Itaconic acid-modified layered double hydroxide as a novel adsorbent for effective removal of Congo red from aqueous solutions

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Itaconic acid-modified layered double hydroxide as a novel adsorbent for effective removal of Congo red from aqueous solutions

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Abstract

Herein, we report the synthesis of Cu-Ca-Al/NO$_3$-based layered double hydroxide through co-precipitation methodology. The prepared layered double hydroxide was then modified with itaconic acid. The physicochemical properties of the prepared materials were studied using Fourier transform-infrared spectroscopy, scanning electron microscopy, X-ray diffraction analysis, thermogravimetric analysis, and nitrogen adsorption/desorption technique. The prepared materials were then applied as novel adsorbents for the removal of Congo red as a model of an anionic dye from aqueous media. To reach maximum adsorption, the effect of parameters including sample solution pH, adsorbent amount, contact time, and initial concentration of Congo red on the adsorption process was investigated. Kinetic studies were also conducted to study the mechanism of adsorption. In this regard, the kinetic models of pseudo-first-order, pseudo-second-order, Elovich, and intra-particle diffusion were studied. The results showed that the adsorption of Congo red onto Cu-Ca-Al-LDH and LDH-ITA adsorbents followed the pseudo-second-order kinetic model. To evaluate the equilibrium adsorption data, different isotherms including Langmuir, Freundlich, and Dubinin-Radushkevich were also applied. The data revealed that the Freundlich isotherm provided the best fit with the equilibrium data of both adsorbents. Maximum adsorption capacities of 81 and 84 mg g$^{-1}$ were obtained using Cu-Ca-Al-LDH and LDH-ITA adsorbents, respectively.

Keywords: Cu-Ca-Al/NO$_3$-based layered double hydroxide; Itaconic acid; Adsorption; Congo red; Kinetic and isotherm
1. Introduction

As a growing trend, nanotechnology has attracted huge interest among scientists in various scientific fields such as catalysis [1-3], energy conversion and storage [4], sample preparation [5-8], and adsorption [9-15]. The great interest in the field of nanotechnology arises from the extraordinary physical, chemical, thermal, and mechanical characteristics of nanomaterials in comparison with large-size particles. In general, nano-sized materials exhibited high specific surface area, tailorble structure, thermal stability, high chemical and mechanical resistance, and easiness in functionalization. As a subgroup of inorganic layered nanomaterials, layered double hydroxides (LDHs) are ionic lamellar mixed hydroxides that consisted of positively charged main layers and an interlayer region with charge-compensating anions undergoing anion-exchange chemistry [16, 17]. They are generally demonstrated with a stoichiometry of $[M_{2+}^{2+}M_{3+}^{3+}(OH)_{2}]^{x+}(A^{n-})_{x/n} \cdot mH_2O$ [18, 19]. In this formula, $M^{2+}$ and $M^{3+}$ represent divalent and trivalent metals of the layers, respectively, and $A^{n-}$ is charge balancing anion in the interlayer region which can be readily replaced. Owing to their fantastic properties, nowadays LDHs with different compositions have received remarkable attention from academia and industry. They are exhibited important properties such as ion exchange capability, acid-base properties, and adsorption capacity. They are also low-cost materials and their properties can be easily tailored. The use of these materials in drug delivery [20], catalysis [21], energy conversion and storage [22], environmental remediation [23, 24], and sample preparation [25, 26] have been reported.

Despite the unique characteristics of LDHs, various functionalization strategies have been reported for the modification of LDHs to increase their performance and applications. Considering the surface properties of LDHs, they are easily agglomerated, usually incompatible with organic substances, and have low efficiency for specific applications. LDHs functionalization can drastically improve their performance and properties. Until now,
various functionalization strategies have been used for the modification of LDHs. Some common functionalization strategies included intercalation, hybrid assembly, surface modification, size and morphology regulation, layer composition tuning, and defect introduction which are discussed in detail in a reported review by Laipan et al [27].

