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Equilibrium, kinetics and thermodynamic studies for separation of malic acid on layered double hydroxide (LDH)

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ABSTRACT

The adsorption equilibria of malic acid onto layered double hydroxide (LDH) was studied. In the experimental context of this study, firstly LDH with a highly crystalline structure was synthesized with the co-precipitation method and characterized. In the adsorption experiment some important effects such as, adsorption equilibrium, influence of quantities of LDH as adsorbent, effect of adsorption temperature, and influence of starting concentration of malic acid were investigated. The removal of malic acid was 96.73% the highest percentage for 1 g LDH at 298 K. The results obtained from the experiment were used to plot Langmuir, Freundlich, and Temkin adsorption isotherms. It has been found that experimental data about solid–liquid equilibria of malic acid with LDH and isotherm equations were appropriate. The equilibrium data show that the adsorption isotherm is compatible with Langmuir isotherm (R^2 is 0.9992 at 298 K). Adsorption depended on the starting malic acid concentration at various temperatures (298, 308, 318 K), respectively. The temperature dependence of adsorption process is associated with changes in several thermodynamic parameters such as standard Gibbs energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of adsorption and were calculated. Elovich and other kinetic model equations were applied to the obtained data from the experiment.

1. Introduction

Malic acid is a C_4 carboxylic acid and intermediate of the tricarboxylic acid cycle [1]. It is a valuable product which has a wide range of usage in pharmaceuticals, polymer and food industries. Two of the main uses of malic acid in the food industry are as flavoring and an aging agent of wine [2]. Beside's use as an essential compound for cellular mechanisms, malic acid can be used for treatments for different diseases in the pharmaceutical field such as; hyper ammonemia and chronic pain [3,4]. Moreover, poly(β)malic acid is used in polymeric drug systems as well [5].

Malic acid produced by fermentation from fumaric acid usually amounts to about 10% of the weight of the aqueous solution [1,6]. The recovery of carboxylic acid from aqueous solutions is an important matter for industries because it directly effects the cost of production. Sometimes purification steps can cost 60 to 70% of the total production [1]. Liquid extraction is an alternative way for recovery of malic acid but conventional solvents such as alcohols, ketones ethers and alyphatic hydrocarbons aren't effective due to their low distribution coefficient [7,8]. There are some other methods in literature like reactive extraction, liquid membrane permeation, electrodialysis and supercritical fluid extraction [1,2,8–12]. As an alternative purification step in our study layered double hydroxide (LDH) was used for the recovery of malic acid from aqueous media.

LDH's, also called hydrotalcite like minerals, are a class of inorganic nanomaterials, whose structure can be explained like brucite layers. The general formula of LDH is $[M^{II}_{1-x}\cdot M^{III}_{x}\,(OH)_2]^{x+}[A^{n-}_{x/n}\cdot yH_2O]^{x-}$ where M^{II} and M^{III} are divalent and trivalent metal cations, and A^{n-} is an n-valent anion [13–15]. LDH has exhibited similar physical and chemical properties like clay minerals, so they have attracted attention for being used as catalysts, catalyst and ceramic precursors, traps for anionic pollutants, ion exchangers, additives for polymers, being used in electrochemsitry and photochemistry [15,16]. They have high adsorption or intercalation capacities like clay minerals [17]. Therefore, the objective of this

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study was to investigate the adsorption properties of LDH, which is a new polymeric adsorbent for concentrating the malic acid solution. LDH was synthesized by a co-precipitation method, and its adsorption mechanism was also examined.

In this study, the adsorption of malic acid from aqueous solutions with LDH was investigated. The experiment's data have been used for calculating the equilibrium isotherm, and kinetic and thermodynamic parameters.

2. Materials and methods

2.1. Materials

Aluminum chloride hexahydrate ($AlCl_3$—$6H_2O$), magnesium chloride hexahydrate ($MgCl_2$—$6H_2O$) and sodium hydroxide (NaOH) were all purchased from Sigma-Aldrich (Germany). Malic acid (MA) was purchased from Merck (Germany). These chemicals and the other reagents were chemically pure grade, and all solutions were prepared to use deionized water. The purity of the substances studied provided in Table 1 as mass fraction.

2.2. Synthesis of Mg–Al–LDH

Mg—Al—Cl LDH was synthesized under a nitrogen atmosphere at room temperature using the coprecipitation method, similar to the method previously described [14,16]. Briefly, $MgCl_2{\cdot}6H_2O$ (3 mmol) and $AlCl_3{\cdot}6H_2O$ (1 mmol) were dissolved in 10 mL of deionized water and quickly poured into the 40 mL NaOH solution (6 mmol) with vigorous stirring under a nitrogen atmosphere at room temperature. Then the solution containing the slurry was stirred for 30 min and aged for 1 h and the resulting slurry was collected via centrifugation (5 min, 4500 min^{-1}). The precipitate was washed with deionized water twice and resuspended manually in 50 mL of deionized water. Then the solution was treated hydrothermally at 100 °C for 24 h to obtain homogen size. LDH crystallites were obtained via centrifugation and dried under a vacuum [18].

