Colloids and Surfaces A 525 (2017) 64–76

Contents lists available at ScienceDirect

Colloids and Surfaces A

journal homepage: www.elsevier.com/locate/colsurfa

Preferential adsorption of various anionic and cationic dyes from aqueous solution over ternary CuMgAl layered double hydroxide

Dipshikha Bharali, Ramesh C. Deka*

Department of Chemical Sciences, Tezpur University, Napaam 784028, India

ARTICLE INFO

Keywords:
CuMgAl LDH
Adsorption properties
Anionic and cationic dyes
Second order kinetic model

ABSTRACT

To investigate the effect of Cu on structural and adsorption properties of CuMgAl LDH towards the efficient removal of organic dye contaminants from aqueous solution, a series of CuMgAl LDHs with different molar ratio of Cu/Mg were synthesized via co-precipitation method. The synthesized materials were characterized by using various techniques such as powder X-ray diffraction (PXRD), Fourier transformed infrared (FTIR), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), N_2 adsorption–desorption, transmission electron microscopy (TEM) and diffuse-reflectance UV–vis (UV-DRS) spectroscopy. The presence of Cu greatly enhanced the adsorption capacity of the adsorbents for efficient removal of organic dye pollutant from aqueous solution. The adsorption performance of the Cu-rich LDH was examined for preferential adsorption of various anionic and cationic dyes such as methyl orange, bromothymol blue, erichrome black-T, Congo red, methylene blue and rhodamine B from aqueous solution. The anionic dyes were adsorbed in higher amount over the ternary LDH compared to that of cationic dyes. The influence of various reaction parameters like contact time, adsorbent dosage, initial dye concentration and solution pH on adsorption process was studied thoroughly. The adsorption process was analyzed by using various isotherm models and the Langmuir isotherm model showed the best fitting to the isotherm data. The kinetics study showed that the adsorption process followed second order kinetic model. The successful interaction of dye with the adsorbent surface was studied by FTIR spectroscopy. The adsorbent was stable and active upto three successive cycles.

1. Introduction

From the environment point of view, the organic dye contaminants releases from various sources such as textile, paper, painting, plastic, cosmetics, pharmaceutical and food industries become the serious issue in all over the world. When the contaminants are discarded into the environment causes severe environmental pollution, affecting the human health as well as the aquatic life [1–5]. When the contaminants are released into the water, due to its highly colorant nature it reduces the light penetration and visibility through the water surface and thus affects the photosynthetic cycle essential for the aquatic life. It also increases the chemical oxygen demand (COD) and makes the aquatic life very dangerous [6–8]. Due to their synthetic origin and aromatic structure, dye molecules are very stable and non-degradable in nature due to which it is difficult to remove the dyes from waste water [9,10]. Many of the dyes are toxic, mutagenic and carcinogenic in nature and thus their release into the environment becomes a serious issue [11–13]. Therefore, it is important to develop an efficient technique for removal of dye pollutants before discharging into the environment.

The adsorption process is one of the most reliable and widely adopted techniques for removal of dyes from aqueous solution which have advantages over various other techniques like coagulation [14], chemical oxidation [15], adsorption [16–18] and photocatalysis [19–21] in terms of simplicity, economically feasible and highly efficient technique with simple ease of operation [22–25]. Moreover, availability of various types of adsorbents also makes the adsorption process as an efficient technique for dye removal. The use of different types of adsorbents such as activated carbon [26], fly ash [27], chitosan [28,29], zeolites [30] and clays [31–33] for removal of dyes from aqueous solution are well known. Among all these, layered double hydroxides (LDHs) are considered to be an efficient adsorbents with the advantages of economically feasible, high adsorption capacity and anion exchange properties [34–36].

