A Novel Coated of Mg/Fe Layered Double Hydroxide on Date Palm Stones

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Abstract. Mg/Fe layered double hydroxide coated low cost activated carbon (AC-Mg/Fe) was synthesized to be as a novel material by a co-precipitation method. The using of Scanning electron microscope (SEM), Energy Dispersive Spectroscopy (EDS), X-Ray Diffraction Analysis (XRD) and Specific surface area of materials by Brunauer–Emmett–Teller analysis (BET) were employed for characterize the synthesized coated adsorbent. The XRD and SEM displayed that the particles on the surface of low cost activated carbon are regular and good-defined, and the structure of LDHs is typical lamellar. The crystallite size of the coated adsorbent according to the XRD analysis was to be 96.7 nm. The contents of the Fe and Mg after modification increase noticeably according to the EDS analysis. From BET analysis, it was an increasing in the specific surface area of the adsorbent from 22.57 m²/g (before synthesize) to 81.77 cm/g (after synthesize). This analysis resulted in successfully coated Mg/Fe layered double hydroxide (Mg/Fe-LDH) on activated carbon for preparing of a high capacity adsorbent and magnetic sorbent for easy separation by magnetic field.

1. Introduction
In recent year, for removing of heavy metals from wastewater, the techniques for alternative removing was the adsorption. Thus, there has been an increase in demand for technologies that are sustainable in terms of economy, efficiency, energy and environment such as adsorption [1,2]. Natural materials, low cost activated carbon derived from agriculture waste coated by other inorganic adsorbents such as magnesium oxide, manganese oxide, aluminum oxide, and ferric oxide to produce Layered double hydroxides (LDHs), which are consider as a novel type of adsorbent that improving a wastewater treatment [3].

In the last years, due to the possible applications of the hydro-talcite-like compounds or layered double hydroxides (LDHs) (were to be a class of anionic clays) as sorbents, catalyst supports or catalyst and as ion exchangers, they has got considerable interest from both academia and industry [4].

In spite of the LDHs presented as minerals in nature, they can be synthesized comparatively economical and simplicial. The LDHs have a high capacity of anion exchange (2–3 meq.g⁻¹) and large surface area, which considered the most interesting properties, and these properties are comparable to those of good thermal stability and anion exchange resins [5]. The low cost activated carbon (AC), which produced from chemical and physical modification processes like activation of natural date palms stones (PS), show high removal efficiency for heavy metal compared with PS [6]. So the adsorption capacity for individual PS or AC or Mg/Fe LDH is lower than Mg/Fe LDH modified with organic or inorganic
material. From previous studies, the use of AC coating by Mg/Fe–LDH as an adsorbent for heavy metals has not been reported [7,8]. So, this low cost and good adsorbent with high surface area derived from agriculture waste is modified by Mg/Fe LDH to produce an economic and effective novel adsorbent for removal of heavy metals from wastewater. The preparation of this novel adsorbent by co-precipitation method and study the adsorption process of it are the main objective of this work in order to produce economic high sorption capacity for removing heavy metal and elimination from agriculture waste.

2. Experimental works & procedures

2.1 Preparation of low cost activated carbon (AC)
The date palms stones were originally collected from the local markets, these stones were washed thoroughly with tap water, and dried naturally in the sun light for 5 days, then the stones ground using a mechanical grinder with sizes from (0.5 to 1.1 mm). The ground stone then were placed in a furnace to be activated physically at temperature of 340 º C with flow of 500 mL min⁻¹ of (N₂ and CO₂) respectively with duration 2 h for each gas.

2.2 Synthesis of LDH coated on low cost activated carbon (AC-Mg/Fe)
The co-precipitation method was used to prepare LDHs at the room temperature. The method was conducted by using different AC dosage (0.05, 0.1, 0.3, 0.5, 1, and 2 g/50 mL) and different molar ratio of (Mg/Fe) (1/1, 2/1, 3/1 and 4/1) of solution containing Mg(NO₃)₂·6H₂O and FeCl₃·6H₂O with stirring at 200 rpm for 1 h. The pH of the solution fix to 7 by adding Na₂CO₃ (0.2 mole) and NaOH (2 Mole). The obtained solids, after filtering and washing in deionized water, were dried for 24 h at 80 ºC. In order to prepare the Mg/Fe-LDH in optimum AC dosage and molar ratio (AC-Mg/Fe), the Pb²⁺ and Cu²⁺ adsorption capacity was compared in different conditions of preparation.