As an important environmental concern in both developing and industrial countries, the lack of clean water due to the disposal of various toxic compounds into the environment caused drastic concerns about the creature’s health. As an unpleasant result of the industrialization process, water pollution is an international problem, and nowadays scientists, and policymakers are beginning to take more notice of this vital problem to find a suitable solution. Among the well-known pollutants, synthetic organic dyes are one of the important groups of water pollutants. The release of these contaminants is an increasing and serious global challenge from the environmental point of view. These relatively complex organic molecules are widely used in different industries such as leather tanning, food processing, paper making, cosmetics, textile, and plastics. As a water-soluble member of synthetic dyes, Congo red is used in a huge quantity in textile and biochemistry based industries [28]. It is a benzidine-based anionic dye that was discovered by Paul Bottinger in 1883. Generally, benzidine-based dyes are toxic and highly carcinogenic. Congo red is known to metabolize to benzidine, which is a carcinogen and mutagen compound for humans. Due to the high toxicity and carcinogenicity of Congo red, its use is banned in many countries [29].

Until now, various decontamination techniques including biological, chemical, and physical treatments have been adopted to remove toxic compounds especially synthetic organic dyes from environmental media in both industrial and municipal wastewaters [30]. In this regard, the application of membrane separation, adsorption, chemical oxidation, chemical coagulation, biological degradation, etc. is reported [15]. Among the treatment techniques,
the adsorption strategy provided a simple, low cost, and relatively fast methodology with high efficiency. This conventional strategy is used in advanced wastewater treatment due to its ease of operation, and flexibility in adsorbent design. This method also produces no harmful by-products and prevents sludge formation during the removal process [15]. Until now, various synthetic and natural adsorbents have been used for the adsorption of organic dyes which is discussed in some useful review reports [31-33]. Notably, developing adsorbents with improved characteristics to be used for the adsorption process is an ongoing trend.

Herein, we present the synthesis and characterization of a novel adsorbent of itaconic acid-modified Cu-Ca-Al layered double hydroxide for adsorption purposes. The Cu-Ca-Al layered double hydroxide was synthesized at first and then modified with itaconic acid through a simple approach. To study the applicability of the prepared materials for adsorption purposes, Congo red as an anionic dye was selected to be removed from the aqueous solution. Kinetic studies were also conducted for the prepared materials. To the best of our knowledge, this is the first report to study the potential application of itaconic acid-modified Cu-Ca-Al layered double hydroxide for adsorption purposes.

2. Experimental section

2.1. Materials and methods

Aluminum nitrate nonahydrate (Al(NO$_3$)$_3$.9H$_2$O, ≥98.0%), calcium nitrate tetrahydrate (Ca(NO$_3$)$_2$.4H$_2$O, ≥99.0%), copper(II) nitrate trihydrate (Cu(NO$_3$)$_2$.3H$_2$O, ≥99.0%), sodium carbonate (Na$_2$CO$_3$), sodium hydroxide (NaOH), and itaconic acid (C$_5$H$_6$O$_4$) were purchased from Sigma-Aldrich. Acetic acid (99.5%) and ortho-phosphoric acid (85%) were obtained from Merck (Darmstadt, Germany). The stock standard solution of Congo red (2000 mg L$^{-1}$)
was prepared in water. Working standard solutions were prepared daily by diluting the stock solution. Deionized water was prepared by a lab-made water purification system.

2.2. Apparatus

A double beam UV–Vis spectrophotometer (UV-1601 Shimadzu, Japan) was applied for the determination of dye concentration in the sample solutions at the wavelength of 499 nm. The XRD data were recorded with the help of a Rigaku-DMax 2500 diffractometer (Japanese science and science company, Tokyo, Japan) with Cu $K_{\alpha}$ radiation at a wavelength of 1.540 Å and the generator working at 40 kV. Diffractograms were recorded between 2θ of 5-70°. The FT-IR spectra were recorded on a Jasco-FT-IR-350 (Tokyo, Japan) spectrometer with a wavenumber range from 400 to 4400 cm$^{-1}$, using the KBr pellet technique. Scanning electron microscopy (SEM) was performed on a JSM-6510 Series scanning electron microscope (JEOL, Tokyo, Japan). Nitrogen adsorption/desorption analysis was performed using a Belsorp-mini II (BEL Japan Inc., Osaka, Japan) at the temperature of 77 K. Thermogravimetric analysis was performed on an STA 503 (Bahr GmbH, Hullhorst, Germany) analyzer, at a heating rate of 10 °C min$^{-1}$ from room temperature to 800 °C under an inert atmosphere.

