the models (Fig. 6). The values of the constants for isotherm models at 298 K for the removal AO8 onto SMZBA are presented in Table 4.
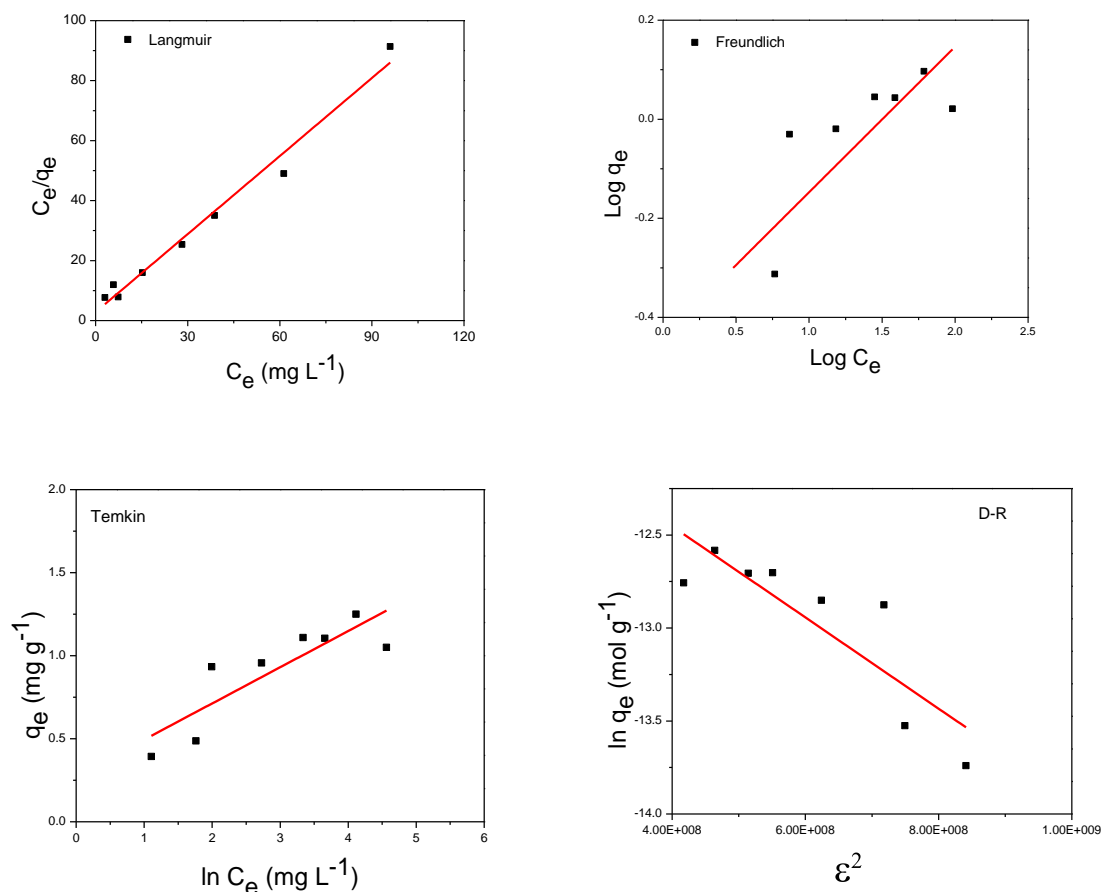
Fig 6. *Linearized (A) Freundlich, (B) Langmuir, (C) Temkin and (d) D-R isotherms for AO8 adsorption on SMZBA*

Table 4. *Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherm constants for the adsorption of AO8 on SMZBA*

Langmuir	
Q_0 (mg g^{-1})	1.15
b (L mg^{-1})	0.306
R	0.990
Freundlich	
K_F (mg g^{-1})(L mg^{-1})$^{1/n}$	0.362
n	3.41
R	0.842
Temkin	
K_t (L g^{-1})	3.56
B_T	0.217
b_t (KJ mol^{-1})	1.14
R	0.863
D-R	
β (mol^2 J^{-2})	2.45x10^{-9}
K_{DR} (mol g^{-1})	1.04x10^{-5}
R	0.861

As seen in Table 4, the Langmuir isotherm fits quite well with the experimental data (correlation coefficient R = 0.99). This indicates that the Langmuir model was very suitable for describing the adsorption equilibrium of AO8 on SMZBA. Compared with the correlation coefficient value of the linear plot of Langmuir isotherm, those of Freundlich model, Temkin model, and D–R model

were found less satisfactory (R < 0.86). The best correlation coefficients were, in decreasing order, Langmuir > Temkin > D-R > Freundlich models. The value of Freundlich constant n larger than 1 point out the favorable adsorption conditions.

The values of error analysis for Langmuir, Freundlich, Temkin and D-R isotherm models at are presented in Table 5. Apparently, it can be concluded that the most applicable isotherm to describe acid orange 8–SMZBA adsorption system is Langmuir. The values of regression coefficients, R and the non-linear error functions are in agreement to one another.

Thermodynamic data such as adsorption energy can be evaluated from Langmuir equation [36]. According to thermodynamic law, $\Delta G°$ of adsorption is calculated as follows:

$$\Delta G°ads = - R \, T \, \ln K_L \quad (3)$$

were $\Delta G°$ is free energy of adsorption (kJ mol^{-1}), T is the absolute temperature (K), K_L is the Langmuir equilibrium constant (L mol^{-1}) and R is the gas constant (8.314 J K^{-1} mol^{-1}). Using Langmuir isotherm, the free energy value was evaluated as - 28.8 kJ mol^{-1}. A negative $\Delta G°$ value indicates that adsorption of AO8 from aqueous solution onto SMZBA is spontaneous in nature.

Table 5. *Isotherm error deviation data related to the adsorption of AO8 onto SMZBA*

	R	ARED	SSE	MPSED	HYBRID	SAE	X^2
Langmuir	0.990	17	0.143	28	4.03	0.898	0.187
Freundlich	0.842	92.7	7.88	95.5	124	7.24	153
Temkin	0.863	17.3	0.168	20.7	3.68	1.04	0.209
D-R	0.861	17.1	0.235	20.2	4.36	1.11	0.270

4. CONCLUSION

In the present work, it was found that HDTMA-modified zeolite that was synthesized from coal bottom ash (SMZBA) showed high retention capacity for Acid Orange 8, an anionic azo dye, from aqueous solutions. The kinetic data agreed well with the pseudo–second order rate equation. Five isotherm models were studied and the Langmuir model was the most appropriate for fit of the equilibrium experimental data (higher values of coefficients of determination and through error analysis). The negative value of the free energy change calculated indicates the spontaneous nature of the adsorption and confirms the affinity between the SMZBA and the Acid Orange 8.

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