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Effect of pH on the adsorption of Sunset Yellow FCF food dye into a layered double hydroxide (CaAl-LDH-NO_3)

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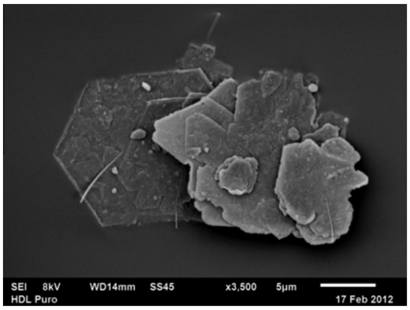
HIGHLIGHTS

- pH affects the adsorbent surface charge and the degree of anionic dye dissociation.
- CaAl-LDH-NO_3 is an effective adsorbent for the removal of Sunset Yellow FCF food dye from aqueous solutions.
- Lower pH potentially causes dissolution of the CaAl-LDH-NO_3.

GRAPHICAL ABSTRACT



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ABSTRACT

Effluents that are discarded by food industries are important sources of water pollution because they can contain large concentrations of organic matter and have intense color. The “batch” method for evaluating the adsorption of Sunset Yellow FCF food dye into a CaAl-LDH-NO_3 layered double hydroxide (LDH) system was investigated. The CaAl-LDH-NO_3 was coprecipitated at variable pH and characterized by X-ray diffraction, infrared spectroscopy and scan electron microscopy. Adsorption experiments were carried out as a function of pH, contact time and dye concentration. The results showed that pH affects the adsorbent surface charge and the degree of anionic dye dissociation. The effective pH range for dye removal was between 4.0 and 10. Lower pH potentially causes dissolution of CaAl-LDH-NO_3. The Langmuir equation adequately describes the equilibrium data. The best-fits showed a maximum adsorption of 398.41 mg/g or 0.88 mmol/g.

1. Introduction

Environmental changes due to human action have reached extremely worrisome levels. These actions result in a significant reduction in soil, air and water quality. Over the years, the problem of environmental pollution has become worse, which makes it a matter of public interest. Environmental pollution endangers the health of the community and of future generations. Thus, environmental pollution is identified as one of the largest problems of modern society [1,2].

Color is the most obvious water pollution indicator. Synthetic dyes represent a relatively large group of organic chemicals that are found in practically all spheres of our daily life. Annually, approximately 7×10^5 tons of dyes are produced, and approximately 7×10^4 tons/year are discarded by industries, including the textile, rubber, food, paper and plastic industries [1,3,4].

Because of their high organic matter concentrations and their intense colors, the effluents discarded by the food industry are an important source of pollution for water bodies. When discharged into streams, these effluents reduce the transmission of sunlight into the depleted dissolved oxygen zone [5–7] and may cause changes in aquatic biota (particularly near the release point). Thus, it becomes necessary to remove these materials before they are mixed with natural and unpolluted water bodies [3].

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The removal of color from wastewater is a major environmental problem because it is difficult to treat colored wastewaters with conventional methods [4]. Among the various types of processes for dye removal (physical, chemical, biological methods, electrochemical oxidation and adsorption methods), the adsorption process is one of the most efficient [8–11]. Activated carbon is the most popular adsorbent due to its high adsorption capacity for organic and inorganic pollutants [4]. Moreover, the use of low cost materials for adsorption has attracted attention as a color removal technique. For example, natural clays, bagasse fly ash, chitosan and other adsorbents have been used [11–15].

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds, have attracted considerable attention in recent years because of their potential industrial uses, which include their use as adsorbents, ion exchangers, catalysts and drug carriers [16–20]. These compounds are a class of layered compounds that are derived from the structure of mineral brucite, $Mg(OH)_2$, can be represented with the general formula $[M^{2+}{}_{(1-x)}M^{3+}{}_x(OH)_2](A^{n-})_{x/n}\cdot zH_2O$, where M^{2+} and M^{3+} are any divalent and trivalent metal cations, A^{n-} is the interlayer anions, and x is $M^{3+}/(M^{2+} + M^{3+})$ molar ration.

There is an interesting group of LDHs named as hydrocalumite, $Ca_2Al(OH)_6Cl(H_2O)_2\cdot nH_2O$. A net positive charge on the sheets originates from the partial replacement of Ca^{2+} with Al^{3+} ions, forming $[Ca_2Al(OH)_6Cl]^+$ layer. In hydrocalumite-like compounds, the large difference in ionic radii (Ca^{2+}, 99 pm; Al^{3+}, 56 pm) leads to a strong distortion of the local Ca^{2+} environment from a regular octahedron to a heptavalent coordination and gives rise to an ordering of the divalent and trivalent cations in a corrugated brucite-like layer [21]. The hydrocalumites attracted far less attention, perhaps because of the relative difficulty in synthesizing pure forms of the material and the somewhat less efficient calcination/rehydration behavior [22]. Consequently, the literature tends to contain little detail on anion exchange, pillaring and dehydration/rehydration behavior of the calcium–aluminum LDH species.