2.3. Synthesis of Cu-Ca-Al-LDH

The Cu-Ca-Al-LDH was prepared according to the following procedure. At first, 976 mg of Cu(NO$_3$)$_2$·3H$_2$O (4 mmol), 954 mg of Ca(NO$_3$)$_2$·4H$_2$O (4 mmol), and 1.532 g of Al(NO$_3$)$_3$·9H$_2$O (4 mmol) were dissolved into 100 mL of deionized water. In another container, 100 mL of an aqueous alkaline solution containing 150 mmol L$^{-1}$ of NaOH and 50 mmol L$^{-1}$ of Na$_2$CO$_3$ was prepared. Then, the two prepared solutions were slowly added to a 500 mL round bottom glass flask. The pH of the solution was kept between 10 and 11 during
the addition. After the addition, the mixture was stirred at room temperature for 60 min. Then, the temperature of the solution was enhanced to 60 °C and maintained for 18 h. Afterward, the slurry was cooled and filtered. The prepared material (Cu-Ca-Al-LDH) was washed several times with deionized water and dried in an oven at 85 °C.

2.4. Synthesis of LDH-ITA

For the preparation of LDH-ITA, 976 mg of Cu(NO$_3$)$_2$·3H$_2$O (4 mmol), 954 mg of Ca(NO$_3$)$_2$·4H$_2$O (4 mmol), and 1.532 g of Al(NO$_3$)$_3$·9H$_2$O (4 mmol) were dissolved into 100 mL of deionized water. Then, 100 mL of an aqueous alkaline solution containing 150 mmol L$^{-1}$ of NaOH and 50 mmol L$^{-1}$ of Na$_2$CO$_3$ was prepared. The two prepared solutions were then slowly added to a 500 mL round bottom flask at room temperature (the pH of the solution was kept in the range of 10-11). The mixture was stirred for 60 min, heated to 60 °C, and then, 50 mL of water containing 2.5 g of itaconic acid was poured into the round bottom flask and stirred for 60 min. The mixture was maintained at this step for 18 h without stirring. The obtained slurry was filtered, washed with deionized water, and dried at 80 °C.

2.5. Adsorption experiments

The batch adsorption experiments were conducted to study the adsorption behavior of Congo red onto the prepared adsorbents. For the experiments, 5 mL of an aqueous solution of Congo red (with the desired concentration) was poured into a 25 mL Erlenmeyer flask containing the accurately weighed amount of adsorbent. The adsorption was carried out in a water-bath shaker (298 K) at a shaking speed of 220 rpm for a specific period. After separation of the adsorbent from the solution, the concentration of Congo red in the solution was determined with the help of the UV–Vis spectrophotometer at 499 nm. All the samples
were filtered through filter papers before analysis. The removal efficiency was calculated using the following equation (Eq. 1):

\[
RE (\%) = \frac{C_i - C_e}{C_i} \times 100
\]  

(1)

In this equation, \(C_i\) and \(C_e\) are the initial and equilibrium concentration of Congo red in the solution (mg L\(^{-1}\)), respectively. The adsorption capacity \((q_e, \text{mg g}^{-1})\) was computed according to the following equation (Eq. 2):

\[
q_e = \left(\frac{C_i - C_e}{W}\right) \times V
\]  

(2)

In this equation, \(W\) is the adsorbent amount (mg) and \(V\) is the solution volume (mL).

3. Results and discussion

3.1. Synthesis and characterization of the materials

In this study, Cu-Ca-Al-LDH was prepared in a simple strategy. For the modification of the prepared LDH, itaconic acid was applied. Due to their ability to establish a hydrogen bond between surface hydroxyl groups and functional groups of organic dyes, as well as their ion exchange ability, Cu-Ca-Al-LDH and LDH-ITA can be used as adsorbents to remove organic dyes from aqueous media. Scheme 1 reveals the structure of these materials and possible interactions during adsorption of Congo red by them form the aqueous solution.
Scheme 1 The schematic representation for structure of Cu-Ca-Al-LDH and LDH-ITA and their application for adsorption of Congo red from the aqueous solutions.

