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Removal of Metronidazole from Aqueous Medium by Adsorption on Co-Zr LDH †

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Abstract: Metronidazole is an antimicrobial, antibacterial and antiprotozoal drug that is applied to treat many infections. However, it has been considered as a pollutant in water bodies. In this study, Co-Zr layered double hydrodxide (LDH) was synthesized using cobalt and zirconium metal salts by mechanochemical method. Layered double hydroxides are generally described as $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}{\cdot}mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively. Here, we used divalent and tetravalent metal cations and A is an n-valent interlayer guest anion. The LDH was characterized by XRD, FE-SEM and IR methods, and then was used to adsorb metronidazole in aqueous solution. We have optimized the pH to obtain the maximum adsorption capacity which was determined by UV-VIS spectroscopy. The results showed that this adsorbent had better performance than previous studies.

Keywords: Co-Zr LDH; metronidazole; adsorption; mechanochemical

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1. Introduction

In the world wide, due to human, industrial and agricultural activities, large amounts of toxic organic and inorganic pollutants have entered the wastewater and aquatic ecosystem [1]. These pollutants include pharmaceuticals products, cosmetics and products of domestic in aqueous solutions [2]. Amongst pharmaceutical products including antibiotics, anti-inflammatory drugs, painkillers, antidepressants, antihistamines, anti-cancer drugs, etc [1], antibiotics are a group of chemical compounds used to treat and prevent infections of microorganisms and growth of other bacteria [3]. These compounds are toxic to aqueous solutions due to the presence of benzene rings in their structure or new compounds and are usually not completely eliminated by conventional purification processes. Meanwhile, they become more toxic and turn unknown due to reactions with chemicals used to refine water [4].

Metronidazole is an antibiotic used to treat anaerobic bacteria and protozoan bacteria and as a food additive. It has been detected frequently in drinking water, meat industry effluents and wastewater treatment plants. Due to its high solubility in water and low biodegradability, this substance shows severe toxic effects [1].

Various methods such as oxidation, electrical decomposition, ozonation, biodegradation and photocatalytic decomposition have been used for wastewater treatment, but adsorption is the most appropriate method due to its inhibitory toxic properties and limited transfer to aqueous systems [5]. In addition, gamma radiation was used for the decomposition and mineralization of metronidazole, for which according to the results, the toxicity of by-products was higher [3].

Adsorption is a water treatment process that is used to remove a broad range of organic and inorganic pollutants, and is widely used both in the laboratory and on the field. The application of this process in urban water treatment is well established [6].

Layered double hydroxides of two-dimensional anionic clays consist of brucite-like layers and exchangeable charge balancing interlayer anions with structural formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}.mH_2O$ [7], where M (II) and M (III) are divalent and trivalent cations, respectively, A is the interlayer anion of charge n, and x represents the molar fraction of trivalent cations [8]. Water molecules are also present to stabilize the structure in interlayer spaces [9].

Various anions can be placed interlayer domain, but due to the easy replacement of monovalent anions, they prefer any organic or inorganic anions [8].

Features such as large surface area, high anion exchange capacity and flexibility in the interlayer spaces of LDH make these materials suitable for effective uptakes of anionic contaminants through adsorption [6]. LDHs can adsorb anions in aqueous solution in three ways including direct absorption, anion exchange and hydration of calcined LDH [9].

In this study, we applied Co-Zr LDH, synthesized by a new green method, to adsorb metronidazole from aqueous solution at different pHs.

2. Experimental

2.1. Materials

Metal salts and NaOH were purchased from Merck. The chemical properties of Metronidazole are shown in Table 1. Deionized water was used in all stages of the work.

Table 1. Chemical properties of Metronidazole [10].

Property	Values
CAS ID	443-48-1
IUPAC Name	2-(2-methyl-5-nitroimidazol-1-yl) ethanol
Chemical Formula	$C_6H_9N_3O_3$
Molar mass	171.15 g/mol
Specific gravity	1.5
Solubility in water (at 25°C)	11 g/l
pKa	2.57, 15.42
$Log K_{ow}$	−0.02
Melting point	158 – 160°C
Boiling point	405.4°C

2.2. Synthesis of Co-Zr LDH

Co-Zr LDH was synthesized by a mechanochemical method. Briefly, zirconium and cobalt salts ($ZrCl_4$, $Co(NO_3)_2{\cdot}6H_2O$) were added to an agate mortar. Then, 2.5 mol NaOH was slowly added to the mortar and the mixture was ground for 50 min. The color was changed from light pink to brown. The resulting brown precipitate, was washed with deionized water and dried in a vacuum oven.

