Journal of Hazardous Materials 190 (2011) 659–668

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Physicochemical characterization and adsorption behavior of Ca/Al chloride hydrotalcite-like compound towards removal of nitrate

Mahamudur Islam[a,*], Rajkishore Patel[b]

[a] Department of Chemistry, Purushottam Institute of Engineering & Technology, Purushottam Vihar, 10th km, Highway – 10, Mandiakudar, Kansbahal, Rourkela 770034, Orissa, India
[b] Department of Chemistry, National Institute of Technology, Rourkela 769008, Orissa, India

ARTICLE INFO

Article history:
Received 19 October 2010
Received in revised form 4 March 2011
Accepted 28 March 2011
Available online 6 April 2011

Keywords:
Hydrotalcites
Nitrate
Isotherms
Kinetics
Adsorption

ABSTRACT

The objective of the present research was to synthesize, characterize and to investigate adsorption of nitrate from synthetic nitrate solution by Ca–Al–Cl HTlc. In the present study Ca–Al–Cl HTlc was synthesized by co-precipitation method and was characterized using SEM, XRD, FTIR and TGA–DSC. To assess the practical usefulness, a detailed removal study of nitrate was carried out. The removal of nitrate was 84.6% under neutral condition using 0.35 g of adsorbent in 100 mL of nitrate solution having initial concentration of 10 mg/L. Adsorption kinetic study revealed that the adsorption process followed first order kinetics. Adsorption data were fitted to linearly transformed Langmuir adsorption isotherm with R^2 (correlation coefficient) > 0.99. Thermodynamic parameters were also calculated to study the effect of temperature on the removal process. In order to understand the adsorption type, equilibrium data were tested with Dubinin–Radushkevich isotherm.

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1. Introduction

Hydrotalcites, also known as layered double hydroxides or ionic clays are based upon the brucite [Mg(OH)2] structure in which some of the divalent cations are replaced by trivalent cations (e.g. Al^{3+}, Fe^{3+}, Cr^{3+}, etc.) resulting in a layer charge. This layer charge is counter balanced by anions such as carbonate, nitrate, sulphate or chloride in the interlayer spaces. In hydrotalcites a broad range of compositions of the type $[M_{1-x}{}^{2+}M_x{}^{3+}\,(OH)_2][A^{n-}]_{x/n}\cdot yH_2O$ are possible, where M^{2+} and M^{3+} are the di and trivalent cations in the octahedral positions within the hydroxide layers with x normally between 0.17 and 0.33. A^{n-} is an exchangeable interlayer anion [1]. The degree of anionic replacement in the hydrotalcites depends on the structural characteristics, e.g. the nature of the interlayer anion and crystallinity. Exchange conditions like pH and carbonate contamination from environment are also important limitations. Due to the high affinity of hydrotalcites towards carbonate ion, materials with intercalated carbonate ions have relatively smaller exchange capacities unless being calcined. High pH conditions must be applied to maintain the stability of hydrotalcites, however, OH^- intercalation is competitive in this case. The technological applications of hydrotalcite and calcined hydrotalcite have attracted much attention in recent years [2–5].

Hydrotalcite-derived mixed oxides are used as antacids, catalysts and catalyst supports, because of their high surface area, phase purity, basic surface properties, and structural stability [5]. Hydrotalcite-derived oxides catalyze higher alcohol synthesis from CO/H_2 [6], oxidation of mercaptans [7] and water gas shift reactions [8]. Also, Mg–Al mixed oxides prepared by oxidative decomposition of hydrotalcite precursors have been used in base-catalyzed aldol condensations [9,10], alkylations [11], Knoevenagel condensations [12], double-bond isomerization, and alcohol dehydrogenation and coupling. There are many other important uses of hydrotalcites such as in the removal of environmental hazards in acid mine drainage [13,14] and a mechanism for the disposal of radioactive wastes [15]. The use of hydrotalcites as ion exchangers and adsorbents has drawn the attention of researchers.

Among the many uses is the removal of toxic anions from aqueous systems. Nitrate in water is quite harmful in food and drinks of young children and can be quite toxic. Nitrate is a wide spread contaminant of ground and surface water due to excessive use of nitrogenous fertilizer in agricultural activities and disposal of untreated sanitary and industrial wastes [16–18]. Elevated nitrate concentrations in drinking water are linked to health problems such as methemoglobinemia in infants and stomach cancer in adults. US Environmental Protection Agency (EPA) has set the maximum contamination level as 44 mg/L of $NO_3{}^-$ [19,20]. Current technologies for removal of nitrate, like ion-exchange and reverse osmosis, are not selective to nitrate, generate secondary brine wastes and require frequent media regeneration. In recent years chemical methods of nitrate removal using zero-valent metals like iron (Fe^0),

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[*] Corresponding author. Tel.: +91 88952 70088; fax: +91 6624 280625.
E-mail address: mahamudur.islam@gmail.com (M. Islam).

0304-3894/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2011.03.094

magnesium (Mg^0) and aluminum (Al^0) has been studied intensively [21–27]. However, challenges like high dose requirement, long reaction time, presence of anaerobic condition and rapid deactivation of metal surface due to hydroxide precipitation. The use of biological reactor seems to be the most promising technique in the treatment of high nitrate concentration. However, maintaining biological processes at their optimum conditions is difficult, and the problems of contamination by bacteria [28] have to be solved to make such processes safe enough to utilize for drinking water treatment. On the other hand, adsorption is a very feasible process but there are not many adsorbent available for removal of nitrate since nitrate is very selective towards adsorption. Among a few adsorbents, hydrotalcite like compounds may prove beneficial for adsorption of nitrate.

