

Removal of indigo carmine and green bezanyl-F2B from water using calcined and uncalcined Zn/Al + Fe layered double hydroxide

Hassiba Bessaha, Mohamed Bouraada and Louis Charles Deménorval

ABSTRACT

Layered double hydroxide Zn/(Al + Fe) with a molar ratio of 3:(0.85 + 0.15), designated as ZAF-HT, was synthesized by co-precipitation. Its calcined product CZAF was obtained by heat treatment of ZAF-HT at 500 °C. The calcined and uncalcined materials were used to remove the acid dyes indigo carmine (IC) and green bezanyl-F2B (F2B) from water in batch mode. The synthesized materials were characterized by X-ray diffraction, scanning electron microscopy, Brunauer–Emmett–Teller analysis, Fourier transform infra-red spectroscopy and thermogravimetric/differential thermal analysis. The sorption kinetic data fitted a pseudo-second-order model. The adsorbed amounts of the calcined material were much larger than ZAF-HT. The maximum adsorption capacity of CZAF was found to be 617.3 mg g⁻¹ for IC and 1,501.4 mg g⁻¹ for F2B. The isotherms showed that the removal of IC and F2B by ZAF-HT and CZAF could be described by a Langmuir model. The thermodynamic parameters were also calculated. The negative values of standard free energy ΔG° indicate the spontaneity of sorption process. The reuse of CZAF was studied for both dyes and the calcined material showed a good stability for four thermal cycles.

Key words | acid dyes, adsorption, intercalation, layered double hydroxides, mixed metal oxides

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INTRODUCTION

Synthetic dyes have long been used in various industries, such as textiles, cosmetics, paper, leather, pharmaceuticals and foods (Yuan *et al.* 2009). During and after the dyeing process, huge amounts of dyes are released as industrial discharges into the environment causing serious problems. They are aesthetic pollutants, and the coloration of water by dyes reduces the penetration of light which affects photochemical activities (McMullan *et al.* 2001). As a result, the aquatic ecosystem is destroyed. Moreover, it has been reported that many dyes are toxic, carcinogenic and mutagenic for aquatic organisms, even at very low doses, and may cause severe damage to human beings, such as dysfunction of the kidneys, reproductive system, liver, brain and central nervous system (Mittal & Gupta 1996).

Chemical, electrochemical and photochemical methods, reverse osmosis, coagulation and aerobic and anaerobic biodegradation have been used to remove dye compounds from water and wastewater (Zhu *et al.* 2005; El Gaini *et al.* 2009). However, photodegradation methods may not fully mineralize synthetic dyes, due to their resistance, and also may produce persistent degradation products which are toxic and carcinogenic for aquatic organisms (Lourenco *et al.* 2001). Furthermore, treatment of dyes in water by chemical or electrochemical methods, reverse osmosis and coagulation is not widely applicable because of economic considerations (Zhu *et al.* 2005; El Gaini *et al.* 2009). However, the adsorption process has widely been used to remove different types of dye from water using less expensive adsorbents. This process has several advantages over others, such as high efficiency, no harmful by-products and simplicity of operation.

Layered double hydroxides (LDHs), also known as hydrotalcite-like materials or anionic clay, can be good

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doi: 10.2166/wrd.2016.042

adsorbents for removal of organic and inorganic pollutants because of their high capacity for anion exchange and high layer charge densities (Extremera *et al.* 2012; González *et al.* 2015). LDHs are scarce in nature, but can be prepared easily and in large quantities in the laboratory using inexpensive precursors (Seftel *et al.* 2008). Their general formula is $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2(A^n)_{x/n}m\text{H}_2\text{O}]$, where M^{2+} and M^{3+} are di- and trivalent metal cations, A^n is an exchangeable organic or inorganic anion with negative charge n , m is the number of interlayer water molecules and $x = M^{3+}/(M^{2+} + M^{3+})$ is the layer charge density of the LDH (Kameda *et al.* 2015). LDHs can be used to remove pollutants by anionic exchange with the original interlayer anions. However, the latter process is not always feasible, especially when the initial interlayer anions have a strong affinity toward the LDH layers, e.g. carbonates ions.

Calcination transforms LDHs into mixed metal oxides with high specific areas and homogeneous dispersion of metal cations (Ni *et al.* 2007). The calcined-LDHs (CLDHs) are also used as adsorbents to remove anionic contaminants from water via a specific property called 'memory effect'. The CLDHs regain their original structure by the intercalation of anionic species such as acid dyes (Lv *et al.* 2006).