3. Results and Discussion

3.1. FT-IR Spectroscopy

The FT-IR technique has been used to identify the nature and symmetry of interlayer anions. The peaks of 1383 cm^{-1} and 845 cm^{-1} were related to the tensile and flexural vibrations of interlayer nitrate anions. The peaks at 593 cm^{-1} and 490 cm^{-1} confirmed the existence of M-O-M bonds. The peak at 1638 cm^{-1} was related to the flexural vibration of water. The presence of tensile OH of water was detected at 2924 cm^{-1}, as shown in Figure 1a. Figure 1b shows the IR spectrum after LDH uptake in which metronidazole was loaded at pH 8.

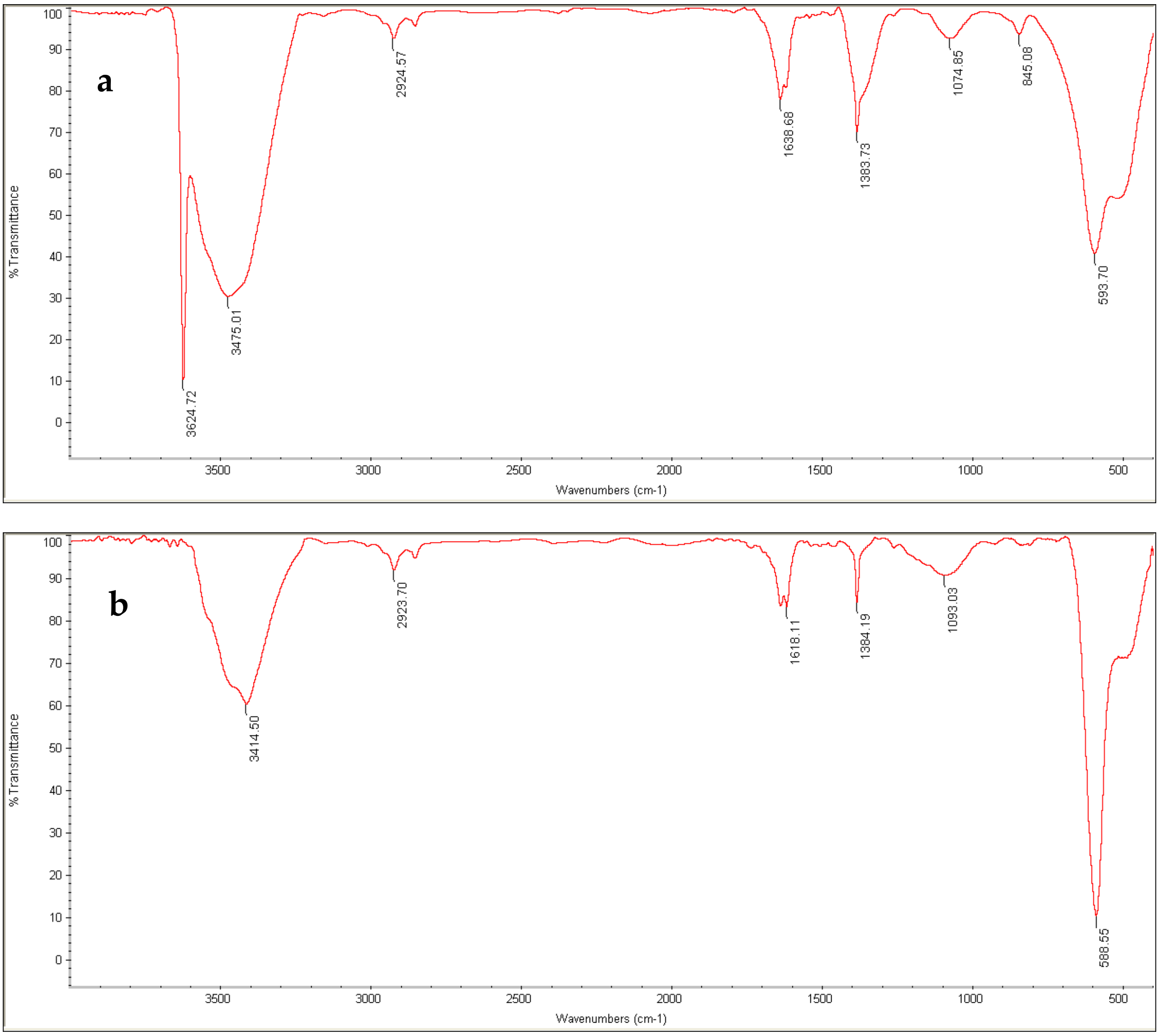

Figure 1. IR spectra of the (**a**) Co-Zr LDH, (**b**) Co-Zr LDH loaded with metronidazole.

