RESEARCH ARTICLE

CURRENT
NANOMATERIALS
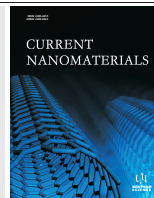
Adsorption of Solophenyl Dyes from Aqueous Solution by Modified Nanozeolite from Bottom Ash and its Toxicity to *C. dubia*

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Abstract: ***Background***: It is known that wastewater from textile industries are responsible for producing large amounts of highly contaminated effluents by various types of synthetic dyes. These compounds can be toxic, and in some cases, are carcinogenic and mutagenic and its removal is recommended.

Application: In the area of water purification, nanomaterials have been applied for removal of several compounds. Of the four classes of nanomaterials, zeolites have demonstrated good results for the removal of dyes. Nanozeolite synthesized from bottom ash and modified with hexadecyltrimethylamonium (ZMB) was used as adsorbent to removal of Solophenyl Navy (SN), Solophenyl Turquoise (ST) and their hydrolyzed forms (SNH and STH, respectively) from simulated textile wastewater.

Method: The physical-chemical characterization of materials was presented by using relevant analytical methods (XRD, SEM, BET surface area, *etc*.). Effects of parameters such as initial dye concentration, contact time and equilibrium adsorption were evaluated. The adsorption kinetics followed the pseudo-second-order model.

Results: Langmuir isotherm model shows the best fit for most dyes-ZMB systems. In order to identify if ZMB presented toxicity for the environment, bioassay and toxicity identification evaluation (TIE) with *C. dubia* were performed. The leached of ZMB was toxic to daphinids (11.3 TU).

Conclusion: TIE results appointed that the main cause of the toxicity could be due the surfactant and metal ions presents in aqueous solution.

1. INTRODUCTION

Solophenyl Navy (SN) and Solophenyl Turquoise (ST) are blue-coloured, water-soluble direct dyes. Their chemical structure contains one phthalocyanine metal, a copper ion. These dyes are used for coloring cellulosic fibers, particularly cotton. In Brazil, SN and ST dyes are widely used in commercial laundries and in textile industry to dye jeans. They are also combined with other dyes to create new colors [1, 2].

Direct dyes are the largest class (60-70%) of dyes with the greatest variety of colors [3]. They have been used to dye cellulose for over 100 years. Owing to the ease of their application and the wide gamut of colors available at a modest cost, direct dyes are still a popular dye class [4]. Most direct dyes have disazo and trisazo structures, with each color dominated by unmetallized structures [5], generally copper.

Copper is the third most commonly used metal in the world [6] and is known to have a number of negative effects [7].

It has long been known that after treatment with salts of metals, such as chromium, aluminum, iron, *etc*., can give not only varied shades, but can also improve the light and wash-fastness properties of many direct dyes [4, 5]. After chelation with the metal ion, the dye formed has a large molecular complex, less soluble in water, more stable photolytically, and with an increase in the lightfastness [8].

It is estimated that about 10–50% of the reactive dyes are lost during dyeing and enter the industrial effluent system. The conventional treatment using activated sludge applied by textile industries does not efficiently remove dyes, which are thus discharged into the environment [9-11]. Even at very low concentrations (10 - 50 mg/L) water-soluble azo dyes can cause waste streams to become highly colored. Aside from their negative aesthetic effects certain azo dyes and biotransformation products have been shown to be toxic, and in some cases these compounds are carcinogenic and mutagenic [7, 12-14]. Approximately, it was determined that 130 of 3200 azo dyes in use have produced carcinogenic aromatic amines because of reductive degradation [15].

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Acute toxicity can be defined as toxicity elicited immediately following short-term exposure to a chemical. In accordance with this definition, two components comprise acute toxicity: acute exposure and acute effect [13]. Effects encountered with acute toxicity commonly consist of mortality or morbidity. From a quantitative standpoint these effects are measured as the LC_{50}, EC_{50}, LD_{50}, or ED_{50}. The LC_{50} and EC_{50} values represent the concentration of the material to which the organisms were exposed that cause mortality (LC_{50}) or some other defined effect (EC_{50}) in 50% of an exposed population. Since ecotoxicology focuses upon the adverse effects of chemicals in the environmental, acute toxicity in this discipline is more commonly described by the LC_{50} or EC_{50} [16, 17].

One of the most important processes used to identify causes of toxicity is the toxicity identification evaluation (TIE). TIEs involve a series of procedures designed to decrease, increase, or transform the bioavailable fractions of sediment contaminants to assess their contributions to sample toxicity [18-20]. The three phases of the TIE process (characterization, identification, and confirmation) comprise a weight-of-evidence approach to determine the causes of toxicity.