In the present study, ZAF-HT LDH was synthesized by co-precipitation and calcined at 500 °C (CZAF). The adsorptive performances of the calcined and the uncalcined materials were tested on the uptake of two anionic dyes, indigo carmine (IC) and green bezanyl-F2B (F2B), from aqueous solution in batch mode. The effect of various sorption factors, such as kinetics, solution pH, isotherms and temperature, was investigated. The thermodynamic parameters of change in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated. The reusability study of CZAF for both dyes for four thermal cycles was also studied.

METHODS

Materials and reagents

IC (purity 99%) was produced by Ciba Society (Zurich, Switzerland) and F2B, was provided by the company Soitex, Tlemcen, Algeria. The dyes were used as received. Dye

solutions were prepared by dissolving an accurately known amount of dye (1 g L^{-1}) in distilled water and subsequently diluting to required concentrations. Aluminium chloride hexahydrate (purity 99%) and urea (purity 98%) were obtained from Sigma-Aldrich, Germany. Zinc chloride (purity 98%, Paureac, Spain) and ferric chloride (purity 99%, Chemopharma, Austria) were used as received.

Synthesis of ZAF-HT and CZAF

Zn/(Al + Fe) DLH with a molar ratio of 3/(0.85 + 0.15) was synthesized by co-precipitation according to the literature with some modifications (Mantilla *et al.* 2010). A mixture of 0.06 moles of ZnCl_2 , 0.017 moles of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.003 moles of FeCl_3 was dissolved in 200 mL of deionized water. The latter solution was added dropwise to a glass reactor vessel containing 100 ml of urea solution (20% w/v) as precipitant agent, with vigorous stirring. The pH of the suspension was adjusted to 10.5 by using 2 M NaOH. The resulting precipitate was vigorously stirred for 4 h at room temperature and then heated at 90 °C under reflux for 36 h. The material obtained was separated by centrifugation, washed thoroughly with deionized water several times until the precipitate was free from Cl^- (AgNO_3 test) and air-dried at 100 °C overnight. This material, designated as ZAF-HT, was ground and sieved to obtain a particle size of <0.250 mm. A portion of ZAF-HT was calcined in air at 500 °C for 4 h and designated as CZAF.

Characterization of the materials

The samples were characterized by several physical and chemical techniques. Powder X-ray diffraction (XRD) patterns were recorded using a Phillips X'Pert MPD diffractometer with monochromatic $\text{CuK}\alpha = 1.5418 \text{ \AA}$ (40 kV, 30 mA). Fourier transform infra-red (FTIR) spectra were obtained in a transmission mode on a Nicolet Avatar 330 FTIR spectrometer by using KBr disks containing 1wt % samples. The spectra were recorded with 2 cm^{-1} resolution in the range 4,000–400 cm^{-1} . Thermogravimetric analysis (TGA) of solid samples was conducted using a NETZSCH STA 409 PC/PG simultaneous thermal analyser, heated from 20 to 900 °C at a heating rate of 10 °C/min under a N_2 flow rate of 50 mL/min. The Brunauer–

Emmett–Teller (BET) specific surface areas and pore sizes of the samples were determined by N₂ adsorption–desorption isotherms using a Micromeritics ASAP (2010). The particle morphologies of ZAF-HT and CZAF were observed by scanning electron microscopy (SEM) using a Hitachi S-2600N variable pressure scanning electron microscope.

Adsorption equilibrium experiments

The removal of IC and F2B was studied in batch mode at room temperature and at atmospheric pressure. The effects of contact time, solution pH, initial concentration of the dyes and temperature on the adsorption process were investigated. A suspension containing 25 mg of ZAF-HT or CZAF was added to 50 ml of IC or F2B solution with initial concentrations of 250 and 750 mg L⁻¹, respectively. The suspensions were stirred for various time intervals (0.5–24 h) without adjusting the initial pH of solution. To study the effect of pH, the suspension pH was adjusted in the range 5.0–9.5 by adding 1 N HCl or 1 N NaOH. Samples were stirred during equilibration and then centrifuged. The concentrations of dyes in the supernatant were determined by visible spectrophotometry on a HACH DR/4000 U spectrophotometer at 610 nm and at 646 nm for IC and F2B, respectively. The equilibrium sorption amount Q_e (mg g⁻¹) (Equation (1)) and the removal percentage of the dyes (R %) (Equation (2)) were calculated using the following equations:

$$Q_e = \frac{(C_i - C_t)}{m} \times V \quad (1)$$

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

where C_i (mg L⁻¹) and C_e (mg L⁻¹) are the initial and the equilibrium concentration of dyes, respectively, C_t (mg L⁻¹) is the concentration of the dye solution at time t , V (L) is the solution volume and m (g) is the adsorbent mass.

