



Adsorption of humic acid from aqueous solutions on organo Mg-Fe-SDS

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Abstract

In this study, Organophilic LDH was prepared by interposing a surfactant (sodium dodecylsulfate, SDS 0.1 M) and applied for the removal of humic acid from solutions in batch system, the synthesized adsorbent (Mg-Fe-SDS) was characterized by FTIR, X-ray diffraction, and BET. Several adsorption kinetics models (pseudo-first order, pseudo-second order, n^{th} -order and intraparticle diffusion) were tested against the experimental results. The calculation of the corresponding parameters show that results are best fitted with n^{th} -order ($n \in \mathbb{R}^+$), $n \neq 1$ model with a determination coefficient close to 1 and a relatively small root mean square error. Among the available mathematical models used to describe the isotherms experimental results (Langmuir, Freundlich and many-parameters models). The three models that are proposed show a better performance than Freundlich, Langmuir. The calculation of the parameters of the different adsorption models was performed on MATLAB using genetic algorithms. Thermodynamic analysis of sorption isotherms suggest that sorption process of humic acid is spontaneous ($\Delta G^\circ < 0$), with a positive enthalpy variation, characteristic of an endothermic process.

Keywords: ZnS; doped, co-doped, FP-LAPW, GGA+mBJ

I. Introduction

Humic acids have a strong effect on the properties of natural water since they represent most of the dissolved organic matter with 50% to 90% of dissolved organic carbon [1]. These molecules affect the taste and color of water [2], and represent a source of nutrients to bacteria and trap heavy metals, pesticides and herbicides [3]. Recent use of anionic clays (layered double hydroxides (LDH)) as adsorbents showed a particular interest for the elimination of micro-pollutants [4]. LDH have a brucite layer structure where the brucitic layers ($M_{II}(\text{OH})_2$) are positively charged. This is due to the partial substitution of bivalent cations M^{II} by trivalent cations M^{III} [5]. Electroneutrality is ensured by anionic species, which are solvated by water molecules present in sheets interspace [4]. The insertion of anionic surfactants modifies the hydrophilic property of the clay which becomes hydrophobic and capable of adsorbing organic pollutants [6]. In the present work, SDS based organophilic LDH, calcined at 773 K are used for the elimination of humic acid. A particular interest is given to the investigation of kinetic and thermodynamic equilibrium as well as adsorption thermodynamics to provide a description of the fixation mode using recently proposed multi-parameters adsorption models.

2. Method

2.1 Materials

Sodium dodecylsulfate (SDS, 0.1 M), HCL (0.1 M), NaOH (0.1 M), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, Na_2CO_3 , and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. All reactants from Panreac Química SA Castellar del Valles Barcelona, Espana.

2.2 Preparation of humic acids

Commercially available humic acid (Acros) is used in the experiments. A solution with a concentration of 1 g/L is prepared by dissolving 1 g of humic acid in 62.5 mL of NaOH solution (2 N), followed by addition of distilled water to obtain 1 l of solution. The latter is mixed during 24 h then filtered through a 45 μm filter and finally protected from light and kept at a temperature of 277 K [7].

2.3 Synthesis of Mg–Fe– CO_3 phase

Mg–Fe phase with a ratio of $\text{Mg/Fe} = 2$ was prepared by adding a basic solution of NaOH (2 M) and Na_2CO_3 (1 M) to a mixture of two salts, namely $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (0.66 M) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.33 M). Optimum parameters that would lead to crystallized LDH consist of $\text{pH} = 10$, a temperature of 298 K, and a mixing time of 6 h. The resulting suspension is mixed overnight to enhance material crystallization followed by washing, drying at 338 K, and grinding to obtain Mg–Fe– CO_3 .

Subsequently, LDH are calcined at 773 K during 5 h to improve structural properties and texture, then a decarbonation and dehydration to obtain Mg-Fe-C with enhanced anionic exchange properties [8].

2.4 Preparation of organophilic LDH

Calcined LDH were added to a solution of surfactant, namely sodium dodecylsulfate (SDS, 0.1 M) with solid to solution ratio equal to 1 g/50 mL. The mixture constantly mixed and heated up to 338 K in an oil bath, while maintaining nitrogen reflux to minimize CO_3^{2-} amount in the solution [9]. The resulting solid is washed five times with distilled water, then dried at 338 K and grinded to obtain Mg-Fe-SDS.