The main problem found in the decontamination of textile wastewaters in the removal of colour, since at the present time there is no single process capable of adequate treatment, mainly due to the complex nature of dyes effluents [21, 22]. Adsorption has been reported to be superior to others treatments for the removal of dyes from wastewater. Activated carbon is the most widely used adsorbent. However, its applications are sometime restricted due to its higher cost. Therefore, efforts have been directed towards developing low-cost alternative adsorbents [23].

Ash is formed by combustion of coal in coal-fired power station as a waste product. Efficient disposal of coal ash is a worldwide issue due to its massive volume and harmful risks to the environment. As a technique for recycling coal ashes, synthesis of zeolites from coal fly ash has attracted a great deal of attention. The synthesis of zeolites has produced an environmentally friendly and economically viable way of recycling coal fly ash. Zeolites synthesized from fly ash have been found to be efficient adsorbents for the removal of dye contaminants from aqueous effluents [23-27]. However, studies involving zeolite from bottom ash have not been done very extensively.

Previous study has reported the adsorption of ST and SN dyes and its hydrolyzed forms from water onto surfactant-modified nanozeolites from coal fly ash, as well as the toxicity of the leached zeolitic material and the toxic identification [24]. In order to continue these studies, in the present work, the removal of Solophenyl dyes from aqueous solutions and toxicity studies were evaluated using surfactant-modified zeolite from bottom ash as adsorbent under same conditions

2. MATERIALS AND METHODS

2.1. Preparation of Simulated Wastewater

All chemicals used for experimental studies were of analytical grade. The Solophenyl Navy BLE 250% (SN) and Solophenyl Turquoise BRLE 400% (ST) dyes manufactured by HUNTSMAN Corporation were used without further purification and their chemical structure is shown in Fig. (**1**). The stock solutions contained 30% of the industrial formulation of the dyes (0.067g of dye and 1.005 g of NaCl in 10 mL of water) [28]. The hydrolysis procedure, similar to the industrial process, was carried out to prepare hydrolysed dyes. Hydrolysed ST (STH) and SN (SNH) were prepared by mixing each stock solution (5 g L^{-1}) in 40% NaOH (pH 11-12). The solutions were heated at 70-80°C for 90 min. The pH was decreased to 5 using HCl 31% [29].
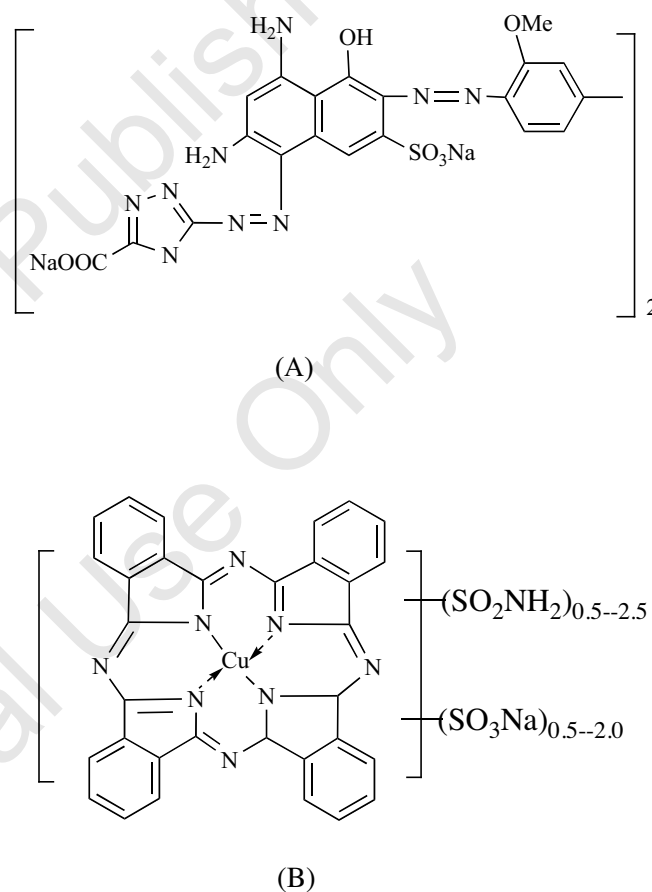
(A)

(B)

Fig. (1). Chemical structures of (**A**) Solophenyl Navy SN dye (MW1100 g/mol); (**B**) Solophenyl Turquoise dye (MW 775.17 g/mol).

2.2. Synthesis of Surfactant-modified Zeolite from Bottom Ash

The sample of coal Bottom Ash (BA) was obtained from a coal-fired power plant located at Figueira County, in Paraná State, Brazil. In the synthesis experiment, 10 g of BA was heated to 90°C in oven for 24 h with 160 mL of 3 mol L^{-1} NaOH. After finishing of the process, the suspension was filtered and the solid zeolitic material (ZB) was repeatedly washed with distilled water until the pH ~ 10 and dried at 100 °C for 24 h [30]. Zeolite modified with surfactant (ZMB) was prepared by mixing 10 g of ZB with 400 mL of 1.8 mmol L^{-1} of HDTMA-Br (hexadecyltrimethylammonium bromide, molar mass 364.46 g mol^{-1}, Merck). The mixture

was placed on agitation for 7 h and the solid phase was filtered and subsequently dried at 100°C for 24 h [31].