The characterization or identification of MA, LDH and MA–LDH were analyzed by FTIR. The zeta potential (surface charge) and mean particle diameter of LDH were determined with Zetasizer Nanoseries (Malvern Instruments, UK) in deionized water at 25 °C.

2.3. Adsorption experiments

The adsorption experiments were done to determine the effect of important variables such as, time, amount of adsorbent, initial acid concentration and temperature. For each experimental run, 5 mL stock acid solution of 100.80 g L^{-1} initial malic acid concentration and 0.1 g adsorbent were taken in a 50 mL flask. This mixture was kept agitated at a constant speed and temperature, in a thermostatic shaker at 298 K. The sample was taken out periodically every 15 min for 150 min, which was adequate to reach equilibrium, then centrifuged, and the aqueous phase was titrated (±0.01uncertainty) with 0.1 M NaOH solution, with a phenolphthalein indicator. For determining the temperature effect on adsorption, four different initial acid concentrations (25.30, 50.70, 75.40, 100.80 g L^{-1}) and 0.1 g. LDH were mixed. The samples were shaken at 298, 308 and 318 K and then the aqueous phases were analyzed to verify the effect of adsorbent concentration on the adsorption, 5 mL. solution was added to 0.05–1 g LDH and the experiment was completed according to the procedure.

3. Results and discussions

LDH was synthesized by a co-precipitation method and the zeta potential and mean particle diameter of LDH were determined. In addition, the use of LDH as an adsorbent for recovery of malic acid from aqueous solutions was studied. For this purpose, the effects of different conditions such as contact time, values of concentrations of malic acid, temperature, were investigated and the parameters of adsorption kinetics, thermodynamics and equilibrium were obtained by using the experimental results.

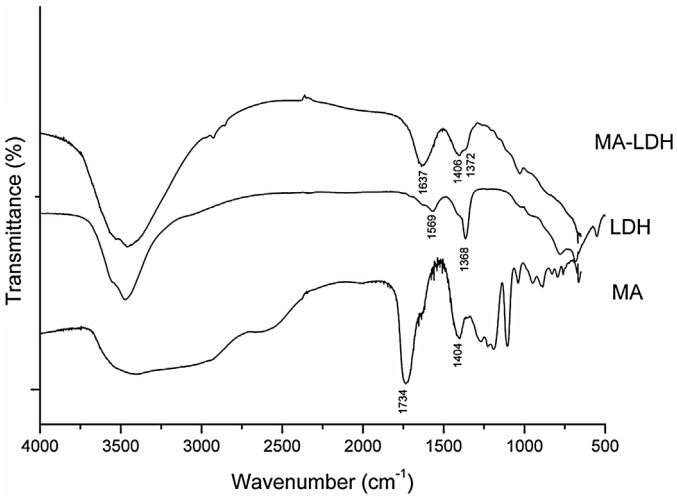

Fig. 1. FTIR Spectra of MA, LDH and MA–LDH.

3.1. Synthesis, FTIR, surface charge and mean diameter analysis of LDH

The nanoclays are used for the removal of heavy metals and organic polluting or for the recovery of the organic materials. The LDH structures, which are synthetic anionic clays, consist of a wide range of chemical inorganic salts and offer multivalent anions within the interlayer space because of their strong electrostatic interaction. They are preferred because of their low costs, reusability, high sorption capacities, easy recovery and large surface area. LDHs display the various particle sizes according to the synthetic route [19].

Therefore, our aim is to prove that the synthesis of LDH is a particular nanosize and appropriate surface charge. In this study the mean diameter and surface charge of LDH as an adsorbent, are 383.6 nm and 39 ± 2.5 mV, respectively. Moreover, their polydispersity index are 0.231, so their size homogeneity are appropriate for being used as an adsorbent.

The FTIR spectra of MA, LDH and MA–LDH are given in Fig. 1. The sharp absorption band at 1734 cm^{-1} which was attributed the stretching vibrations of carboxylic acid (C=O bond) in the MA structure was shifted to the small and broad adsorption band at 1637 cm^{-1}, which was probably ascribed to the intramolecular hydrogen-bonded carboxylic acid groups of MA adsorbed by LDH (Fig. 1). Moreover, the other sharp absorption band at 1404 cm^{-1} was related to the stretching vibrations of C—OH bond in the MA structure, was seen in the FTIR spectra of MA–LDH. These results confirmed that the MA was adsorbed by LDH [14,20].

3.2. Adsorption studies

3.2.1. Influence of time on adsorption of malic acid

Influence of adsorption time was examined to find the time of equilibrium. It has been determined that 150 min are sufficient for 298 K. The amount of LDH was 0.1 g. Results for time of equilibrium are listed in Table 2. Influence of adsorption time experiments were used to obtain the kinetic parameters.