2.5 Adsorption kinetics of humic acid

The investigation of the kinetics of adsorption of a component onto an adsorbent enables to assess the influence of contact time on the adsorbed quantity (Eq. (1)). The main objective of this research is to evaluate the time necessary to reach adsorption equilibrium for different concentrations. All results obtained are reported on a $Q_t = f(t)$ plot with:

$$Q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where C_0 is the initial concentration of humic acid AH (mg/L), C_t is the residual concentration at time t (mg/L), V is the volume of the aqueous solution (L) and m the mass of clay. (g).

2.6 Adsorption isotherm

Adsorption isotherms are drawn at room temperature using suspensions with 10 mg of adsorbent in 10 mL solutions with increasing humic acid concentration. The suspensions with pH = 5 are agitated during 6 h then centrifuged.

The total equilibrium concentration of humic acid (C_e) is measured from the supernatant. where C_0 is the initial concentration of humic acid (mg/L), C_e is the residual equilibrium concentration (mg/L), V is the volume of the aqueous solution (L), and m is the mass of clay.

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

2.7 Effect of pH on adsorption

pH represents an important parameter for the adsorption process. It affects the charge of the adsorbent surface and the ionization of different functional groups as well as the adsorbate. The investigation of humic acid adsorption onto materials in seawater is carried out under pH values between 2 and 12. A mass of 10 mg of each material is added to 10 mL of solution with an initial concentration of 10 mg/L.

3. Characterization

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Diffraction patterns of Mg-Fe-CO₃ sample, before calcination, after calcination and after exchange by SDS are represented in figure 1. X-ray diffraction results for Mg-Fe-CO₃ are typical of those of LDH structures encountered in the literature [10]. These symmetrical peaks at (003), (006) and (009), as well as asymmetrical at (015), (018), (110) and (113) indicate that our product is crystallized and similar to those reported in the literature [10]. Mg-Fe-C shows that calcination modifies the crystalline structure of LDHs by causing dehydration, dihydroxylation and decarboxylation. Mixed oxides of MgO type are also formed at $2\theta = 42, 93^\circ$ and $62, 22^\circ$. These oxides, which are formed after calcination, are weakly crystallized and exhibit peak broadening on the XRD diagram in accordance with available literature [11]. After intercalation of SDS surfactant (figure 1), the crystalline structure reappears (memory effect) and shows characteristic peaks that correspond to initial LDH reflections.

Mg-Fe-CO₃ diagram (figure 2) shows a wide band at $\sim 3440\text{ cm}^{-1}$, which corresponds to a stretching vibration of lamellar hydroxide groups bonded to different metals [10, 12]. A small vibration band observed at $\sim 3000\text{ cm}^{-1}$ corresponds to the stretching of water molecules [13]. A vibration band, observed at $\sim 1630\text{ cm}^{-1}$, can be attributed to the deformation of interposed water molecules [12]. A vibration band around 1353 cm^{-1} corresponds to asymmetric stretching of interlamellar carbonates (CO₃-2) [10, 11]. Vibration bands in the range $800\text{--}500\text{ cm}^{-1}$ are attributed to valence vibrations of Mg-O, Fe-O [11]. The presence of SDS ions in the interfoliar space is represented by the two peaks at ~ 2909 and $\sim 2844\text{ cm}^{-1}$ for the Mg-Fe-SDS phase. These two peaks characterize both symmetric and asymmetric stretching of C-H bond that belongs to the linear chain of interposed SDS. The presence of sulfonate groups at $\sim 105(\text{S}=\text{O})$ asymmetric) and $\sim 1193\text{ cm}^{-1}$ ($\nu(\text{S}=\text{O})$ symmetric) is also noticeable [15].

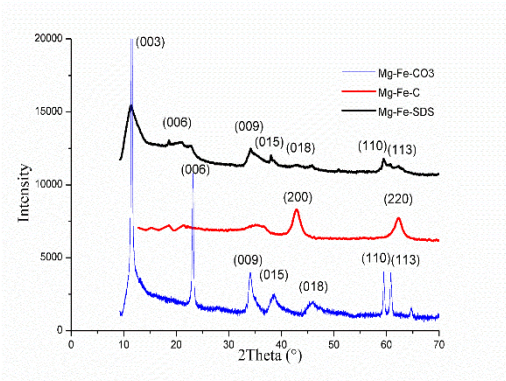


Figure 1. XRD diagrams: Mg-Fe-CO₃, Mg-Fe-C and Mg-Fe-SDS.