Temperature effect

The temperature effect was studied on suspensions of CZAF in IC and F2B solutions with initial dye concentration of 260

and 800 mg.L⁻¹, respectively (solid/solution ratio = 0.5 g L⁻¹). The suspensions were stirred during the equilibrium time at three constant temperatures (25, 35 and 45 °C) and then centrifuged, and the residual concentrations were determined as above.

Reusability study

The regeneration of CZAF was based on a thermal recycling method. After the adsorption of dyes (IC or F2B), the material was recovered and calcined at 500 °C for 4 h, and then the calcined product was dispersed into a known concentration of dye solution. The residual concentration of dye was determined as above. This procedure was repeated three times.

RESULTS AND DISCUSSION

Characterization of materials

The XRD patterns of ZAF-HT, CZAF before and after sorption experiments are shown in Figure 1. The XRD pattern of the original LDH showed sharp and symmetrical peaks with some asymmetrical peaks at a high angle, indicating good crystallinity (You et al. 2002). The interlayer distance of ZAF-HT at 003 reflection was 7.645 Å (d_{003}), which is higher than value reported by Mantilla et al. (2009). The XRD spectra of the calcined sample (CZAF) at 500 °C confirmed that the layered structure was destroyed where

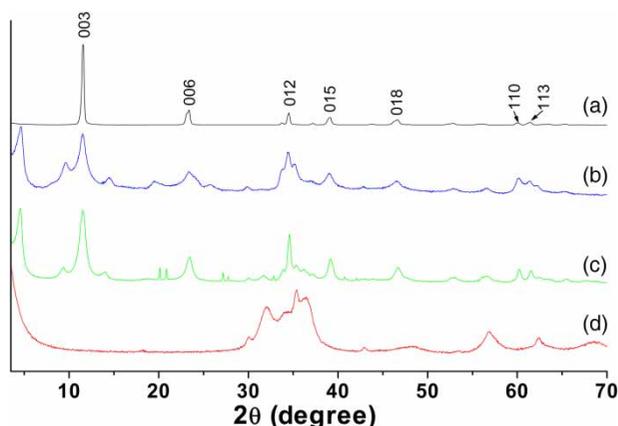


Figure 1 | XRD patterns: ZAF-HT (a), ZAF-IC (b), ZAF-F2B (c) and CZAF (d).

the carbonates anions and water molecules of the interlayer space had decomposed. New diffraction lines appeared (Figure 1(d)) which can probably be associated with the presence of the mixed metal oxides as seen in Mantilla *et al.* (2010). After the retention of IC and F2B by CZAF, a new peak was observed at weak 2 θ . However, the intensity of the peaks (003) and (006) decreased slightly indicating some reductions in the crystallinity after calcination and rehydration (Zhu *et al.* 2005). Moreover, the interlayer distance was increased from 7.645 Å in ZAF-HT to 18.652 Å after the adsorption of IC and to 19.031 Å after the uptake of F2B. These values may suggest that the dye molecules were inserted vertically into the interlayer space (Chen *et al.* 2012).

The intercalation of IC and F2B was also shown by FTIR spectra (Figure 2). The ZAF-HT spectra showed an intense broad band at 3,460 cm^{-1} corresponding to the stretching vibration of the metal hydroxide layer and interlayer water molecules. The shoulder near 3,200 cm^{-1} is associated with the H-bond stretching vibration of the interaction between CO_3^{2-} and water molecules in the interlayer space (Dula *et al.* 2002). The weak peak at 1,637 cm^{-1} can be attributed to the H_2O bending vibration of interlayer water (Chen *et al.* 2012). The strong peak observed at 1,362 cm^{-1} was assigned to the ν_3 vibration of the interlayer carbonate anions (Yuan *et al.* 2009). The bands in the range 500–700 cm^{-1} probably were due to metal–oxygen–metal vibrations.

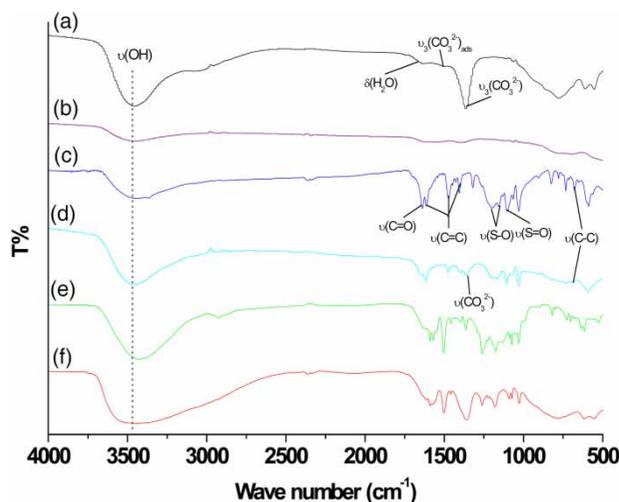


Figure 2 | FTIR spectra: (a) ZAF-HT; (b) CZAF; (c) IC; (d) ZAF-IC; (e) F2B; (f) ZAF-F2B.