2.3. Dyes Removal Studies

Adsorption experiments were carried out by bath technique. In the batch procedure, 10 mL of a known initial dye concentration was agitated with 0.1g of ZMB at 120 rpm for 5 up to 120 min. The supernatant was centrifuged and analyzed using UV spectrophotometer (Carry IE-Varian) by measuring the absorbance at λmax = 604 nm for SN and SNH and λmax = 611 nm for ST and STH, respectively in pH 5. Adsorption isotherms were carried out by contacting 0.1 g of ZMB with 100 mL of SN, ST and its hydrolyzed forms with concentrations ranging between 10 to 50 mg L^{-1}.

In order to investigate the transient mechanism of adsorption, characteristic constants were determined using the linearized form of pseudo-first order and pseudo-second order. The data of the isotherm adsorption equilibrium were fitted using the linear and nonlinear equations of Langmuir, Freundlich and Temkin models [24, 32].

2.4. Characterization Techniques

The physico-chemical characteristics of ZMB were determined using standard procedures. Bulk density was determined by helium pycnometer (Micromeritcs Instrument Corporation). The surface area (BET) was determined by N2 adsorption isotherm with relationship using NOVA 1200 (Quantachrome Corp.). Before adsorption experiments, the samples were degassed at 150°C for 12 h to remove volatile and moisture in a degasser (Nova 1000 Degasser). The specific surface area was obtained by five points at p/p° between 0.05 and 0.20 applying the Brunauer–Emmet–Teller equation to the adsorption data. The phases of the zeolite were determined by X-ray diffraction analyses (XRD) with an automated Miniflex II X-ray Diffractometer- Rigaku diffractometer with Cu anode with Kα radiation at 40 kV and 20 mA over the range (2θ) of 5–80o with a scan time of 1o/min. The chemical composition of zeolite was determined by a RIX-3000 RIGAKU X-ray fluorescence spectrometer (XRF) equipped with an Rh X-ray tube (operated at 50 kV-60 mA). Scanning Electron micrograph was obtained by using XL-30 Philips Scanning Electron Microscope (SEM). The Cation Exchange Capacity (CEC) value was determined using ammonium solutions. The sodium ion concentration of the resulting solution was determined by optical emission spectrometry with inductively coupled plasma - ICP-OES (Spedtroflame - M120). The pH of zeolite was measured as follows: 0.1 g of samples were mixed with 10 ml of distilled water and shaken for 24h at 120 rpm.(Ética - Mod 430). After filtration, the pH of solution was determined by a pH meter (MSTecnopon - Mod MPA 210) and the conductivity was measured using a conductivimeter (BEL Engineering - Mod W12D).

2.5. Toxicity Evaluation

In order to investigate the potential toxic effects by the zeolitic modified material in environment, acute toxicity tests were performed. Sample of zeolite modified material (2g) were agitated with 10mL of culturing media in the equilibrium time for each dye. The supernatant was filtrated and

the leached used in the tests. The brood stock of *Ceriodaphnia dubia* used in the bioassays and all toxic testes were realized at Commonwealth Scientific and Industrial Research Organization (CSIRO), Australia, laboratories. Acute bioassay (48h) is generally followed the standard test methods for *Daphnia sp.* acute immobilization test outlined by OECD guideline 202 [33]. Tests were conducted in triplicates in 50 mL glass vial containing 25 mL of test solution and 5 neonates (< 24h old) per vial. Assays were conducted in 1:2 dilutions of leached samples (100, 50, 25, 12.5 and 3.12%) in moderated hard water (MHW, a laboratory prepared water containing 230 mg/L $CaCO_3$ and enriched with 2 mgL^{-1} selenium, as Na_2SeO_4). Cultures were fed a tri-algal mix consisting of Ankistrodesmus sp., Chlamydomonas sp. and Pseudokirchneriella subcapitata and a mixture of yeast, cereal leaves and trout chow (YCT). The culture water was replaced and the cultures were fed three times per week. All the concentrations used for these tests were in their real concentration (measured by spectrophotometer before and after tests). A control (MHW) and a positive control ($CuSO_4$ $5H_2O$) were used to monitor the health of the test organisms. Tests were conducted at 20±1 1ºC with a photoperiod of 16:8 h light to darkness and the test solutions were not renewed for the period of the test. Chemical analyses were performed on water samples for each concentration tested plus control, by Liquid Chromatography-Mass Spectrometry (LCMS) (Thermo Surveyor). A gradient pump, auto sampler and diode array detector – DAD) coupled to a mass spectrometer Thermo LXQ Linear Ion Trap with electrospray ionization (ESI+) and a diode array detector were used. The test endpoint was immobilization after 24-h and 48-h, which was defined as the failure to move within 15 s of the beaker being gently swirled. For acute toxicity tests, the median lethal concentration (LC_{50}) values with 95% confidence limits (*p* <0.05) were calculated by Trimmed Spearman–Karber (TSK) analysis for lethal tests [34]. EC_{50} values were transformed to toxic units ($TU=100/EC_{50}$).