LDHs are commonly known as the hydrotalcite-like compound due to their structural similarities with hydrotalcite clays [37]. The general formula for LDHs can be represented as, $[M_{1-x}{}^{II}\ M_x{}^{III}\ (OH)_2]\ (A^{n-})_{x/n}{\cdot}mH_2O$, where M^{II} are divalent metal cations, such as Mg, Ni, Co, Cu, and Zn; and M^{II} are trivalent metal cations, such as Al, Cr and Fe; x is

---

* Corresponding author.
E-mail address: ramesh@tezu.ernet.in (R.C. Deka).

http://dx.doi.org/10.1016/j.colsurfa.2017.04.060
Received 8 February 2017; Received in revised form 21 April 2017; Accepted 25 April 2017

the molar ratio of $M^{III}/(M^{II} + M^{III})$ whose value ranges between 0.2–0.33 and A^{n-} is the exchangeable interlayer anion compensating the excess positive charge in the interlayer region of LDH such as CO_3^{2-}, NO_3^{-}, SO_4^{2-}, Cl^{-}, Br^{-}, I^{-}, OH− etc and *m* is the amount of water molecules present in layered structure [38–40]. LDHs are widely known as a good anion exchanger due to its highly anion exchangeable properties and also have drown considerable attention in various fields as adsorbents [41,42], catalysts [43–46] or catalyst supports [47–50], drug carriers [51–53] and polymer additives [54,55]. LDHs are also known as anionic clays whose properties can also be modulated by varying the compositions of the materials, types of the metal cations and interlayer anions [56,57].

In this work, we have reported the study of preferential adsorption of a series of organic dye pollutants over ternary CuMgAl LDH and also studied the effect of Cu on the structural as well as the adsorption properties of the LDH. Here, we have synthesized a series of ternary CuMgAl LDHs with different Cu:Mg molar ratio using co-precipitation method. A series of anionic dyes like methyl orange (MO), bromothymol blue (BTB), erichrome black-T (EBT) and Congo red (CR); and cationic dyes like methylene blue (MB) and rhodamine B (RhB) were used for the adsorption study. The influence of different adsorption parameters such as contact time, adsorbent dosage, initial dye concentration and solution pH on the adsorption process was studied and discussed thoroughly. The adsorption process was also analyzed with various adsorption isotherms and kinetics models.

2. Experimental section

2.1. Materials

$Mg(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, NaOH, Na_2CO_3, HCl and absolute ethanol were purchased from Merck, Mumbai. Methyl Orange ($C_{14}H_{14}N_3NaO_3S$), Bromothymol blue ($C_{27}H_{28}Br_2O_5S$), Eriochrome black T ($C_{20}H_{12}N_3NaO_7S$), Congo red ($C_{32}H_{22}N_6Na_2O_6S_2$), Methylene blue ($C_{16}H_{18}ClN_3S \cdot 2H_2O$) and Rhodamine B ($C_{28}H_{31}ClN_2O_3$) were purchased from RANKEM, New Delhi. All the chemicals were used without further purification and dye solutions were prepared using deionized water.

2.2. Synthesis of LDHs

A co-precipitation method was employed to synthesize a series of CuMgAl LDHs with (Cu + Mg):Al ratio of 3:1. Here we have changed the Cu:Mg concentrations such that (Cu:Mg) ratios were (0:3), (1:2), (1:1) and (2:1), accordingly denoted as CuMgAl1, CuMgAl2, CuMgAl3 and CuMgAl4, respectively. The synthesis was carried out by adding two solutions of one containing a mixed salt solutions of $Cu(NO_3)_2 \cdot 3H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ and another containing aqueous solution of NaOH and Na_2CO_3 under continuous stirring. During the addition, pH of the solution was kept remained constant at 10 using 1 M NaOH and stirred for 1 h at room temperature. After that, the mixture was aged in the mother liquor at 80 °C for 24 h. The resulting products were filtered, washed thoroughly with deionized water until pH of the filtrate was 7 and dried at 80 °C in the oven for 15 h.