The structure of the prepared materials was further studied using various characterization techniques including FT-IR spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), N\textsubscript{2} adsorption/desorption, and thermogravimetric analysis (TGA).

The FT-IR spectra of the prepared Cu-Ca-Al-LDH and LDH-ITA are shown in Fig. 1. In the case of Cu-Ca-Al-LDH, the broadband located at 3435 cm\textsuperscript{-1} is associated with the stretching vibration of O-H groups in the brucite-like layer and interlayer molecules. The weak band located at around 1633 cm\textsuperscript{-1} is related to the bending vibration of interlayer water molecules [34]. The band at 1421 cm\textsuperscript{-1} can be assigned to the characteristic vibration mode of
NO$_3^-$ anions in the interlayer of the prepared Cu-Ca-Al-LDH. A series of complicated bands in the range of 400-1000 cm$^{-1}$ (such as 876, 712, 604, 515, 445 cm$^{-1}$, etc.) can be attributed to the vibrational modes of the lattice resulting from M–O, O–M–O, and M–O–M bonds in which the M represents Cu, Ca or Al [35]. In the case of modified LDH-ITA, the broadband related to the stretching vibration of hydroxyl groups and water molecules in the interlayer space can be seen at 3473 cm$^{-1}$. The band at 1421 cm$^{-1}$ disappeared in the case of LDH-ITA, indicating that most of the NO$_3^-$ ions were replaced by itaconic acid anions. An absorption band at 1384 cm$^{-1}$ indicated the presence of some carboxylate anions in the modified hydrotalcite structure. The bands located at 1646 cm$^{-1}$ and 1431 cm$^{-1}$ are related to the absorption bands of the carboxylic ions (asymmetric and symmetric stretching absorptions). The band at 1565 cm$^{-1}$ is related to the C=C stretching vibration [36, 37]. These bands indicated the intercalation of itaconic acid.

![FT-IR spectra of the Cu-Ca-Al-LDH and LDH-ITA.](image)

**Figure 1.** FT-IR spectra of the Cu-Ca-Al-LDH and LDH-ITA.

The XRD patterns of the prepared Cu-Ca-Al-LDH and LDH-ITA are shown in Fig. 2a. In the case of Cu-Ca-Al-LDH, it exhibited characteristic peaks located at $2\theta = 23.1^\circ$, 29.5$^\circ$, 35.6$^\circ$, 38.6$^\circ$, 39.5$^\circ$, 43.1$^\circ$, 47.5$^\circ$, 48.5$^\circ$, etc. which is in accordance with previous reports [38]. In this regard, the peaks at 35.6$^\circ$ and 38.6$^\circ$ correspond to CuO. The presence of
characteristic peaks related to CaCO$_3$ (23.4°, 29.5°, 36.9°, 39.5°, 43.1°, 47.5°, and 48.5°) is
detected in the XRD pattern, which is in agreement with the previous reports on the synthesis
of Ca–Al LDHs [39, 40]. In the LDH-ITA, some diffraction peaks disappeared or weakened.
In contrast, some diffraction peaks became stronger or new peaks appeared. These
observations combined with the earlier FTIR analyses indicated that itaconic acid was
incorporated into the Cu-Ca-Al-LDH structure.

**Figure 2.** The XRD patterns (a) and the TGA thermograms (b) of the prepared Cu-Ca-Al-
LDH and LDH-ITA.

The TGA curves of the prepared Cu-Ca-Al-LDH and LDH-ITA are shown in Fig. 2b. In
the case of Cu-Ca-Al-LDH, a mass loss between 30 to 235 °C (about 2.7%) is mainly due
to the removal of physically-adsorbed and interlayered water [36]. Another mass loss
occurred between 235 to 580 °C (about 3.7%) which may be attributed to the decomposition
of the lamina –OH groups. In this stage, the layered structure of the Cu-Ca-Al-LDH was
gradually degraded. A final mass loss occurred in the range of 580 to 800 °C (about 22.6%).
This mass loss is related to the dehydroxylation of the Cu-Ca-Al-LDH laminates and the
formation of copper, calcium, and aluminum oxides. The Cu-Ca-Al-LDH exhibited a total
mass loss of 29.0%. In the case of LDH-ITA, when the temperature was increased to near
200 °C, decomposition of itaconic acid began. The mass loss of LDH-ITA is considerably
higher than that of the unmodified Cu-Ca-Al-LDH. The LDH-ITA showed a total mass loss of 40.0% from 30 to 800 °C.