2.6. Toxicity Identification Evaluation Test

In order to clarify which toxicants were causing the observed toxicity in the leached, those concentrations characterized as toxic were further analyzed by Toxicity Identification Evaluation procedures (TIE) [35]. The tests were performed in the leached of ZMB raw samples, used as a base line test, and after manipulation with solid phase extraction (SPE) and ethylenediaminetetraacetic acid (EDTA). The methodology for preparations of the samples followed the same order described before (item 2.4). In order to reduce the bioavailability of metals, EDTA (1 g L^{-1}) was added in each beaker and left to interact for 2 h. *C. dubia* neonates were then added to the beaker. Raw samples were passed through solid-phase extraction (SPE) using column C18 Waters Oasis® HLB (6cc/500mg) and nonpolar organic compounds were separated. After both manipulations the same parameters used in item 2.4 were used.

3. RESULTS AND DISCUSSION

3.1. Toxicity Evaluation Studies

The results observed in this work appointed that the effective concentration that caused effect for *C. dubia* for the

raw leached of the surfactant-modified zeolite from bottom ash was found to be 11.3 TU (11.4-11.1 TU). Regarding the TIE procedures, Fig. (**2**) shows results for the raw leached before and after manipulation with SPE and EDTA.

As observed in Fig. (**2**), the raw leached sample showed relevant toxicity for *C. dubia*. After manipulation with EDTA and SPE both were able to eliminate the toxicity in the samples tested. These results suggest the toxicity of the leached raw wastewater was influenced by SPE and EDTA manipulation and the toxicants are mostly metals, reduced by EDTA and non-polar organic compounds, reduced by SPE manipulation. The results of liquid chromatography on the raw samples showed several anions were present, such chloride, nitrate and sulphate. However, the analyzed anions found were not in concentrations high enough to cause the observed toxic effects in *C. dubia*, with the exception of Br-. The value found for Br- is above the EC_{50} values found in literature (0.18 mgL^{-1} 24 h, for *D. magna* [36], still the results of chemical analysis on cultivation water for *C. dubia* showed high values of Br- after 48h test (3.8 mgL^{-1}) which did not cause the observed toxicity.

Therefore, the toxicity found for the leached of surfactant-modified zeolite from bottom ash could mainly be due to two reasons. After the contact with water, the residual surfactant (used for surface modification) could be found in the effluent, and for this reason, the leached may contain HDTMA+ cations. The HDTMA-Br has been reported as toxic, especially for daphnidios [37-39]. Other reason appointed could be due to the mixture of different low concentrated metals, as Al, Ti, Fe and Cu, all found in the samples tested. The literature reports the join action of metals, with concentration close to their no observed effect concentrations (NOECs), could be toxic to different aquatic organisms [22, 40, 41].

TIE tests pointed out that after manipulation with EDTA chelation, the metal mixture did not show toxicity for *C. dubia* in the concentrations tested. The metals appear to exert their toxic effect by binding one or more reactive groups of enzymes and proteins on the structure or metabolism. Chelating agents are compounds that compete with these groups promoting chemical bonding with the metal and not with the normal protein or enzyme. After the treatment with SPE, the toxicity for the raw leached of ZBM was eliminated. The process of SPE retained non-polar organic species, such as HDTMA+, in the cartridge resulting in reduced toxicity in the samples tested. In a previous work, similar results concerning TIE approach with surfactant-modified zeolite from fly ash were observed [24].

3.2. Dyes Removal Studies

The effect of contact time on adsorption process was investigated at various initial dyes concentrations. It can be seen from Fig. (**3**) that the contact time necessary to reach the adsorption equilibrium was 60 min for SN and ST and 20 and 30 min for SNH and STH, respectively. The removal of all dye was very rapid in the first 5–10 min of contact time.

The equilibrium time of SN and ST onto modified zeolite from bottom ash was 3 times less than the results presented in literature for modified zeolite from fly ash (ZMF) at the same conditions [24]. The values of external cation exchange capacity (ECEC) were 0.628 and 0.266 meq g^{-1} for ZMF fly ash and ZMB, respectively. ECEC characterizes the exchange capacity of the zeolite surface for bulky surfactants. Consequently, ZMB adsorbs less surfactant than ZMF, even with the identical amounts of surfactant used in the modification, and so this modified adsorbent is less effective for removal of these dyes. The values of kinetic constants for ST and SN and its hydrolysed forms adsorption onto ZMB are presented in Table **1**.