3.2. Powder X-Ray Diffraction

X-ray powder diffraction for Co-Zr LDH was taken by the BRUKER device and the results were acceptable, according to the literature [11]. X-ray powder diffraction showed Co -Zr LDH plates (003), (006), (012), (015), (018), (110) and (113) in 2θ 11.72, 23.559, 34.653, 39.273, 46.824, 60.229, 61.619, respectively (Figure 2).

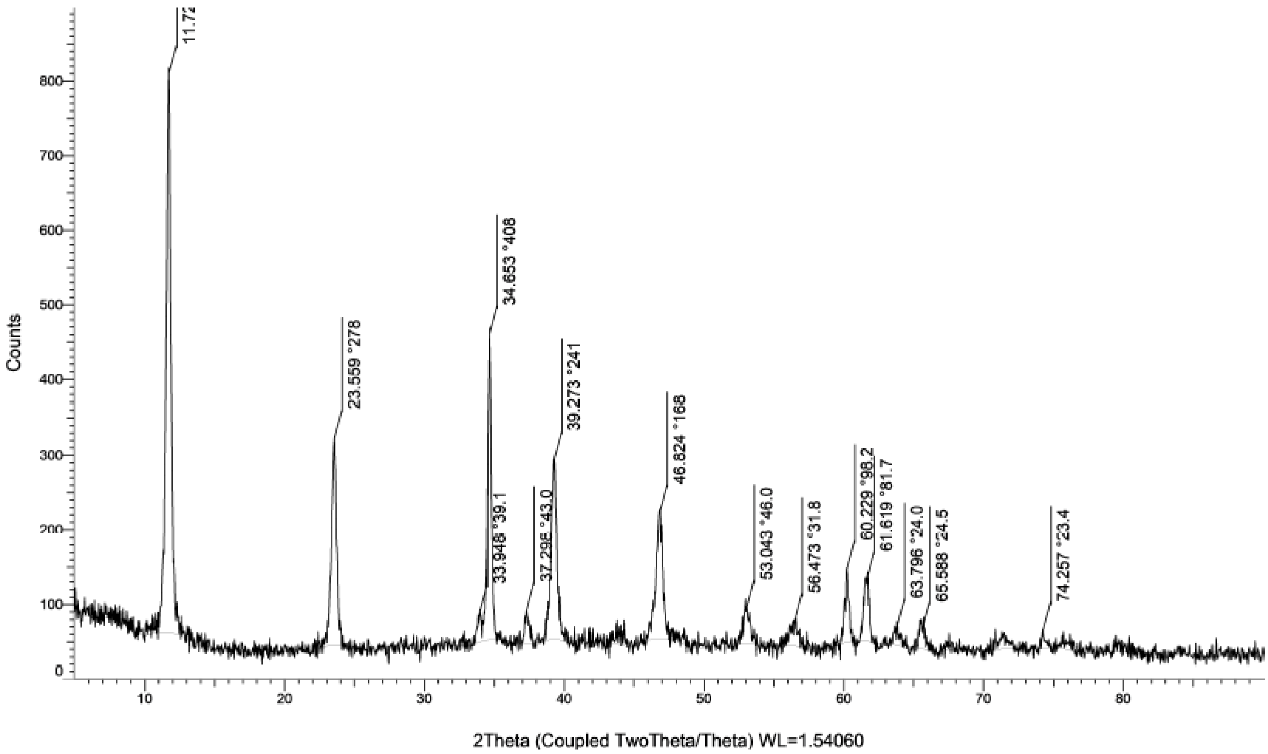

Figure 2. PXRD pattern of the Co-Zr LDH.

3.3. Scanning Electron Microscopy (SEM)

SEM imaging was taken using a ZEISS device. According to the images of the SEM, the well-formed plates and interlayer spaces was evident (Figure 3).

