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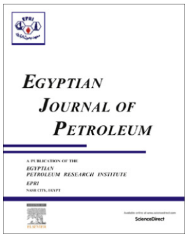

FULL LENGTH ARTICLE

Mn(II) removal from aqueous solutions by Co/Mo layered double hydroxide: Kinetics and thermodynamics

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Abstract This paper deals with the experimental investigation related to the Mn(II) removal from aqueous solutions by the adsorption onto a synthesized Co/Mo layered double hydroxide (Co/Mo-LDH). The adsorption behavior was studied as a function of initial Mn(II) concentration (40–145 mg/L), contact time (15–90 min), solution pH (2–9) and adsorbent mass (0.05–0.35 g per 1.0 L). All adsorption processes were rapidly carried out at different temperatures (298, 308 and 318 K) and constant stirring rate 160 rpm. The results showed that the Co/Mo-LDH is a very promising material for removing of Mn(II) from the aqueous solutions. Particularly, the solution pH range of 4–7 has the most significant effect on the adsorption capacity. The results revealed that the maximum adsorption capacities were 20.2, 26.75 and 38.1 mg/g from the initial Mn(II) concentration (145 mg/L) at pH 5, adsorbent mass (0.2 g/1.0 L), and contact time (60 min) at different temperatures, 298, 308 and 318 K, respectively. The adsorption kinetics data are well fitted by the pseudo-second-order model, while the adsorption isotherms data were better fitted by the Langmuir equation. Also, this paper discusses the thermodynamic parameters of the adsorption and the results demonstrate that the adsorption process is spontaneous and endothermic.

1. Introduction

Manganese can be found in natural waters in its most reduced and soluble form, the Mn(II) ion and in the oxidized form MnO_2 (pyrolusite), respectively. If not oxidized, Mn(II) ions can easily escape through water treatment processes and can gradually be oxidized to insoluble manganic dioxide MnO_2 in the distribution system causing several problems such as water discoloration, metallic taste, odor, turbidity, biofouling and corrosion, staining of laundry and plumbing fixture [1].

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Abbreviations

q_t	amount of adsorption capacity q_t (mg/g)	n	heterogeneity factor related to sorption intensity
q_e	equilibrium adsorption capacity, mg/g	k_1	pseudo-first-order rate constant for the adsorption process
C_0	initial concentration, mg/l	k_2	pseudo-second-order rate constant for the adsorption process
C_t	concentration after time t, mg/l	$\Delta G°$	Gibbs free energy for the adsorption process, kJ mol^{-1}
m	mass of the adsorbent, g	$\Delta H°$	enthalpy change for the adsorption process, kJ mol^{-1}
v	volume of solution, L	$\Delta S°$	entropy change for the adsorption process, kJ mol^{-1} K^{-1}
C_e	equilibrium adsorption concentration, mg/l	R	ideal gas constant, kJ mol^{-1} K^{-1}
K_L	Langmuir constant related to the sorption capacity, L/mg	T	temperature, K
b	Langmuir constant related to the energy of adsorption, mg/g		
K_F	Freundlich constant related to sorption capacity, L/mg		

For high intake manganese having adverse neurotoxic health effect, World Health Organization (WHO) recommends guideline value of 0.4 mg/L to protect against neurological damage [2]. European Union (EU) and the Environmental Protection Agency (EPA) have established the level of 0.05 mg/L for manganese [3,4]. So if concentrations are higher than these standards, then water must be treated before using it for drinking purposes. The excessive concentrations of Mn will result in metallic taste in water, staining of different products like clothes, paper and plastics [5]. Manganese can also cause build up in pipelines, water heaters and pressure tanks. The deposition of manganese in the distribution systems can cause reduction of pipe diameter and eventually clogging of pipe will take place [6].

Oxidation and precipitation is the most common method to remove Mn(II). Such method is based on the Mn(II) oxidation to its insoluble manganic dioxide, followed by clarification and/or filtration. Manganic dioxide is also found to adsorb the manganese ion which can be progressively oxidized with time [7]. Encouraging results for manganese removal have also been obtained by GAC adsorption [8] and biological processes [9,10], with removal up to 95%.

Nano-adsorbents are quite efficient for the fast adsorption of heavy-metal ions and organic molecules from aqueous solutions because of their high specific surface areas and the absence of internal diffusion resistance [11]. Layered double hydroxides (LDHs) are a class of nanostructured inter-layer anionic clays [12] and constitute a class of lamellar ionic compounds containing a positively charged layer and exchangeable anions in the interlayer [13].

While, the ordinary LDH is usually prepared from divalent and trivalent cations, the Co/Mo-LDH from bivalent and hexavalent cations was prepared as a new type of LDH [14]. This type of novel LDH nanoparticles was applied to the Fe(II) removal from aqueous solutions. Thereafter, the kinetics and thermodynamics of Fe(II) removal by Co/Mo-LDH were studied [15].

The objectives of the present study are synthesis of Co/Mo $(CO_3)^{2-}$-LDH nanoparticles, applying them for Mn(II) removal from aqueous solutions, determining the adsorption rate and capacity and thereafter, studying the kinetics and thermodynamics parameters of the adsorption processes.

2. Materials and methods

2.1. Materials

All chemicals with a purity of greater than 99.9% were purchased as follows: Manganese chloride ($MnCl_2 \cdot 4H_2O$) was purchased from Loba Chemie Co., anhydrous ($MoCl_5$), $CoCl_2 \cdot 6H_2O$, and ammonium carbonate $(NH_4)_2CO_3$ were purchased from Sigma–Aldrich (Germany) and NH_4OH (34%) was purchased from Merck Germany.

2.2. Preparation of Co/Mo-LDH

The method of Co/Mo$(CO_3)^{2-}$-LDH preparation was previously published [14]. In typical synthesis, a controlled co-precipitation method is applied based on increasing the rate of addition of NH_4OH and $(NH_4)_2CO_3$ into the Co and Mo cations at 60 °C. A solution A, 59 mmol of $MoCl_5$ and $CoCl_2.6H_2O$ with Co/Mo molar ratio of 0.25, was first prepared in 100 ml de-ionized water, while solution B was prepared from NH_4OH (10 mmol) and $(NH_4)_2CO_3$ (20 mmol) in 50 ml de-ionized water. Then solution B was gradually added into solution A successively till reaching a pH of about 9 with adjusted rate of addition to be through an aging time of 24 h at 60 °C under vigorous stirring. Finally, the formed puffy precipitate was filtered, washed with de-ionized water till the negative Cl ions are removed and dried at 60 °C overnight.

2.3. Characterization of Co/Mo-LDH

Here three main analytical techniques are presented for the prepared Co/Mo-LDH with respect to the Mn(II) adsorption process because the sample was previously proofed, tested and published as will be referenced in the preparation part. The XRD powder diffraction patterns have been performed with Bruker AXS-D8 Advance (Germany) using nickel filtered copper radiation (λ = 1.5405 A) at 60 kV and 25 mA with scanning speed of 8° in 20 min^{-1} over diffraction angle range. Fourier transfer infrared (FT-IR) spectra were recorded on ATI Mattson Genesis series (KBr disk method) apparatus, Model 960 M009 series. While the surface morphologies of