Regarding the hydrolyzed dyes, the equilibrium times found for removal of SNH and STH were lower than those of SN and ST, possibly due to the reduction of the size of the molecule of both dyes after the hydrolysis

The correlation coefficient R^2 for the linear plots (not shown) of the pseudo-second order model is higher than the correlation coefficients R^1 for the pseudo-first order, suggesting that the adsorption kinetic is better represented by the pseudo-second order model. The experimental adsorption capacity values ($q_{e\ exp}$) were found to be in agreement with
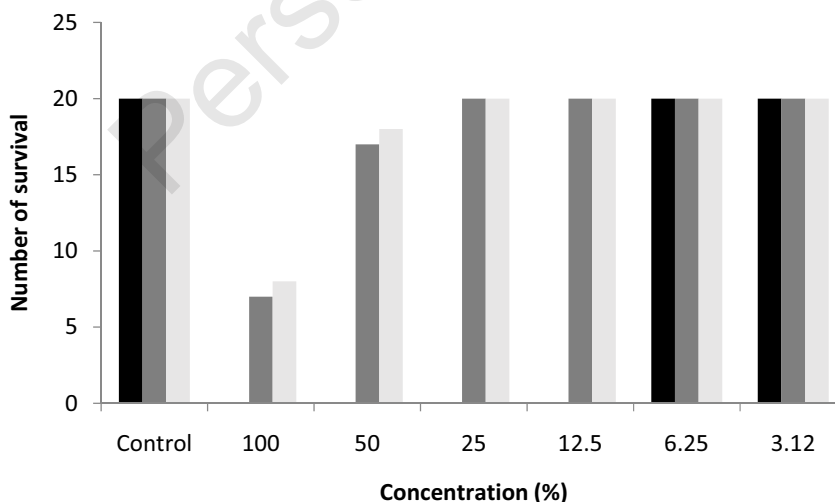

Fig. (2). Toxicity Identification Evaluation for leached of surfactant-modified zeolite from bottom ash on raw leached (black) and after manipulation with ethylenediaminetetraacetic acid (EDTA) (grey) and solid-phase extraction (SPE) (light grey).
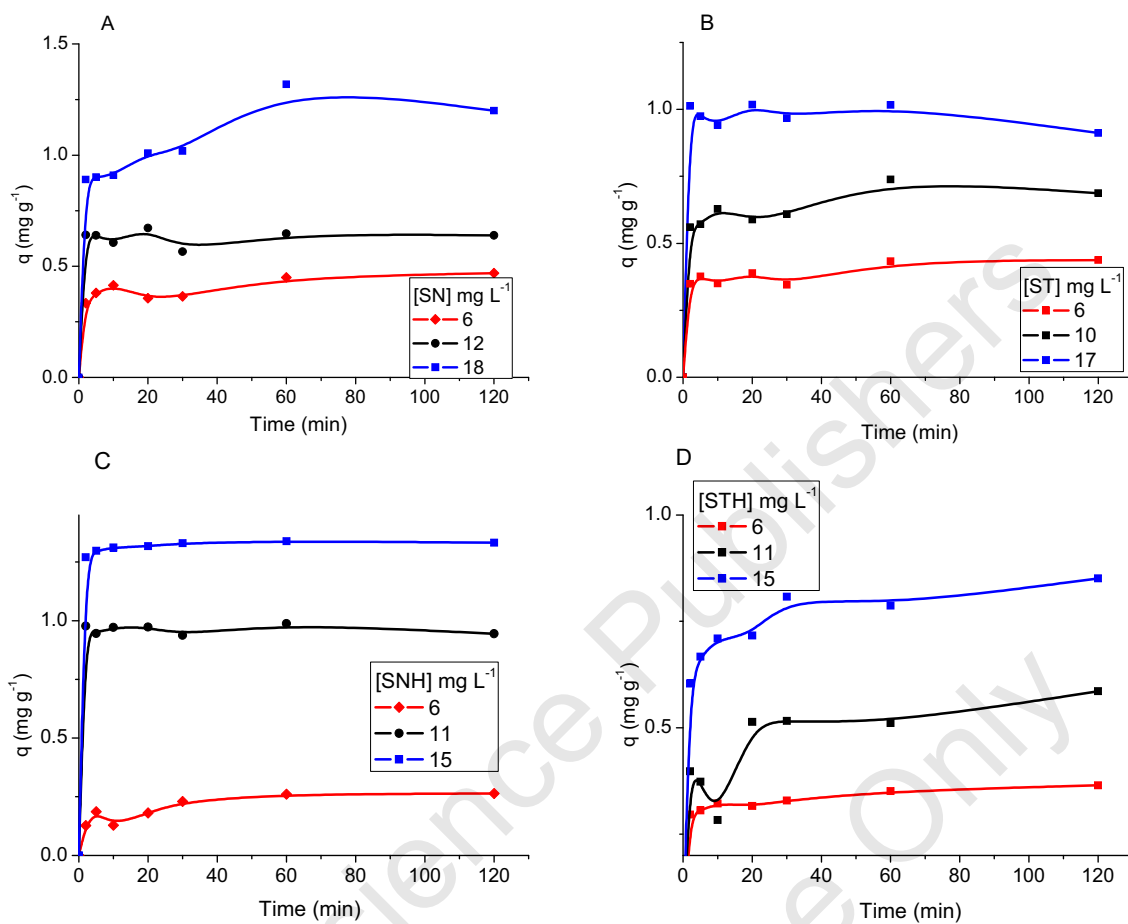
Fig. (3). Effect of agitation time and initial concentration on the adsorption capacity of Solophenyl Navy (**A**), Solophenyl Turquoise (**B**), Solophenyl Navy Hydrolysed (**C**) and Solophenyl Turquoise Hydrolysed (**D**) by ZMB   (T= 25 °C; pH = 5).