Although few studies have examined the synthesis of various HTlcs and the way in which they interact with various anions, the synthesis of Ca/Al chloride hydrotalcite and its application for efficient removal of nitrate has not been examined previously. So, the present research was aimed to synthesize and characterize Ca/Al chloride hydrotalcite. The effect of various parameters on the effectiveness of treating nitrate contaminated water with Ca/Al chloride was unknown. Therefore, in this study, Ca/Al chloride was added to nitrate solutions and the effect of different variables (calcinations temperature, dose, time, pH, initial nitrate concentration, effect of other anions, etc.) on the removal of nitrate from solution by Ca/Al chloride was examined.

2. Experimental

2.1. Reagents and chemicals

Potassium nitrate used in the present study was of analytical grade and was obtained from Merck. 1000 mg/L stock solution of nitrate was prepared by dissolving 1.6305 g of KNO_3 in 1 L distilled water. The required concentration of nitrate solution was obtained by serial dilution of 1000 mg/L nitrate solution. The measuring cylinder, volumetric flask and conical flask used were of Borosil.

2.2. Synthesis of Ca/Al chloride hydrotalcite

Ca–Al–Cl hydrotalcite was prepared by co-precipitation method at pH 10 [29]. In this method two solutions, solution-I containing 0.75 M $CaCl_2$ and 0.25 M $AlCl_3$ and solution-II containing 1 M NaOH and 1 M NaCl, 200 ml each of these two solutions were added simultaneously to a 1 L beaker containing 100 mL of distilled water at a flow rate of 50 mL per hour at 80 °C under vigorous stirring. An inert atmosphere was maintained throughout the addition by bubbling nitrogen gas from a cylinder. The pH of the solution was maintained at 10 by the addition of 2 M NaOH. The slurry was then refluxed at 90 °C for 24 h. It was then filtered and washed thoroughly with distilled water till the washings were neutral. The precipitate was then dried in nitrogen atmosphere for 8 h. The HTlc obtained was calcined at different temperature (50–400 °C) in nitrogen atmosphere for 8 h.

2.3. Characterization of Ca/Al chloride hydrotalcite

BET surface area of the sample was measured using QUANTACHROME Autosorb I. The sample was degassed at 100 °C in vacuum. Helium was used as carrier gas and the surface area was measured by nitrogen adsorption–desorption method at liquid nitrogen temperature. Thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) was carried out using NETZSCH STA 409C. 30 mg of the sample was used and alumina was used as reference. TGA and DSC curve was obtained from 25 °C to 800 °C at a rate of 10 °C/min. Scanning electron micrographs of the sample was obtained by JEOL JSM – 6480LV scanning electron microscope. The sample was coated with platinum for 30 s at a current of 50 mA before the SEM micrograph was obtained. Chemical analysis of HTlc was carried out by dissolving 0.5 g of material in 1:1 HCl, followed by the estimation of Al by precipitating it with NH_4Cl and NH_4OH. Then the residual solution contained Ca which was estimated by standard EDTA [29,30]. Powder XRD of the material was obtained by using PHILLIPS X'PERT X-Ray diffractometer with Cu Kα radiation (35 kV and 30 mA) at a scan rate of 1°/min and was analyzed using standard software provided with the instrument. FTIR of the sample was obtained using Perkin Elmer FTIR spectrophotometer (SPECTRUM RX – I).

Table 1
Synthesis of various samples of hydrotalcite like compounds (HTlcs).

Uncalcined layered double hydroxides (LDHs)	Percentage removal of nitrate from 100 mg/L solution
Ca–Al–Cl	65.2
Mg–Al–CO_3	3.6
Zn–Cr–Cl	11.2
Mg–Mn–CO_3	3.8
Mg–Cr–Cl	9.8
Ca–Cr–Cl	5.2

2.4. Batch experiments

The nitrate removal experiments from its aqueous solution by HTlc were carried out using standard 10 mg/L, 50 mg/L and 100 mg/L NO_3^-. The adsorption experiments were carried out in 250 mL glass conical flask with stopper by adding 0.1–0.8 g of HTlc in 100 mL of synthetic nitrate solution. Stoppers were provided to avoid change in concentration due to evaporation. All the experiments were carried out at ambient temperature (25 ± 2 °C). After continuous stirring over a magnetic stirrer at about 400 rpm for a predetermined time interval, nitrate concentration was determined by Nitrate ion selective electrode (Orion Ionplus Sureflow Nitrate Electrode) and Orion 720 A+ ion analyzer. Two standards were prepared that bracket the expected sample range and which differ in concentration by a factor of ten. Measurements were done by taking 10 mL of each standard and sample into separate 50 mL beaker and 10 mL of nitrate interference suppressor (930710). All the sample and standards were maintained at same temperature to avoid interference due to difference in temperature. A number of parameters such as reaction time, adsorbent dose, concentration of nitrate, pH, affecting the removal of nitrate ion have been varied widely in order to optimize the removal process.

3. Results and discussion

3.1. Characterization

A number of HTlc samples were prepared and examined for the removal efficiency of nitrate. This was done by adding a 0.5 g sample of each HTlc to 100 mg/L nitrate solution, stirring for 8 h, filtering the solution and analyzing for residual nitrate. The result of the study is presented in Table 1. The percentage removal of nitrate was 65.2% for Ca–Al–Cl. It is evident from the table that Ca–Al–Cl exhibited maximum removal of nitrate from synthetic nitrate solution. All other HTlcs used, exhibited poor nitrate removal efficiency (less than 12%). So, Ca–Al–Cl was selected for further study.

To study the effect of calcination temperature on the removal of nitrate, sample of Ca–Al–Cl HTlc was calcined at different temperatures (50–400 °C in nitrogen atmosphere) for 8 h. 0.5 g of calcined samples were added to 100 mL of 100 mg/L nitrate solution and percentage removal of nitrate was studied. The result of the study

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