2.3. Characterization methods

For identification of crystalline phase, powder X–ray diffraction (PXRD) patterns of the samples were recorded on a Rigaku Multiflex instrument with nickel-filtered CuKα (λ = 0.15418 nm) radiation source at 30 kV and 15 mA in steps 0.05 within 2θ range of 5–70°. Fourier Transform Infra–red (FTIR) spectra were recorded on a Nicolet Impact I–410 FTIR spectrophotometer in the wavelength range of 4000–500 cm^{-1} using KBr pellet. The thermogravimetic analyses (TGA) were carried out on a Thermal Analyzer (Model TGA-50, Shimadzu). The samples were heated in the temperature range from 20 to 600 °C at the heating rate of 10 °C min^{-1} under N_2 flow. The diffused reflectance UV–vis (DRUV–vis) spectra of the samples were measured on Shimadzu Corporation (UV–2450) UV–visible spectrophotometer. Scanning Electron Microscopy (SEM) images were obtained on JEOL JSM-6390 LV Scanning Electron Microscopes operating at an accelerating voltage of 15 kV. Brunauer–Emmett–Teller (BET) surface area and pore size distribution of the samples were measured by the N_2 adsorption-desorption technique and Barrett–Joyner–Halenda (BJH) method using a Quantachrome Instruments (Model: NOVA 1000e) within the precision of ± 5%. Transmission electron microscopic (TEM) images were obtained on FEI–Technai (G2 F20S–TWIN) instrument operating at an accelerating voltage of 200 kV. The images were recorded with a slow-scan CCD camera. Prior to the analysis, the sample preparation was carried out by dispersing the powdered sample in ethanol and coated on a copper grid using a very dilute suspension.

Table 1
Chemical composition and textural properties of various LDH samples.

LDH Samples	Cu:Mg ratio		d_{003} (Å)	Unit cell parameters[b] (Å)	S_{BET} (m^2/g)
	Solution	Solid[a]		*c*	
CuMgAl1	0:3	0:3.1	7.69	23.07	131
CuMgAl2	1:2	0.9:2.1	7.79	23.37	102
CuMgAl3	1:1	1:1.1	7.97	23.91	89
CuMgAl4	2:1	2.1:1	8.42	25.26	60

[a] Determined by AAS.
[b] $c = 3d_{003}$.

2.4. Adsorption experiments

Batch adsorption experiments were carried out by mixing 5 mg of the adsorbent with 20 mL of 20 mg/L dye solution at room temperature and pH 7 for 180 min. The adsorbent was separated by centrifugation and the concentration of the residual dye in the sample solutions were analyzed using the Shimadzu Corporation UV–visible spectrometer (UV–2550) at their respective absorbance maximum. The effect of various parameters such as contact time, adsorbent dosage, initial dye concentration and pH of the dye solution on adsorption process was also investigated. The pH effect was studied over a wide range of pH (3–11) by adjusting the dye solutions using 0.1 M NaOH and 0.1 M HCl solutions. The adsorption kinetics was investigated by withdrawing the dye samples at a particular time intervals of 5, 10, 20, 30, 60, 90, 120 and 180 min. The adsorption isotherm was carried out using a constant amount of the adsorbent of 5 mg and 20 mL of dye solutions with different initial concentrations (ranging from 10–70 mg/L). The dye removal (%), adsorption capacity at equilibrium, q_e (mg/g) and adsorption capacity at time *t*, q_t (mg/g) were calculated according to the following equations,

$$\text{dyeremoval}(\%) = \frac{C_o - C_t}{C_o} \times 100\% \tag{1}$$

$$q_e = \frac{(C_o - C_e)V}{m} \tag{2}$$

$$q_t = \frac{(C_o - C_t)V}{m} \tag{3}$$

where, C_o, C_e and C_t are the dye concentrations in mg/L at initial, equilibrium and time *t*, respectively. *V* is the volume of the dye solution in L and *m* is the mass of the adsorbent in g. For data consistency, each experiment was carried out twice.