Table 1.   Kinetic parameters for the removal of Solophenyl Navy (SN), Solophenyl Turquoise (ST), Solophenyl Navy Hydrolysed (SNH) and Solophenyl Turquoise Hydrolysed (STH) onto ZMB.

Dye	Concentration (mg L^{-1})	Pseudo-first-order			Pseudo-second-order			
		k_1 (min)$^{-1}$	qe_{cal} (mg g^{-1})	$R_1^{(1)}$	k_2 (g mg^{-1} min^{-1})	qe_{cal} (mg g^{-1})	$R_2^{(2)}$	qe_{exp} (mg g^{-1})
SN	6	4.01x10^{-2}	0.181	0.413	1.24	0.472	0.997	0.365
	10	24.8x10^{-2}	5.97	0.971	3.01	0.641	0.999	0.647
	17	1.43x10^{-2}	0.0846	0.999	0.273	1.24	0.996	1.31
ST	6	0.0856x10^{-2}	0.00212	0.141	0.871	0.444	0.997	0.443
	12	0.817x10^{-2}	0.161	0.482	0.799	0.702	0.998	0.738
	18	37.3x10^{-2}	6.74	0.885	1.41	0.925	0.998	1.016
SNH	6	0.472x10^{-2}	0.0545	0.999	1.36	0.277	0.996	0.181
	11	15.6x10^{-2}	0.885	0.973	3.04	0.948	0.999	0.973
	15	44.9x10^{-2}	0.325	0.997	6.09	1.29	0.999	1.31
STH	6	237.2x10^{-2}	1.06	0.709	1.751	0.367	0.999	0.329
	11	23.6x10^{-2}	0.471	0.567	0.432	0.599	0.995	0.516
	15	168x10^{-2}	0.184	0.834	0.588	0.856	0.999	0.808

(1) R$_1$ = Correlation coefficients of pseudo-first-order model; (2) R$_2$= Correlation coefficients of pseudo-second-order model.

those of the theoretical adsorption capacity ($q_{e\ calc}$) that were calculated with the pseudo-second order model for all systems dye-ZMB.

The parameters of the Langmuir, Freundlich and Temkin isotherm models for dyes/ZMB systems were determined by linear and nonlinear regression and are listed in Table **2**. The R^2 values (correlation coefficients of linear equation) for the Langmuir model are closer to unity than those for the other isotherm models, showing that the experimental equilibrium data for most of the systems were better explained by the Langmuir equation, with exception of SNH/ZBM system. The SNH and STH dyes showed higher value of maximum adsorption capacity (Q_0) relative to their non-hydrolysed form. This finding supports the fact that the molecular weight of dyes decreases after hydrolysis process and consequently increases the removal efficiency of ZMB.

3.3. Characterization of the Materials

The physico-chemical properties of BA, ZB and ZMB are given in Table **3**. The major constituents of all materials are silica (SiO_2), alumina (Al_2O_3) and ferric oxide (Fe_2O_3). A significant amount of Na element is incorporated in the final zeolitic materials due to hydrothermal treatment with NaOH solution [42]. The SiO_2 /Al_2O_3 ratio was 1.95, 1.45 and 1.41 for BA, ZB and ZMB, respectively, and this ratio is associated to the cation exchange capacity [42]. The SiO_2/Al_2O_3 ratios for the zeolites were lower than those of raw fly ash suggesting that the hydrothermal treatment contributed to the increase in the cation exchange capacity of those materials. The bulk density values ranged from 1.32 to 1.76 g cm^{-3}. The BET surface area of zeolites was approximately 7-8 times

greater than its precursor material. This area increase is due to the crystallization stage on the spherical particles of the bottom ash after hydrothermal treatment [42].