The retention of IC by CZAF was demonstrated by the appearance of new peaks at 681 cm^{-1} , attributed to the C–C single vibration; at 1,614 cm^{-1} , assigned to the double bonding of the ethylenic band; and the bands at 1,473–1,399 cm^{-1} , which are probably due to the double bonding of the aromatic ring system (El Gaini *et al.* 2009). The C = O vibration band was also present at 1,640 cm^{-1} and the S–O vibration bands appeared at 1,153 and 1,199 cm^{-1} . The band assigned to $\nu(\text{S}=\text{O})$ at 1,104 cm^{-1} was shifted to 1,110 cm^{-1} (El Gaini *et al.* 2009). The intensity of vibration bands decreased after the fixation of the IC dye. The FTIR spectra of F2B and ZAF-F2B showed the presence of many common peaks indicating the uptake of F2B dye by CZAF. The FTIR results were consistent with the XRD patterns.

Nitrogen adsorption–desorption isotherms of uncalcined and calcined samples are shown in Figure 3. The data were presented in arbitrary units, showing only the form of the isotherm and not its real values. According to IUPAC classification, ZAF-HT and CZAF followed by type IV isotherm with H3 hysteresis corresponds to mesoporous solids with slit-shaped irregular pores (Parida & Mohapatra 2012). The surface area for ZAF-HT was 28.59 m^2/g , while for CZAF it was almost double (53.29 m^2/g). SEM images of ZAF-HT and CZAF are shown in Figure 4(a) and 4(b), respectively. It can be seen that ZAF-HT has a planar structure with particles of various sizes. Upon calcination, the structure of hydrotalcite crumbled as the planar forms become fragile and the size of the particles becomes smaller; this change can be attributed to the formation of mixed metal oxide.

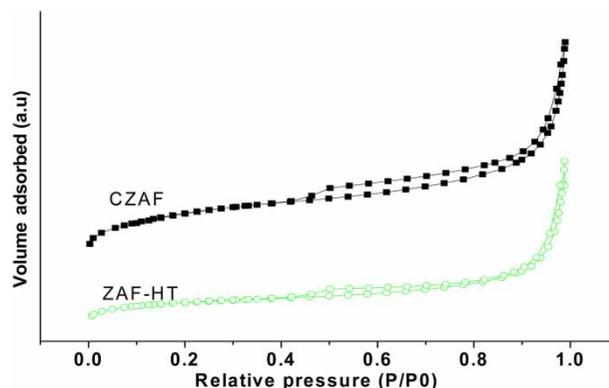


Figure 3 | N_2 adsorption–desorption curves of uncalcined and calcined material.

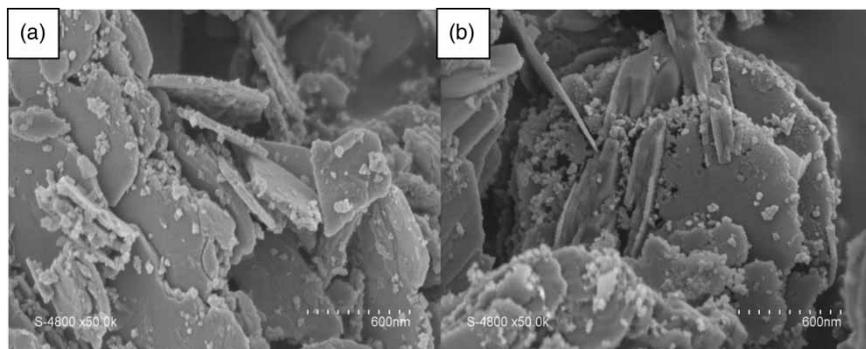


Figure 4 | SEM images: (a) ZAF-HT; (b) CZAF.

Figure 5 shows the thermoanalytical measurements of ZAF-HT to evaluate the different transformations of the sample during the heat treatment. At temperature range 80–220 °C, a small endothermic peak was observed and related to dehydration of water molecules from the internal gallery and the external non-gallery surfaces. In the second region from 220 to 400 °C, about 11% of weight was lost due to the dehydroxylation and the beginning of carbonate decomposition (Seftel et al. 2008).

