

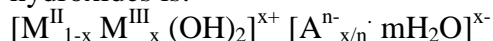
EQUILIBRIUM OF PHENOL AND CHROMATE ADSORPTION ON IONIC LIQUID FUNCTIONALIZED Zn-Al LAYERED DOUBLE HYDROXIDE**Laura Cochechi, Lavinia Lupa, Alin Golban, Rodica Pode***Faculty of Industrial Chemistry and Environmental Engineering, Politehnica University of Timisoara, 300223 Timisoara, 6 Parvan Blv., Romania
e-mail: laura.cochechi@upt.ro***Abstract**

A Zn₃Al-type layered double hydroxide (LDH) was impregnated with methyltri-n-butylammonium chloride (IL) in order to obtain a functionalized material (IL-LDH). Both materials were utilized as adsorbents for phenol and chromate from water. The results show that the functionalized material has better adsorption capacities than the starting material. Four equations (Langmuir, Freundlich, Langmuir-Freundlich and Redlich-Peterson) were taken into consideration in order to describe the adsorption equilibrium.

Introduction

Ionic liquids (IL) are a group of new organic salts that exist as liquids at a low temperature (<100°C). An important feature of ILs is their immeasurably low vapor pressure. For this reasons, they are called “green” solvents, in contrast to traditional volatile organic compounds. ILs have many attractive properties, such as chemical and thermal stability, nonflammability, high ionic conductivity, and a wide electrochemical potential window. Therefore, they have been extensively investigated as solvents or co-catalysts in organic and inorganic synthesis and extractants for metals and organic compounds [1-3]. The main disadvantage of ILs is the possibility of their decomposition in water with release of extractants, therefore the immobilization of the extractants in suitable supports is a solution to prevent these drawbacks [4].

Layered double hydroxides (LDH), also called hydrotalcite-like materials or anionic clays, have layered structure and tunable properties. The general formula of layered double hydroxides is:



where: M^{II} is a divalent cation (Mg²⁺, Mn²⁺, Zn²⁺, Ni²⁺, Fe²⁺, Co²⁺, Cd²⁺, Cu²⁺ etc.), M^{III} a trivalent cation (Al³⁺, Fe³⁺, Ga³⁺, In³⁺, Cr³⁺ etc.) and Aⁿ⁻ charge compensating anions (NO₃⁻, Cl⁻, SO₄²⁻, ClO₄⁻ etc.). Due to the positive charged brucite-like layer and the exchangeable anions and water in the interlayer space, these materials have attracted much attention because of their properties as catalysts, catalyst precursors, adsorbents, flame retardants and matrices for biosensors [5-9].

This paper focuses on the study of equilibrium adsorption of phenol and chromate from water. As adsorbents were utilized two materials: Zn₃-Al – layered double hydroxide and ionic liquid functionalized Zn₃-Al - layered double hydroxide.

Experimental

LDH was prepared from analytical grade reagents by co-precipitation under oversaturation method, described by Cavani et al. [10]. The molar ratio Zn²⁺ : Al³⁺ in the starting solution was 3 : 1. A part of the solid material obtained after synthesis was impregnated with methyltri-n-butylammonium chloride (IL). The impregnation method implies 10 minutes of ultrasonication using a IL : LDH ratio of 1 : 10 (w/w). The phase composition of the samples was established by X-ray diffraction using a Rigaku Ultima IV diffractometer (40 kV, 40 mA) using Cu K α radiation. Fourier transform infrared (FT-IR) spectra were performed over a

range of wavenumber from 4000 to 400 cm^{-1} on a Shimadzu IRPrestige-21 FT-IR spectrophotometer.