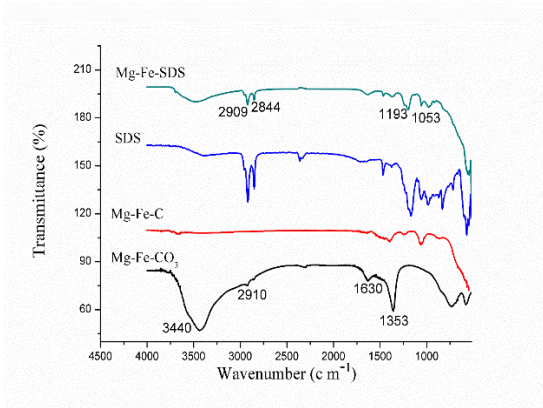


Figure 2. IR spectra of anionic clays.

Table 1. Constants of adsorption kinetics models on different materials ($C_0= 10$ mg/L, $T=298$ K , $pH=5$).

		Mg-Fe-SDS			Mg-Fe-C			
Models	Parameters	Initial concentrations (mg/l)						
		10	30	100	10	30	50	90
Pseudo-first-order model $q_t = q_e(1 - e^{-k_1t})$	Q_e (cal) (mg/g)	9	30	90	8	28	42	70
	$RMSE$	0.7268	1.6112	7.6039	0.3708	2.5974	2.5793	2.4560
	r^2	0.9354	0.9853	0.9332	0.9879	0.9435	0.9677	0.9896
	k_1 (min ⁻¹)	0.2100	0.1611	0.0763	0.0798	0.0899	0.1116	0.1349
Pseudo-second-order model $Q_t = \frac{k_2(Q_e)^2t}{1 + k_2Q_et}$	Q_e (cal) (mg/g)	8.66	29.85	88.78	7.88	27.63	41.72	69.62
	$RMSE$	0.3848	0.7559	3.6864	0.0811	1.4311	1.0807	0.9457
	r^2	0.9771	0.9944	0.9765	0.9990	0.9768	0.9917	0.9976
	k_2 (g/mg/min)	0.0505	0.0143	0.0017	0.0173	0.0056	0.0073	0.0055
n-order model	Q_e (cal) (mg/g)	8.26	29.35	87.59	7.88	26.69	41.59	69.58

$Q_t = 1 - (1 + (n - 1)k_n t)^{\frac{1}{1-n}}$	RMSE	0.1619	0.4090	3.2931	0.0809	0.8875	1.057	0.9420
	r^2	0.9936	0.9977	0.9804	0.9990	0.9885	0.9920	0.9977
	k_n	1.7028	1.7895	0.1992	0.1370	0.3451	0.3752	0.3601
	N	3.2940	2.9355	2.3430	1.9864	2.8749	2.1545	1.9428

3.2 Adsorption isotherm

By adjusting the experimental points on the different new models proposed with several parameters, and based on the values of the coefficient r2 and RMSE, it appears that the values of the coefficient of correlations r2 approaches unity and the RMSE tends towards zero, which clearly shows the precision of the models proposed compared to the Freundlich and Langmuir models. We also note that the adsorption process of HA on different materials is better presented by the proposed model (03) with four parameters. Curves of figure 4 shows the fitting of experimental data with these different models. The adsorption process of humic acid is well represented by the four parameters mode. Parameters calculation was performed on MATLAB using genetic algorithms.

Table .2. Constants of adsorption isotherms of humic acid.

Modèles		Paramètres	Mg-Fe-SDS	Mg-Fe-C
Freundlich	$Q_e = Q_m a C_e^n$	RMSE	18,6165	12,6418
		r^2	0,9322	0,9708
		a	0,1279	0,0755
		n	0,5418	0,5933
		Qe cal (mg/g)	256,139	203,35
Langmuir	$Q_e = \frac{Q_m a C_e}{1 + a C_e}$	RMSE	21,0740	20,2892
		r^2	0,9561	0,9715
		a	0,0947	0,0568
		Qe cal (mg/g)	198,28	161,035
Proposed model 01	$Q_e/Q_m = (1 - \exp(-a C_e^2))^{\frac{1}{2}}$	RMSE	3,6666	5,2482
		r^2	0,9977	0,9951
		a	0,0029	$7,733 \cdot 10^{-0,4}$
		Qe cal (mg/g)	231,15	183,30

Proposed model 02	RMSE	3,6664	5,1180
$Q_e/Q_m=b(1-\exp(-aCe^n))^{1/2}$	r^2	0,9977	0,9953
	a	0,0029	0,0008
	b	1,0004	0,9873
	Qe cal (mg/g)	239,53	185,43
Proposed model 03	RMSE	2,1904	2,9572
$Q_e/Q_m=b(1-\exp(-aCe^n))^m$	r^2	0,9991	0,9983
	a	0,0277	3,3015
	b	0,9960	1,2528
	n	1,3922	0,1558
	m	0,9456	164,883
	Qe cal (mg/g)	238,68	185,33
	Qe exp (mg/g)	238,92	185,28