Effect of contact time and kinetic modelling

The contact time between the pollutants and the adsorbent is an important parameter in treatment by adsorption. Figure 6(a) shows the time effect on the sorption of IC and F2B by CZAF: the adsorbed amount increased with contact time, and remained almost constant after 4 h and 20 h for IC and F2B, respectively,

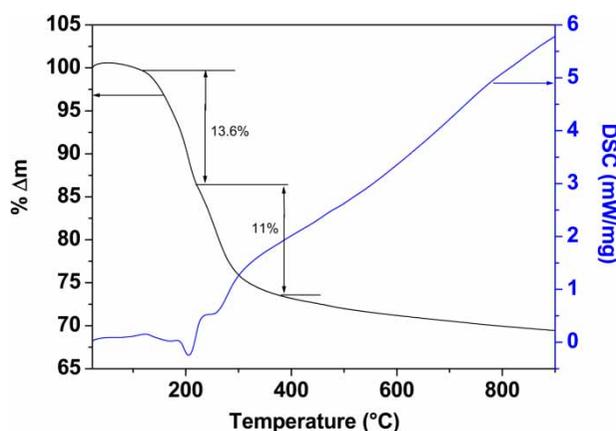


Figure 5 | TGA and differential thermal analysis (DTA) of ZAF-HT.

indicating an equilibrium state. The adsorption capacity of the material at the equilibrium was 488.9 mg g⁻¹ for IC and 1,487.9 mg g⁻¹ for F2B. El Gaini et al. (2009) studied the removal of IC by calcined Mg-Al-CO₃ where the equilibrium time was found to be 20 min. However, Bouraada et al. reported that the sorption of F2B by Mg-Al-SDS takes 2 h to reach the equilibrium state (Bour-aada et al. 2009). Thus, the equilibrium time depends closely on the nature of the adsorbent (structure and chemical composition) and the dye structure.

Adsorption kinetics models were used in order to explain the possible adsorption mechanism. Pseudo-first-order (Equation (3)) and pseudo-second-order (Equation (4)) are the most used models (Mantilla et al. 2009), and they were applied to the experimental data of the uptake of IC and F2B by CZAF material.

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 \times t \quad (3)$$

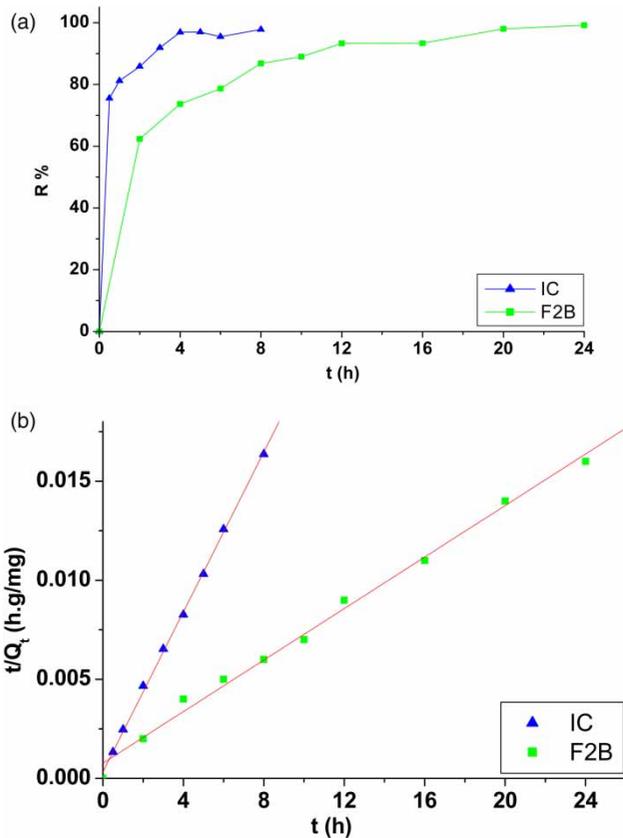
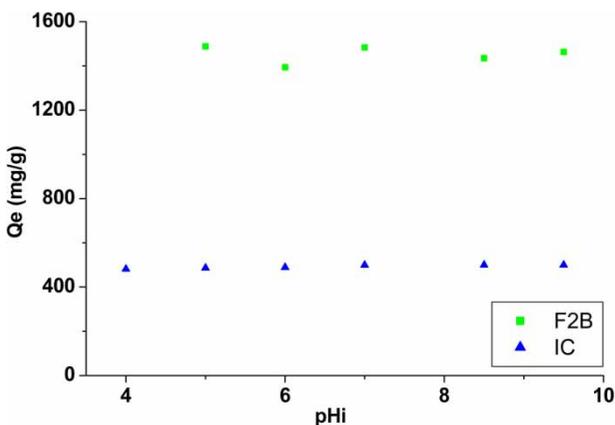
$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (4)$$

where Q_t and Q_e are the adsorbed amount at time t and at equilibrium state, respectively (mg g⁻¹), k_1 : the pseudo-first-order rate constant of adsorption (h⁻¹), and k_2 : the pseudo-second-order rate constant of adsorption (g mg⁻¹ h⁻¹).