The FESEM images of the prepared Cu-Ca-Al-LDH and LDH-ITA are shown in Fig. 3 at three magnifications. The plate-like morphology of both Cu-Ca-Al-LDH and LDH-ITA crystallites is observable in the images. They exhibited a lamellar structure with sharp edges [38]. Also, the prepared Cu-Ca-Al-LDH shows more aggregation in comparison with modified LDH (LDH-ITA). This may be due to the formation of hydrogen bonds on the surface of the Cu-Ca-Al-LDH. In the case of LDH-ITA, the degree of reunion is reduced, and the particle size decreased [36].

![Figure 3. The scanning electron micrographs of the prepared Cu-Ca-Al-LDH (a-c) and LDH-ITA (d-f) with different magnifications.](image)

The N₂ adsorption/desorption isotherms of the prepared Cu-Ca-Al-LDH and LDH-ITA are shown in Fig. 4. As can be seen in Fig. 4, Cu-Ca-Al-LDH showed a combination of type III and IV isotherms with H3-type hysteresis loops according to the IUPAC classification. The LDH-ITA exhibited IV type isotherm with H3-type hysteresis loops. The calculated parameters are shown in Table 1. The prepared Cu-Ca-Al-LDH showed a BET surface area of 15.6 m² g⁻¹ while LDH-ITA exhibited a BET surface area of 24.8 m² g⁻¹. Also, pore
volumes of 0.142 and 0.080 cm$^3$ g$^{-1}$ were obtained for Cu-Ca-Al-LDH and LDH-ITA, respectively.

Figure 4. The N2 adsorption/desorption isotherms of Cu-Ca-Al-LDH (a), LDH-ITA (b), and the BJH pore size distribution curves of the samples (c).

Table 1. Textural properties of the synthesized materials.

| Sample    | BET | BJH |
|-----------|-----|-----|
|           | Surface area | $V_p$ | $r_p$ |
|           | (m$^2$ g$^{-1}$) | (cm$^3$ g$^{-1}$) | (nm) |
| LDH       | 15.6 | 0.142 | 1.64 |
| LDH-ITA   | 24.8 | 0.080 | 1.64 |

3.2. Adsorption studies

3.2.1. The effect of pH on adsorption

To study the effect of sample solution pH on the adsorption of Congo red onto the Cu-Ca-Al-LDH and LDH-ITA adsorbents, sample solution pHs between 5.0 and 9.0 were investigated. This range was selected due to the instability of Congo red below pH 5 [28]. All the experiments were done using 5 mL of an aqueous sample solution containing 50 mg L$^{-1}$ of Congo red with the adsorbent dosage of 10.0 mg. The adsorption was performed at 298 K for 3 h with the help of magnetic stirring at 1500 rpm. After the adsorption procedure, the adsorbent was separated from the sample solution utilizing centrifugation (6000 rpm, 10 min) and the concentration of remained dye in the sample solution was determined using UV-Vis spectroscopy. The data are shown in Fig. 5a. As can be seen in Fig. 5a, with increasing
solution pH from 5.0 to 9.0, a continuous decrease in the removal efficiency of the two adsorbents was observed. The decrease in the Congo red removal efficiency is may be due to that the surface of the adsorbents becomes highly negative when pH increased from 5.0 to 9.0. The negative charge on the surface of the adsorbents results in electrostatically repelling of negatively charged Congo red [28]. Accordingly, pH=5.0 was selected for further experiments.

Figure 5. The effect of pH (a), adsorbent amount (b), and contact time (c) on the adsorption of Congo red by the prepared adsorbents.