The values of pH_{PZC} of ZB and ZMB (Table **3**) were lower than the pH in water, suggesting that the surface was negatively charged in aqueous solution for both nanoadsorbents. In the case of ZMB, the negative charge indicated incomplete formation of bilayer of surfactant on the surface of zeolite ZB [31].

Fig. (**4**) shows X-ray diffraction patters of the modified zeolite from coal bottom ash and modified zeolite saturated with ST and SN dyes. The identification and interpretation of PXRD patterns of the materials are prepared by comparing the diffraction database provided by "International Centre for Diffraction Data/Joint Committee on Power Diffraction Standards" (ICDD/JCPDS). According to Fig. (**4**), ZBM is composed mainly of quartz (ICDD / JCPDS 001-0649) and mulite (ICDD / JCPDS 002-0430) and presented hydroxysodalite (ICDD / JCPDS 011-0401) as well as zeolites. Quartz and mullite are considered as resistant phases and remained in the zeolite sample after hydrothermal treatment.

The scanning electron micrographs (SEM) of BA, ZB and ZMB are shown in Fig. (**5**). Coal bottom ash particles typically had the predominance of spherical shapes at different sizes and smooth surfaces (Fig. **5A**), similar to previous observations from other studies [23-26, 31, 32, 42] According to Fig. (**5B** and **C**), the surface of zeolites is rough, indicating that zeolite crystals were deposited on the surface of bottom ash particles during the hydrothermal treatment [23-26, 31, 32, 42]. However, morphological difference between ZB and ZMB was not observable.

Table 2. Adsorption isotherms parameters for Solophenyl Navy (SN) and Turquoise (ST) and its hydrolyzed forms (SNH e STH) onto ZMB.

	Linear	Non Linear	Linear	Non Linear	Linear	Non Linear	Linear	Non Linear
	SN		ST		SNH		STH	
Langmuir								
Q_0 (mg g^{-1})	0.235	0.256	0.492	0.483	1.26	1.12	1.86	1.59
b (L mg^{-1})	0.201	0.192	0.123	0.129	0.115	0.11	0.193	0.195
R^2	0.997	--	0.998	--	0.759	--	0.964	--
Freundlich								
K_f [a]	0.0552	0.0621	0.0567	0.0681	0.181	0.197	0.347	0.531
N	2.21	2,46	1.44	1.66	2.13	2.22	1.92	2.83
R^2	0.962	--	0.988	--	0.783	--	0.884	--
Temkin								
Kt (L g^{-1})	2.31	2.31	1.51	1.51	0.982	0.982	1.52	1.52
B_t	0.0525	0.0525	0.0984	0.0984	0.260	0.260	0.459	0.459
bt [b]	72	72	251	251	935	935	541	541
R^2	0.950	--	0.990	--	0.776	--	0.877	--

(a) [(mg g^{-1}) (L mg^{-1}) $^{1/n}$]; (b) (kJ mol^{-1}).

Table 3.   Physico-chemical properties of bottom ash (BA), zeolite from bottom ash (ZB) and surfactant-modified zeolite bottom ash (ZMB).

| Properties	BA	ZB	ZMB
SiO_2 (wt. %)	41	32	35
Al_2O_3 (wt. %)	21	22	25
Fe_2O_3 (wt. %)	12	12	11
Na_2O (wt. %)	0.8	12	9.9
CaO (wt. %)	5.6	6.7	5.5
TiO_2 (wt. %)	2.3	2.5	2.2
SO_3 (wt. %)	6.1	8.8	7.4
MgO (wt. %)	1.6	2.9	3
Br (wt. %)	<0.02	<0.02	0.12
SiO_2/Al_2O_3	1.95	1.45	1.41
BET surface area ($m^2\ g^{-1}$)	5.25	39.9	36.0
Bulk density ($g\ cm^{-3}$)	1.32	1.76	1.68
CEC ($meq\ g^{-1}$)[a]	0.0985	1.12	2.51
pH in water	8.1	9.8	9.9
pH_{pzc}[b]	---	8.5	5

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

CONCLUSION

This study demonstrates the application of bottom ash, a solid waste generated in large amounts, as raw material for surfactant-modified nanozeolite synthesis. Surfactant-modified nanozeolite from bottom ash (ZMB) was used for removing Solophenyl dyes and its hydrolyzed forms from simulated textile wastewater. A percentage of dyes removal between 50-70% was achieved. The adsorption kinetics of Solophenyl dyes onto ZMB were found to follow a pseudo-second-order model. The equilibrium adsorption data fitted well with Langmuir isotherm models. The main mechanism controlling adsorption of Solophenyl dyes onto ZMB with incomplete bilayer of HTDMA can be attributed to partition between sulphonates groups and hydrophobic "tail" of the surfactant.