The kinetic parameters of the models were calculated and are reported in Table 1. Based on the values of determination coefficient R^2 , the sorption of the dyes was better expressed by a pseudo-second-order kinetic model (Figure 6(b)). Several studies reported that the adsorption of acid dyes by anionic clay was described by a pseudo-

Table 1 | Parameters of pseudo-first- and the pseudo-second-order models for sorption of IC and F2B by CZAF

Dyes	C_i (mg L ⁻¹)	Q_{exp} (mg g ⁻¹)	k_1 (h ⁻¹)	Q_1 (mg g ⁻¹)	R_1^2	k_2 (mg g ⁻¹ h ⁻¹)	Q_2 (mg g ⁻¹)	R_2^2
IC	250	488.94	0.803	207.06	0.926	0.0124	500	0.999
F2B	750	1,487.9	0.140	1,107.6	0.965	5.5×10^{-4}	1,538.2	0.993

**Figure 6** | (a) Effect of contact time on removal of IC and F2B by CZAF; (b) pseudo-second-order plots for the sorption of IC and F2B by CZAF.**Figure 7** | Effect of pH on adsorption capacity of IC and F2B by CZAF.

second-order model (Ni *et al.* 2007; Bouraada *et al.* 2009; El Gaini *et al.* 2009; Ahmed & Gasser 2012).

Effect of initial pH

The variation of the sorption capacity of CZAF at different initial pH solution is presented in Figure 7. This figure showed that the sorption amount was almost constant in the studied pH range (5.0–9.5) for both dyes. These results are consistent with previous reports (El Gaini *et al.* 2009). Thus, it was decided for the rest of this study to carry out the sorption experiments without pH adjustment (pH_i of IC equal 6.10 and pH_i of F2B equal 5.01).

Sorption isotherms

Sorption isotherms of IC and F2B by CZAF and ZAF-HT are shown in Figure 8. The sorption capacities of CZAF were higher than those of ZAF-HT for both dyes. The adsorption amount of F2B by CZAF was about a hundred times greater than that of ZAF-HT. On the other hand, the mixed oxides metals CZAF regained their original structure by the intercalation of the dye molecules into interlayer space. Moreover, the sorption capacity of F2B by CZAF was three times greater than that of IC. This is probably related to the chemical structure of the dyes and their affinity towards the calcined material. These results suggest that calcined LDHs may be good adsorbents for removal of a wide range of anionic dyes from wastewater (You *et al.* 2002).

The experimental isotherm data were investigated with the most frequently used isotherm models: Langmuir and Freundlich. The linearized formula of Langmuir model (Equation (5)) and Freundlich (Equation (6)) (Zhu *et al.* 2005; Bouraada *et al.* 2009) are expressed by the following equations:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{K_L Q_{\max}} \quad (5)$$

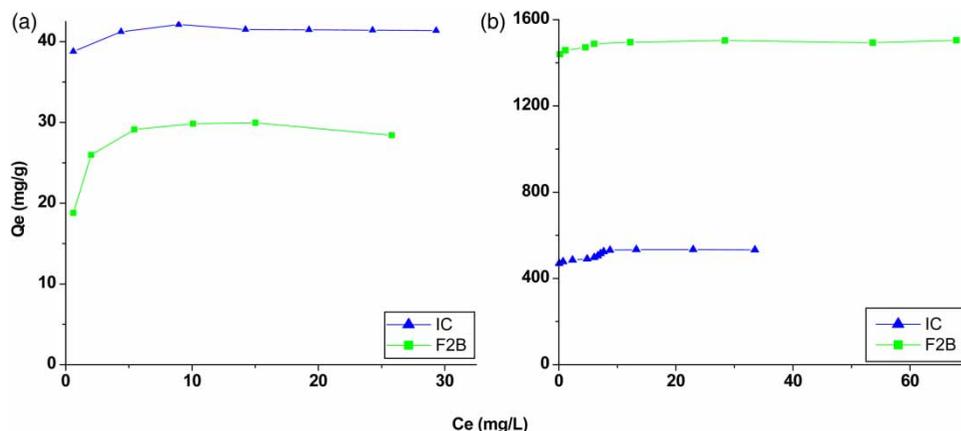


Figure 8 | Sorption isotherms of IC and F2B by (a) ZAF-HT and (b) CZAF.

$$\ln Q_e = \frac{1}{n} \times \ln C_e + \ln K_F \quad (6)$$

where C_e (mg L^{-1}) is the equilibrium concentration of dyes, Q_e is the amount adsorbed at equilibrium, Q_{max} is the maximum monolayer adsorption capacity (mg g^{-1}), K_L is the Langmuir constant refers to energy of adsorption and K_F is the Freundlich isotherm constant (L g^{-1}) related to the adsorption capacity. $1/n$ is the heterogeneity factor that could be obtained from the slope of the plot $\ln Q_e$ versus $\ln C_e$.