3.2.2. The effect of the adsorbent amount

The effect of adsorbent amount on the adsorption of Congo red onto the Cu-Ca-Al-LDH, and LDH-ITA was studied in the range of 1.0-20.0 mg. In these experiments, 5 mL of a standard aqueous solution of Congo red at the concentration level of 50 mg L\(^{-1}\) (pH=5.0) was used. The experiments were performed at 298 K for 3 h with the help of magnetic stirring at 1500 rpm. After separation of the adsorbent from the sample solution (centrifugation at 6000 rpm for 10 min), the concentration of remained dye in the sample solution was determined using UV-Vis spectroscopy. As can be seen in Fig. 5b, the removal efficiency for two adsorbents was enhanced by enhancing the adsorbent amount from 1.0 to 10.0 mg and no further enhancement in removal efficiency was observed for higher adsorbent amounts. Based on the results, 10.0 mg of each of the adsorbents were selected as the adsorbent amount for further experiments.
3.2.3. The effect of contact time

To study the effect of contact time on the adsorption of Congo red onto the Cu-Ca-Al-LDH and LDH-ITA adsorbents, various contact times between 10-250 min were investigated. In the experiments, 5 mL of a standard solution of Congo red at the concentration level of 50 mg L\(^{-1}\) (pH=5.0) with an adsorbent dosage of 10.0 mg was used. The adsorption was performed at 298 K. After separation of the adsorbent from the sample solution (centrifugation at 6000 rpm for 10 min), the concentration of the remained dye in the sample solution was determined. Figure 5c shows the effect of contact time on Congo red removal by the prepared adsorbents. A remarkable enhancement in removal efficiency was observed for the two adsorbents when contact time was increased from 10 to 120 min. Longer times had no significant effect on the adsorption efficiency. The obtained data revealed a relatively fast adsorption process. The high accessible sites of the adsorbents are mainly responsible for this fast adsorption. Based on the results, a contact time of 120 min was used for further experiments to ensure that equilibrium is reached.

3.2.4. The adsorption kinetic studies

To better understanding and study the mechanism of adsorption, kinetic studies were conducted. The kinetic models of pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich, and intra-particle diffusion (IPD) were studied. The used equations are expressed in the following equations:

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{3}
\]

\[
\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \tag{4}
\]

\[
h = k_2 \times q_e^2 \tag{5}
\]
\[ q_t = \frac{\ln (\alpha \beta)}{\beta} + \frac{\ln t}{\beta} \]  

(6)

\[ q_t = k_{dif}(t)^{0.5} + C \]  

(7)

In these equations, \( q_e \) (mg g\(^{-1}\)), \( q_t \) (mg g\(^{-1}\)), \( k_1 \) (min\(^{-1}\)), \( h \) (mg g\(^{-1}\) min\(^{-1}\)), \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)), \( \alpha \) (mg g\(^{-1}\) min\(^{-1}\)) & \( \beta \) (g mg\(^{-1}\)), \( k_{dif} \) (mg g\(^{-1}\) min\(^{-0.5}\)), and \( C \) (mg g\(^{-1}\)) are the adsorption capacity at equilibrium, the adsorption capacity at time \( t \), PFO rate constant, the initial sorption rate in PSO model, PSO rate constant, Elovich constants, IPD rate constant, and a constant, respectively. The results of the fitting are shown in Fig. 6 and Table 2. Data showed that, for both adsorbents, the PSO kinetic model provided better \( R^2 \) values than those obtained by other models. Accordingly, the physiochemical adsorption process can be well described with the PSO model.

**Figure 6.** The kinetic adsorption models of pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich, and intra-particle diffusion (IPD) for adsorption of Congo red by the prepared adsorbents.
Table 2. Parameters obtained by kinetic models for the adsorption of Congo red onto LDH and LDH-ITA.

| Model  | Adsorbent  | $R^2$  | Parameters $^{a}$ |
|--------|------------|--------|-------------------|
| PFO    | LDH        | 0.4668 | $k_1 = 0.0306$  $q_e = 6.6$ |
|        | LDH-ITA    | 0.9347 | $k_1 = 0.0223$  $q_e = 6.5$ |
| PSO    | LDH        | 0.9985 | $k_2 = 0.0068$  $q_e = 18.0$  $h = 2.227$ |
|        | LDH-ITA    | 0.9998 | $k_2 = 0.0073$  $q_e = 20.0$  $h = 2.890$ |
| Elovich| LDH        | 0.9186 | $\alpha = 24.26$ $\beta = 0.4190$ |
|        | LDH-ITA    | 0.9106 | $\alpha = 27.64$ $\beta = 0.3740$ |
| IPD    | LDH        | 0.7977 | $k_{df} = 0.6283$  $C = 9.93$ |
|        | LDH-ITA    | 0.7623 | $k_{df} = 0.6911$  $C = 11.28$ |

$^{a}$The units are as same as mentioned in section 3.2.4.