All adsorption experiments were performed by contacting 50 mL of solutions containing phenol from 5 to 200 mg/L or Cr(VI) from 5 to 100 mg/L with the adsorbents samples corresponding to a solid : liquid ratio of 1g/L. The phenol and chromium removal were conducted in an batch shaker model Julabo, at 25 ± 2 °C, in order to reach the adsorption equilibrium for 6 hours. At equilibrium, the solid was separated by filtration. Phenol and chromate concentrations in aqueous solution were spectrophotometrically determined at 510 nm and 540 nm, respectively, by means of colorimetric methods [11]. Phenol or chromium uptake by the sorbent was calculated by using the following equation:

$$q_e = (C_0 - C_e) V/m$$

where q_e is the adsorption loading of sorbent material at equilibrium (mg/g), V the volume of solution (L), C_0 (mg/L) and C_e (mg/L) the initial and equilibrium concentrations of phenol or Cr(VI), respectively, and m is the mass of adsorbent (g).

Results and discussion

The diffractogram of IL-LDH is presented in Figure 1. The basal peaks corresponding to (003), (006) planes, which are typical of the layered double hydroxides, were present at low 2θ angle values. At 2θ angles ranging from 60 to 65° were present the peaks corresponding to (110) and (113) planes, also characteristic of the layered double hydroxides. The presence of ionic liquid at the LDH surface is envisaged by the FT-IR spectra of the materials, presented in Figure 2. The typical absorption bands for layered double hydroxides were present for both LDH and IL-LDH materials. In addition, the presence of two absorption bands of IL molecule, typical of C-H stretching modes, at 2968 and 2869 cm^{-1} , in the IL-LDH spectra confirm that the IL impregnation of LDH was successful.

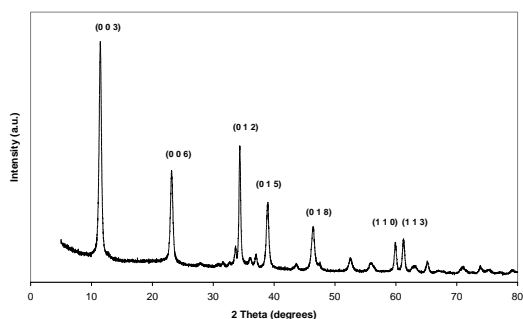


Figure 1. The XRD pattern of IL-LDH

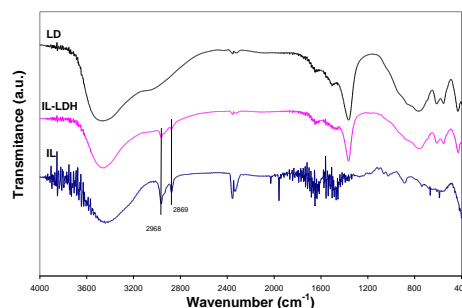


Figure 2. The FT-IR spectra of LDH, IL-LDH and IL

The results of adsorption equilibrium of phenol and chromate onto LDH and IL-LDH are presented in Figure 3 and Figure 4, respective.

The four mathematical models used to describe the adsorption behavior are presented in Table 1. The values of the equilibrium isotherm parameters and correlation coefficients obtained after non-linear regression fitting are listed in Table 2 and Table 3. The correlation coefficients are a measure of the goodness-of-fit and confirm the representation of the experimental data by the Langmuir–Freundlich model.

The maximum adsorption capacities of IL-LDH are higher than that of LDH. The isotherm of phenol adsorption on LDH presented a “S” shape, that suggested a low affinity of phenol for this material, while the isotherm of phenol adsorption on IL-LDH are far from the equilibrium plateau at up 200 mg/L, the maximum concentration employed (Figure 3).

The isotherm of chromate adsorption on LDH presented a typical Langmuir plateau, while the adsorption on IL-LDH have not reach the equilibrium at up 100 mg Cr(VI)/L (Figure 4).