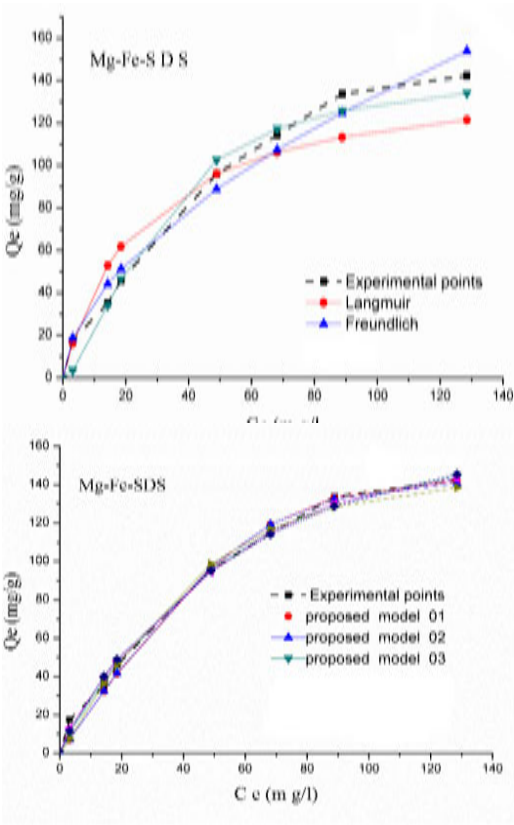


Figure 4. Adsorption isotherms ($t=5$ h, $T=298$ K and $C_0=10$ mg/L).

3.3 Calculation of thermodynamic parameters

Values of free energy ΔG_{0ads} reported in Table (III), suggest that the process is spontaneous while positive values of enthalpy ΔH_0 shows that the process is endothermic favored by increasing temperature fig.5. Positive values of entropy ΔS_{0ads} show that LDH-adsorbate system is less ordered that the molecules [11].

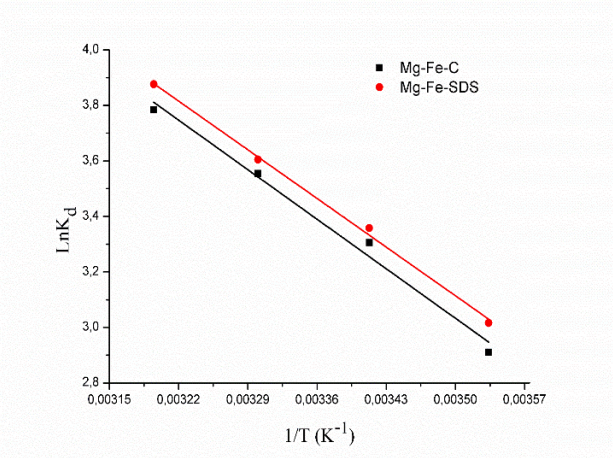


Figure 5. Van't Hoff plot for different materials.

Table 3 Thermodynamic parameters ΔH_0 , ΔS_0 and ΔG_0 related to the adsorption of Mg-Fe-SDS.

Samples	Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol k)
Mg-Fe-SDS	283	-22.48	56.91	270.99
	293	-25.19		
	313	-27.90		

4. Conclusion

Materials characterization confirmed successful synthesis of LDHs. Results of infrared spectra showed LDH characteristic bands with carbonate anions interposed in the interlamellar spacing. Thermal treatment confers to the material a relatively high specific surface. SEM and XRD characterization results show that LDH are crystalline. This crystalline structure reappears (memory effect) after interposing SDS surfactant in LDHs with characteristic peaks that correspond to initial LDH reflections with a slight modification of crystallinity. Results show that

pseudo-first order kinetic model is valid at early stages of the adsorption process, while the pseudo-second order model gives better results. However, the best fit of the experimental results was obtained using the n-order model ($n \in \mathbb{R}^+$) with a determination coefficient close to one. Models of adsorption isotherms that were proposed, particularly 3 parameters model, give better results than classical Freundlich and Langmuir models. A thermodynamics analysis enabled the calculation of enthalpy, entropy and free energy of adsorption and showed that the adsorption process is chemical, spontaneous and endothermic.

5. References

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