The aims of this study were to synthesize layered double hydroxide (LDH) in a $CaAl\text{-}LDH\text{-}NO_3$ system for the removal of Sunset Yellow FCF food dye and to evaluate the dependency of the adsorption on pH and contact time.

2. Experimental

2.1. Reagents

All of the chemicals used were non-pretreated and reagent grade. The Sunset Yellow FCF dye (SY) was kindly provided by Kerry Brazil (Fig. 1).

2.2. Synthesis

The $CaAl\text{-}LDH\text{-}NO_3$ material was prepared by coprecipitation at variable pH. The $CaAl\text{-}LDH\text{-}NO_3$ was prepared in a solution containing 0.10 mol of $Ca(NO_3)_2$, 0.05 mol of $Al(NO_3)_3\cdot 9H_2O$ and 70 mL of distilled water. This solution was slowly added to a solution containing 150 mL of NaOH (2 mol/L) while moderately agitating. The white colored precipitate was dried at 85 °C for 18 h. Lastly, the material was washed until it was neutral and dried at 35 °C for 24 h. Deionized and decarbonated water and under nitrogen atmosphere in order to avoid contamination by carbonate anions.

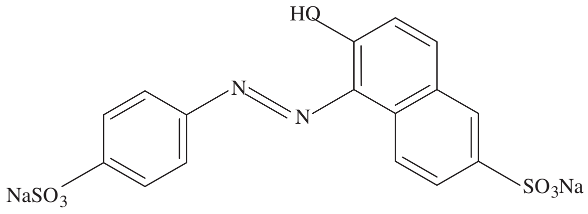

Fig. 1. Chemical structure of Sunset Yellow FCF.

2.3. Adsorption experiments

A batch process was used to evaluate the effects of pH and contact time on the adsorption process of Sunset Yellow dye. Adsorption experiments were performed as a function of contact time by dispersing 200 mg of LDH in 180 mL of distilled water, in sequence 20 mL of dye (500 mg/L) were added to the suspension with vigorously stirring. After selected time intervals, 5.0 mL of the samples were extracted and centrifuged. The dye concentration was determined by UV–Vis spectroscopy. The same procedure was repeated for final dye concentrations of 20 mg/L.

The effect of the initial solution pH on dye adsorption was evaluated by using 20 mL of the dye solution (20 and 50 mg/L) and 20 mg of the adsorbent. The initial solution pH was adjusted with HCl (0.1 mol/L) and NaOH (0.05 mol/L). The system was mechanically stirred (tumbling) for 2 h prior to centrifuging at 5000 rpm.

The isotherm adsorption experiments were carried out at room temperature while the initial concentration of Sunset Yellow ranged from10 to 1000 mg/L, the initial solution pH was adjusted at 4 and 20 mg of the adsorbent. After 2-h adsorption, the mixture was filtered and the residual dye concentration in the filtrate was determined.

The dye concentrations were measured with a UV–Vis spectrophotometer at a wavelength of 480 nm, which corresponded to the maximum absorbance (λ_{max}). The amount of adsorbent was calculated by using the following equation:

$$q_t = (C_o - C_t)V/M \qquad (1)$$

where q_t (mg/g) is the adsorbed amount at time t, C_0 (mg/L) is the initial concentration of the dye, C_t (mg/L) is the concentration of dye at time t, V is the volume of the solution (L) and M is the mass of the adsorbent (g).

2.4. Characterization

Powder X-ray diffraction patterns were collected using a Shimadzu model XD3A diffractometer with Cu Kα radiation (λ = 1.54056 Å, 40 kV e 30 mA), a scan range from 2 = 2 to 80° and at a scan rate of 2 min^{-1}. The identification of crystal phases was carried out by comparing the spectra with those found in the literature. Infrared spectra were recorded on a BOMEM model MB-series instrument in the range of 4000–400 cm^{-1}. In total, 128 scans were collected at a resolution of 4 cm^{-1} for KBr disks containing 1 wt% of samples. Scanning electron microscopy and chemical analyses (SEM/EDS) were obtained with a JOEL JSM-6610 microscope using an accelerating voltage of 10 kV with Thermo scientific NSS Spectral Imaging. The zeta potential was measured with a Zetasizer Nano-ZS (Malvern Instruments). The concentration of dye was determined with a UV-spectrophotometer (SP-220, Biospectro).

3. Results and discussion

3.1. Characterization

The Ca/Al (molar) ratio found for the host material, $CaAl\text{-}LDH\text{-}NO_3$, by EDS was equal to 2, suggesting the following formula: $Ca_2Al(OH)_6NO_3\cdot nH_2O$. The X-ray power diffraction patterns of $CaAl\text{-}LDH\text{-}NO_3$ and CaAl-LDH-SY are shown in Fig. 2. The diffraction