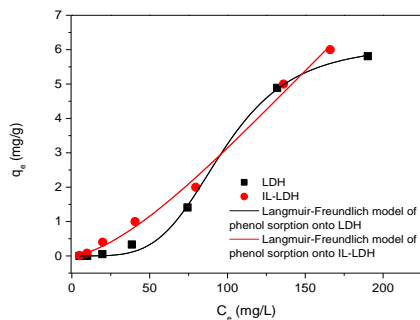


Figure 2. Adsorption equilibrium of phenol

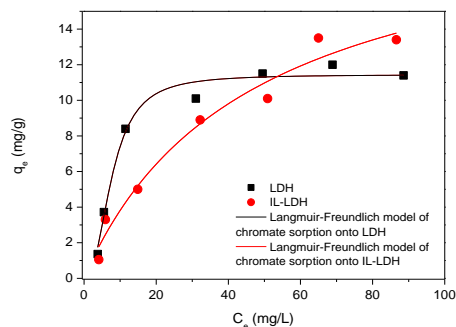


Figure 3. Adsorption equilibrium of chromate

Table 1. The mathematical expressions of the isotherms used for the modelling of the adsorption experiments

Model	Equation
Langmuir (L)	$q_e = q_{\max} \frac{K_L \cdot C_e}{1 + K_L \cdot C_e}$
Freundlich (F)	$q_e = K_F \cdot C_e^{1/n}$
Langmuir-Freundlich (L-F)	$q_e = q_{\max} \frac{(K_{LF} \cdot C_e)^n}{1 + (K_{LF} \cdot C_e)^n}$
Redlich-Peterson (R-P)	$q_e = q_{\max} \frac{K_{RP} \cdot C_e}{1 + (K_{RP} \cdot C_e)^n}$

where q_e is the sorption loading of sorbent material at equilibrium (mg/g); C_e the equilibrium concentration of Cr(VI) (mg/L); q_{\max} maximum sorbed quantity (mg/g); n is the non-homogeneity factor; K – constant).

Table 2. Equilibrium isotherm parameters for phenol adsorption

Model	q_{\max}	K	n	R^2
LDH				
Langmuir	16.9	$2.32 \cdot 10^{-3}$	-	0.8888
Freundlich	-	$6.16 \cdot 10^{-3}$	0.758	0.9549
Langmuir-Freundlich	6.16	32.3	2.32	0.9985
Redlich-Peterson	2.40	$1.36 \cdot 10^{-2}$	3.29	0.9837
IL-LDH				
Langmuir	119	$3.00 \cdot 10^{-3}$	-	0.9664
Freundlich	-	447	0.0926	0.9437
Langmuir-Freundlich	29.7	$5.40 \cdot 10^{-3}$	1.55	0.9947
Redlich-Peterson	24.0	$3.60 \cdot 10^{-3}$	0.56	0.9742

Table 3. Equilibrium isotherm parameters for chromate adsorption

Model	q_{\max}	K	n	R^2
LDH				
Langmuir	14.0	$7.93 \cdot 10^{-2}$	-	0.9278
Freundlich	-	2.47	2.69	0.8243
Langmuir-Freundlich	11.4	$12.9 \cdot 10^{-2}$	2.39	0.9856
Redlich-Peterson	20.2	$4.06 \cdot 10^{-2}$	1.31	0.9508
IL-LDH				
Langmuir	20.9	$2.22 \cdot 10^{-2}$	-	0.9640
Freundlich	-	1.05	1.70	0.9610
Langmuir-Freundlich	21.5	$2.09 \cdot 10^{-2}$	0.98	0.9741
Redlich-Peterson	20.4	$2.32 \cdot 10^{-2}$	0.97	0.9647

Conclusion

A layered double hydroxide Zn_3Al -type was synthesized and functionalized by impregnation with ionic liquid. The two obtained materials were characterized in order to prove the layered structure and the presence of the organic compound (ionic liquid). The structural characterization confirm that the IL impregnation of LDH was successful.

The adsorption experiments of phenol and chromate on the two materials were conducted batchwise. Four equilibrium models were used to describe the adsorption behavior. The non-linear fitting of the experimental data reveals that the Langmuir-Freundlich model approximated the experimental data in all the cases.

The ionic liquid functionalized layer double hydroxide presents higher adsorption capacities than layer double hydroxide alone.

Acknowledgements

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