The parameter values of Freundlich and Langmuir models are reported in Table 2. The sorption of both dyes by ZAF-HT and CZAF fitted very well to the Langmuir isotherm model (Figure 9) with determination coefficient values R^2 very close to 1. The maximum adsorption capacity of the calcined material was found to be 617.3 and 1,501.4 mg g^{-1} for IC and F2B, respectively. These values were compared with other studies (Zhu et al. 2005; Ni et al. 2007; Bouraada et al. 2009, 2014; Ahmed & Gasser 2012) and are shown in Table 3; it can be seen that the

negative charges number of the dye has no significant effect on the maximum adsorption capacity. This allows us to conclude that the nature of the adsorbent and the structure of the adsorbed have a significant influence on the adsorbed amount. Moreover, CZAF material showed a strong ability to remove a huge quantity of dyes.

Effect of the temperature

The sorption of IC and F2B by CZAF was studied at different temperatures (25, 35 and 45 °C) to evaluate the variation of the adsorbed amount. The thermodynamic parameters such as change in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were estimated using Equations (7) and (8):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7)$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (8)$$

Table 2 | Langmuir, Freundlich parameters and determination coefficient R^2 for the uptake of IC and F2B by CZAF and ZAF-HT

	Langmuir				Freundlich		
	Q_{exp} (mg g^{-1})	Q_{max} (mg g^{-1})	K_L (L mg^{-1})	R^2	n	K_F (L g^{-1})	R^2
CZAF-IC	488.9	617.3	0.86	0.991	41.15	488.97	0.754
CZAF-F2B	1,487.9	1,501.4	20.75	1	151.58	1,459.28	0.908
ZAF-IC	41.1	41.41	157.29	1	60.97	39.58	0.794
ZAF-F2B	28.4	28.9	20.84	0.998	8.92	22.07	0.752

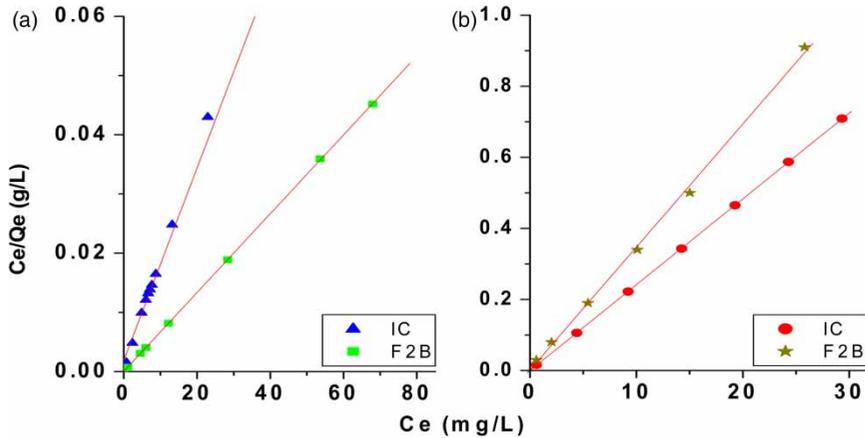


Figure 9 | Langmuir adsorption isotherms of IC and F2B by (a) CZAF and (b) ZAF-HT.

Table 3 | Comparison of the maximum monolayer sorption capacities (Q_{max}) of some dyes on various calcined LDH

LDH nature	Dye	Negative charges number	Q_{max} (mg g ⁻¹)	References
CZAF	IC	2	617.3	This work
CZAF	F2B	Unknown	1,501.4	This work
Zn-Al	Methyl orange	1	200.0	Ni et al. (2007)
Mg-Al	Brilliant blue R	2	613.6	Zhu et al. (2005)
Mg-Al	Yellow thiazole	2	222.2	Bouraada et al. (2014)
Mg-Al	Evans blue	4	107.5	Bouraada et al. (2014)
Mg-Fe	Congo red	2	104.6	Ahmed & Gasser (2012)

where T is the absolute temperature (in K), R is the gas constant (8.314 J mol⁻¹ K⁻¹), and K_d (cm³ g⁻¹) is distribution coefficient of adsorbates between liquid and solid phase. K_d was calculated using Equation (9):

$$K_d = \frac{C_i - C_e}{C_e} \times \frac{V}{m} \quad (9)$$

Figure 10 shows the plots of $\ln K_d$ versus $1,000/T$. The high values of the determination coefficient indicate the good linearity of the plots ($R^2 > 0.995$). The calculated values of ΔG° , ΔH° and ΔS° are shown in Table 4. The negative values of standard free energy indicate the spontaneity of the sorption process, which means a high affinity of CZAF material toward anionic dyes. It was seen also that the value of ΔH° was positive (endothermic) in the sorption of IC, but it was negative (exothermic) for the removal of F2B. These results showed that for IC higher adsorption