3.2.5. The effect of Congo red concentration and adsorption isotherm

To study the effect of Congo red initial concentration, concentrations between 10 and 300 mg L$^{-1}$ (pH=5.0) were studied. An adsorbent dosage of 10.0 mg was applied and the adsorption time was set to 120 min. The obtained data are shown in Fig. 7a. Maximum adsorption capacities of 81 and 84 mg g$^{-1}$ were obtained using Cu-Ca-Al-LDH and LDH-ITA adsorbents, respectively. To study the equilibrium adsorption, Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherm models were investigated. The equations of the linear forms of the applied isotherm models are as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}xk_L} + \frac{C_e}{q_{max}} \quad (8)$$

$$\log q_e = \frac{1}{n} \log C_e + \log k_F \quad (9)$$

$$\ln q_e = \ln q_{max} - B (RT \ln(1 + \frac{C_e}{C_e}))^2 \quad (10)$$

In these equations, $C_e$ (mg L$^{-1}$), $q_e$ (mg g$^{-1}$), $q_{max}$ (mg g$^{-1}$), $k_L$ (L mg$^{-1}$), $n$ & $k_F$ ((mg g$^{-1}$) (L mg$^{-1}$)$^{1/n}$), $B$ (mol$^2$ kJ$^{-2}$), $R$ (j mol$^{-1}$ K$^{-1}$), and $T$ (K) are the concentration of Congo red at
equilibrium, adsorption capacity at equilibrium, the maximum adsorption capacity of adsorbent, the Langmuir constant, the Freundlich isotherm constants for adsorption capacity and adsorption intensity, the Dubinin–Radushkevich isotherm constant, the universal gas constant, and temperature, respectively. Figure 7 and Table 3 show the adsorption isotherms and the calculated parameters. Considering the $R^2$ value, the Freundlich model showed the best fit with the experimental data obtained by both adsorbents. The $R^2$ values of the Freundlich model were obtained 0.9411 and 0.9320 for Cu-Ca-Al-LDH and LDH-ITA adsorbents, respectively. The Freundlich adsorption isotherm model representing multilayer, heterogeneous adsorption sites.

**Figure 7.** The equilibrium isotherm (a) and the isotherm models of Langmuir (b), Freundlich (c), and Dubinin–Radushkevich (d) for adsorption of Congo red by the prepared adsorbents.

**Table 3** The parameters obtained by isotherm models for the adsorption of Congo red onto LDH and LDH-ITA.

| Model   | Adsorbent | $R^2$ | Parameters$^a$ |
|---------|-----------|-------|----------------|
| Langmuir | LDH       | 0.6805| $k_L = 0.0087$, $q_{\text{max}} = 166.6$ |
|         | LDH-ITA   | 0.8782| $k_L = 0.0194$, $q_{\text{max}} = 126.6$ |
| Freundlich | LDH     | 0.9411| $k_F = 1.620$, $n = 1.142$ |
|         | LDH-ITA   | 0.9320| $k_F = 2.945$, $n = 1.289$ |
| D-R     | LDH       | 0.6479| $B = 4.93 \times 10^{-6}$, $q_{\text{max}} = 42.5$ |
|         | LDH-ITA   | 0.6450| $B = 2.34 \times 10^{-6}$, $q_{\text{max}} = 45.6$ |

$^a$The units are as same as mentioned in section 3.2.5.

3.3. Comparison study

Contact time (equilibrium time) and adsorption capacity are two important factors in the adsorption process of an adsorbate species by an adsorbent material. The shorter and higher
the adsorption time and the adsorbent capacity, respectively, the more efficient the adsorption
process. Table 4 compares the adsorption capacities of several adsorbents as well as
the corresponding optimal adsorption conditions. As shown in Table 4, the highest adsorption
capacities were observed at acidic pHs for all adsorbents. Also, compared to the adsorbents
reported in Table 4, adsorbents synthesized in this work have a shorter adsorption time and a
higher adsorption capacity, which indicates the acceptable performance of these adsorbents.
One possible reason for observing this acceptable performance is the adsorption mechanism,
which occurs in both anion exchange and surface adsorption by H-bonding pathway as
depicted in Scheme 1.