3. Results and discussions

3.1 Study the effect of Mg/Fe molar ratio and amount of AC on the preparation AC-Mg/Fe
For selecting the optimum molar ratio of Mg/Fe for preparation AC-Mg/Fe, different molar ratio of Mg/Fe ranging from 1/1 to 4/1 were used (table 1).

Table 1. Removal efficiency for Cu²⁺ and Pb²⁺ at different molar ratio of Fe and Mg at (dosage= 0.04 g/50 ml, pH = 5, adsorption time = 3 hr and contaminant concentration= 10 mg/l)

| Fe | Mg | For Cu²⁺ %  | For Pb²⁺ %  |
|----|----|-------------|-------------|
| 1  | 1  | 70.3        | 54.3        |
| 1  | 2  | 77.33       | 70.3        |
| 1  | 3  | 99.69       | 89.3        |
| 1  | 4  | 60.98       | 50.3        |

As shown in table 1, at molar ratio of Mg/Fe equal three, the removal efficiency for Cu²⁺ and Pb²⁺ on AC was 99.69, 89.3 respectively and they considered the highest value. So the optimum value (Mg/Fe = 3) selected for synthesize coated adsorbent to gain higher adsorption capacities.

Also, for selecting the optimum dosage of AC, different dosages range from 0.05 to 0.5 g were used at 3 Mg/Fe molar ratio (table 2).

Table 2. Removal efficiency for Cu²⁺ and Pb²⁺ at different dosage of activated carbon at (dosage= 0.04 g/50 ml, pH = 5, adsorption time = 3 hr and contaminant concentration= 10 mg/l)

| Dosage | For Cu²⁺ % | For Pb²⁺ % |
|--------|------------|------------|
| 0.05   | 30.02      | 20.2       |
| 0.1    | 46.34      | 36.3       |
| 0.3    | 69.97      | 59.97      |
| 0.5    | 89.69      | 91.66      |
| 1      | 59.09      | 49.09      |
| 2      | 50.43      | 30.4       |
The removal efficiency of Lead and Copper by AC was increased when the dosage of AC increase within the range (0.05 to 0.5) g at 3 Mg/Fe molar ratio as shown in table 2. Therefore, for coating was selected the optimum AC dosage 0.5 g.

3.2 Characterization of the material

3.2.1 Scanning electron microscope (SEM). The AC had structure and high surface area that made it able to be coated by other coating materials such as MgFe-LDH as shown in a SEM analysis. After modification, the MgFe-LDH with size ranging from 83.64 to 24.28 were coated the AC surface. The structure of AC-Mg/Fe is typical lamellar and the particles of it are regular and good defined (Figure 1).

3.2.2 Energy Dispersive Spectroscopy (EDS). High content of the Fe, Mg, O, and C was shown by EDS spectrum of the AC-Mg/Fe. Therefore from this content increase after modification, it was proved that the MgFe-LDH successfully loading on the AC synthesis by co-precipitation method (Figure 1).

3.2.3 X-Ray Diffraction Analysis (XRD). As can be seen only diffraction peaks (2θ=15° and 23°) for the carbon and (2θ=24°, 26.5°, 42.1°, 45°, 51°, 78° and 84°) for the graphite were observed in the AC. For the AC-Mg/Fe, diffraction peaks (2θ=11°, 21.5°, and 29°) refer to layered double hydroxides (Figure 2). The average crystallite size was 96.7 nm calculated by using Debye Sphere's equation.

3.2.4 Specific surface area of materials by Brunauer–Emmett–Teller analysis (BET). After coating the specific surface area increase from 24.5 m²·g⁻¹ for AC to 79.6928 cm²·g⁻¹ for AC-Mg/Fe

![Figure 1. SEM images and EDS spectrum for the (a) AC, (b) AC-Mg/Fe.](image-url)
Figure 2. XRD patterns for AC and AC-Mg/Fe; (●) C; (●), graphite; and (●) Mg/Fe-LDH.

4. Conclusion

Mg/Fe layered double hydroxide coated low cost activated carbon (AC-Mg/Fe) was synthesized by a co-precipitation method. The XRD and SEM displayed that the particles on the surface of low cost activated carbon are regular and good-defined, and the structure of LDHs is typical lamellar. From EDS analysis, it was proved that the MgFe-LDH successfully loading by co-precipitation method on the AC derived from date palm agriculture waste.

5. Reference

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