Regarding ecotoxicity tests, the results showed toxic effect for *C. dubia* (11.3 T.U), and this toxicity could be appointed as the residual surfactant found in the aqueous solution after the treatment with ZMB plus metals. The toxicity was substantially reduced after SPE and EDTA manipulations. TIE tests suggest that the toxicants could be a mixture of metals and organic compounds on the leached of ZMB. Thus, this study suggests that the assay with *C. dubia* is an excellent method for evaluation and identification of toxicity of hybrid organic–inorganic nanoadsorbents.

Taking into account that dying process consumes high quantities of clean-potable water for its processes, it is suggested by the results that ZMB can be used as a tertiary treatment at dyeing industries but the wastewater containing modified-surfactant zeolite bottom must not not be discarded directly into water bodies, but it can be used as non-potable water reuse for industries processes.
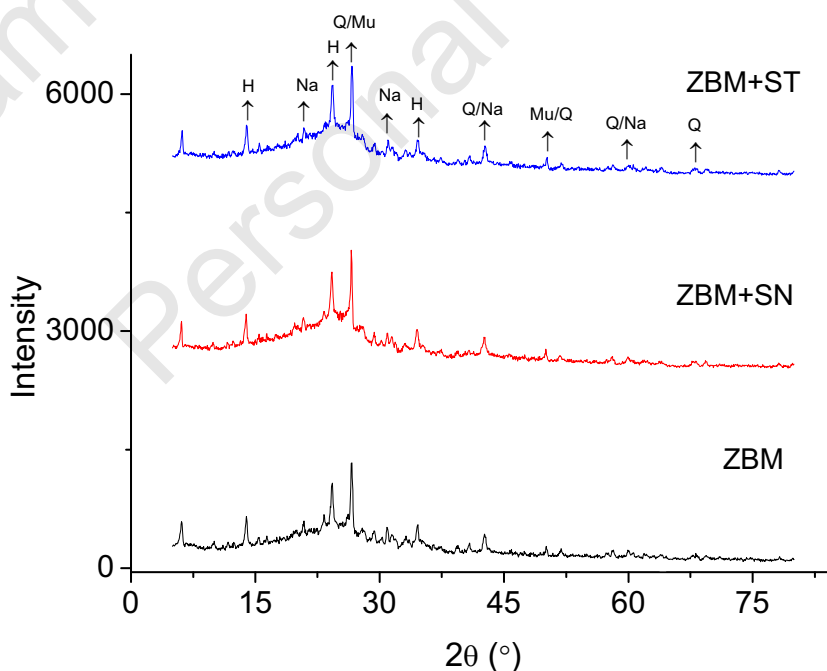
Fig. (4). XDR before adsorption process (ZMB) and after adsorption process with Solophenyl Navy (ZMB+SN) and Solophenyl Turquoise (ZMB+ST) dyes (Q = Quartz; M = Mulite and H =Hydroxysodalite, Na= NaP1).
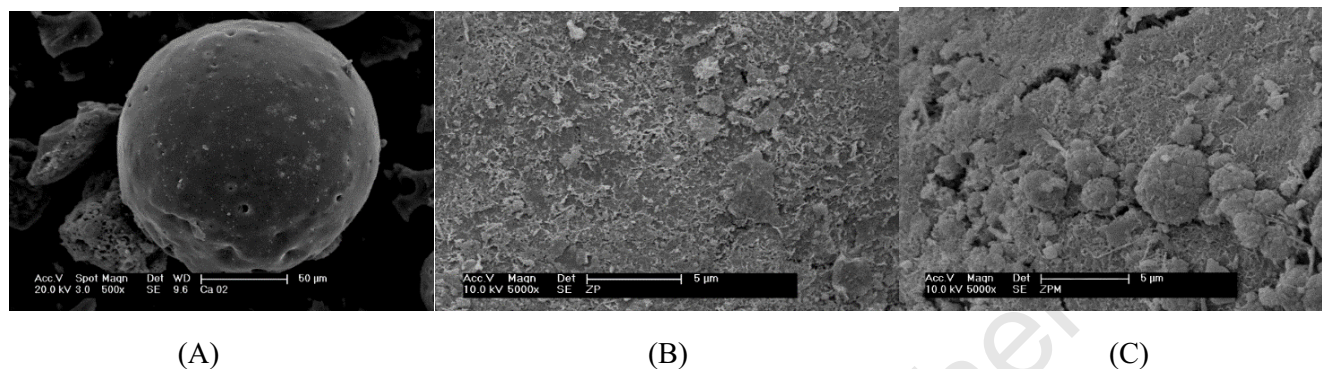
(A)   (B)   (C)

Fig. (5). SEM images of bottom ash (**A**); zeolite from bottom ash (**B**); modified zeolite from bottom ash (**C**).

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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