Table 4. Comparison of a maximum adsorption capacities of Cu-Ca-Al-LDH and LDH-ITA
for removal of Congo red dye by various reported adsorbents.

| Adsorbents          | \(q_{\text{eq}}\) (mg g\(^{-1}\)) | pH   | Equilibrium time (min) | Ref.  |
|---------------------|----------------------------------|------|------------------------|-------|
| Cu-Ca-Al-LDH        | 81                               | 5.0  | 120                    | This work |
| LDH-ITA             | 84                               | 5.0  | 120                    | This work |
| AuNPs-coated AC     | 71                               | 6.5  | 270                    | [41]   |
| AgNPs-coated AC     | 64                               | 6.5  | 270                    | [41]   |
| pTSA-Pani@GO-CNT    | 66                               | 5.0  | 300                    | [42]   |
| Neem leaf powder    | 41                               | 6.7  | 300                    | [43]   |
| hollow ZnFe\(_2\)O\(_4\) microspheres | 16 | 6.0 | 120 | [44] |
| Aspergillus niger biomass | 14 | 6.0 | 1800 | [45] |

\(^a\)NPs: nanoparticles; AC: activated carbon; \(p\)TSA: para toluene sulfonic acid; Pani: polyaniline; GO: graphene oxide; CNT: multiwalled carbon nanotube.

4. Conclusions

In conclusion, Cu-Ca-Al/NO\(_3\)-LDH was functionalized with itaconic acid. Water as an
environmentally-friendly solvent was used in the synthesis procedures. The prepared
materials were applied as novel adsorbents for adsorption purposes. The newly prepared
materials showed good performance toward Congo red removal from aqueous solutions. The
effect of experimental parameters (sample solution pH, adsorbent dosage, contact time, and
initial concentration of the dye) was studied. The kinetic studies showed that the best fit was
achieved with the pseudo-second-order model for the adsorption of Congo red using the two prepared adsorbents. Three isotherm models were used to investigate the equilibrium adsorption studies. The data showed that the Freundlich model showed the best fit with $R^2$ values of 0.9411 and 0.9320 for Cu-Ca-Al-LDH and LDH-ITA adsorbents, respectively. Maximum adsorption capacities of 81 and 84 mg g$^{-1}$ were obtained using Cu-Ca-Al-LDH and LDH-ITA adsorbents, respectively. Finally, the prepared adsorbents showed acceptable characteristics to be considered as effective adsorbents for anionic dye (e.g. Congo red) removal from aqueous media.

**Conflict of interest**

The authors declare no competing financial interest.

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Figures caption

Fig. 1. The FT-IR spectra of the prepared Cu-Ca-Al-LDH and LDH-ITA.

Fig. 2. The XRD patterns (a) and the TGA thermograms (b) of the prepared Cu-Ca-Al-LDH and LDH-ITA.

Fig. 3. The scanning electron micrographs of the prepared Cu-Ca-Al-LDH (a-c) and LDH-ITA (d-f) with different magnifications.

Fig. 4. The $N_2$ adsorption/desorption isotherms of Cu-Ca-Al-LDH (a), LDH-ITA (b), and the BJH pore size distribution curves of the samples (c).

Fig. 5. The effect of pH (a), adsorbent amount (b), and contact time (c) on the adsorption of Congo red by the prepared adsorbents.

Fig. 6. The kinetic adsorption models of pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich, and intra-particle diffusion (IPD) for adsorption of Congo red by the prepared adsorbents.

Fig. 7. The equilibrium isotherm (a) and the isotherm models of Langmuir (b), Freundlich (c), and Dubinin–Radushkevich (d) for adsorption of Congo red by the prepared adsorbents.
**Figures**

*Figure 1*

FT-IR spectra of the Cu-Ca-Al-LDH and LDH-ITA.

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Figure 7

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Supplementary Files

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- Scheme1.png