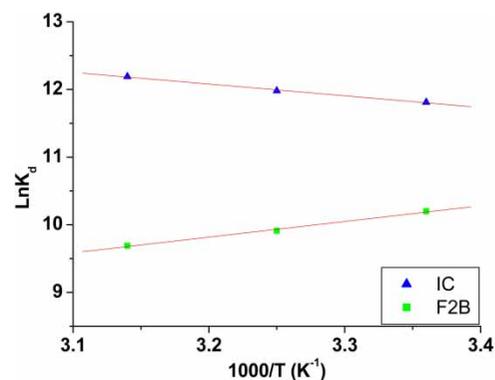


Figure 10 | Van't Hoff plot of the sorption by CZAF of IC and F2B.

occurs at higher temperature, whereas for F2B less adsorption occurs at higher temperature. Positive values of ΔS° showed a high affinity of the material towards the dye molecules and the increasing of the randomness during sorption process (QiuHong et al. 2007).

Table 4 | Thermodynamic parameters for the sorption of IC and F2B by CZAF at several temperatures

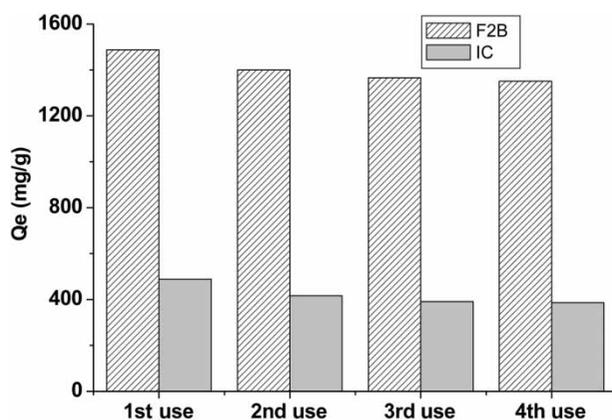
	ΔS° (KJ.mol ⁻¹ .K ⁻¹)	ΔH° (KJ.mol ⁻¹)	ΔG° (KJ.mol ⁻¹)		
			298 K	308 K	318 K
ZAF-IC	0.146	14.360	-29.267	-30.731	-32.195
ZAF-F2B	0.020	-19.273	-25.233	-25.433	-25.633

Reusability of CZAF

Several researchers have studied the possibility of CLDH regeneration by thermal recycling method. The heat treatment of the used CLDHs at around 500 °C can completely decompose the adsorbed organic pollutants and transform the CLDHs for reuse (Shin *et al.* 1996; Crepaldi *et al.* 2002). Figure 11 showed the reusability study of CZAF for both dyes (IC and F2B) for four cycles. The results showed that CZAF exhibits a good stability after four thermal cycles: the adsorption capacities decreased slightly for both dyes and attained 385.7 and 1,365.6 mg g⁻¹ for IC and F2B, respectively for the fourth cycle. After calcination and rehydration, the CLDH crystallinity reduced affecting on the adsorption capacity (Zhu *et al.* 2005). Furthermore, some dye molecules can be presumably interfered with the mixed metal oxides during the heat treatment of CLDHs affecting also their crystallinity.

CONCLUSIONS

In this study, ZAF-HT and CZAF were synthesized and characterized by several experimental techniques (XRD,

**Figure 11** | Reuse of CZAF for the uptake of IC and F2B for four thermal cycles.

BET, FTIR spectroscopy and SEM). The material was used to take up IC and F2B from water in a batch mode. The adsorption capacities of CZAF were found to be 488.94 and 1,487.91 mg g⁻¹ for IC and F2B, respectively. The sorption of IC and F2B does not depend on the pH of the solution. The kinetic data of both dyes fitted the pseudo-second-order kinetic model well, and the isotherm sorption data were described by the Langmuir model. The thermodynamic parameters were calculated and showed that the sorption process was spontaneous in nature. The reusability study of CZAF for the removal of IC and F2B for four cycles showed that the efficiency of the calcined material decreased slightly.

ACKNOWLEDGEMENTS

The authors would like to thank Professor Jersy Zajac, Director of Laboratory AIME-UMR, University of Montpellier, France, for the acceptance in his laboratory allowing us to achieve our characterizations of materials and for inspiring discussions and helpful comments. We would like also to thank all the co-workers cited in the references below for their valuable contributions to the work described here. This work was financially supported by the CNEPRU-Algeria, Project E02220120028.

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First received 22 February 2016; accepted in revised form 8 April 2016. Available online 28 May 2016