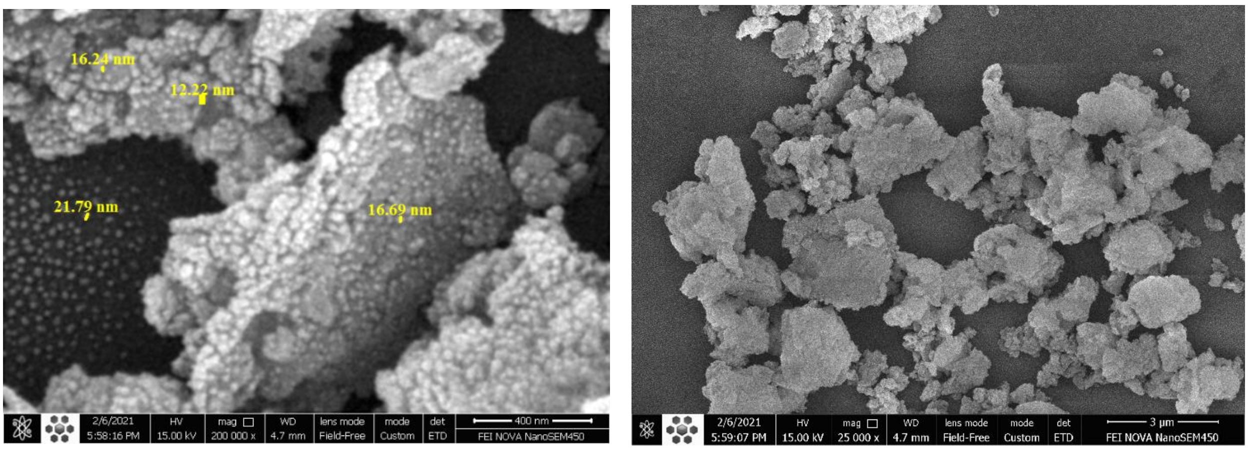

Figure 3. SEM images of Co-Zr LDH.

3.4. Effect of pH on the Adsorption Capacity

By changing the solution pH, the surface charge of the medium and the equilibrium ionization of the solute can be affected. The effect of pH on adsorption capacity was determined using UV spectroscopy. A 150 ppm solution of metronidazole was prepared at pH 4, 6, 8 and 10 (Figure 4). Using Equation (1), the adsorption capacity at different pHs was calculated.

$$q_e = V/m(C_o - C_e) \quad (1)$$

where C_o and C_e are the initial and equilibrium concentrations of Metronidazole (mg/L), respectively, V is the volume of solution (L), and m is the mass of adsorbent (g).

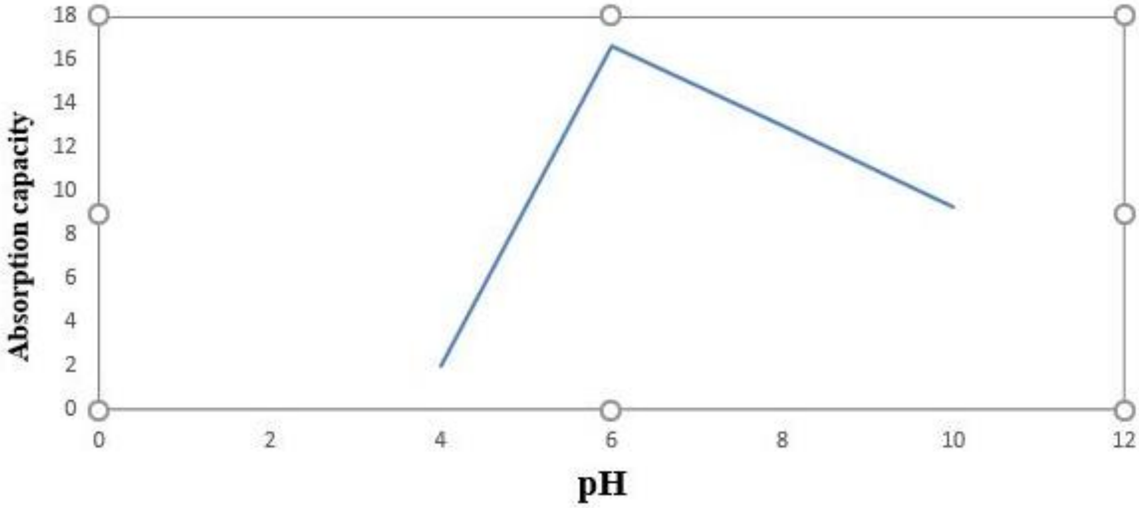

Figure 4. Adsorption capacity diagram at different pH.

4. Conclusions

In this study, Co-Zr LDH was synthesized by a mechanochemical green method. In this path, a solvent free method was taken to prepare a novel kind of LDH using cobalt and zirconium salts in the vicinity of soda at a mortar. The title LDH was used as an adsorbent to absorb metronidazole. According to the results, it was able to successfully absorb metronidazole at pH 6.

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