Stannum : Jurnal Sains dan Terapan Kimia, 6(2) (2024) 109-114

Stannum : Jurnal Sains dan Terapan Kimia

Website: https://journal.ubb.ac.id/index.php/stannum
doi: 10.33019/jstk.v6i2.5481
Research paper

Removal Co(II) Ions in Aqueous Solution using Fe-MCM-41

Penghilangan Ion Co(II) dalam Larutan Berair menggunakan Fe-MCM-41

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Received: July 25, 2024 Accepted: October 28, 2024 Published: October 31, 2024

ABSTRACT

The removal of Co(II) ions using Fe-MCM-41 adsorbent was studied. The removal of Co(II) ions using Fe-MCM-41 adsorbent was studied. Fe-MCM-41 was synthesized by using sonochemical method. Characterization by using XRD of the resulting material showed the peak 2θ about 2.27° as a characteristic of mesoporous material. Then Fe-MCM-41 was interacted with solutions containing Co(II) ions at various concentrations. The Langmuir equation indicated monolayer adsorption could be well-fitted for the adsorption isotherms. The maximum adsorption capacity of Co(II) ions on Fe-MCM-41 was 62.89 mg/g. Therefore, it could be conclude that the concentration of Co(II) ions in an aqueous solution can be reduced by using Fe-MCM-41 adsorbent.

Keywords: adsorption, Co(II), Fe-MCM-41, heavy metal

INTRODUCTION

Heavy metal water pollution is still an environmental issue that concerns many researchers worldwide. Heavy metals have high toxicity, are non-degradable, and bioaccumulate, making them harmful to organisms. Many industries, including battery manufacturing, pigments and paints, metallurgy and mining, and electronics, widely use cobalt as a heavy metal (Briffa et al., 2020; G. Wang et al., 2020; Q. Wang & Yang, 2016).

Cobalt, an essential trace element, is required in small amounts for biocatalysis, within the organism. Cobalt deficiency can affect vitamin B12 formation, reducing red blood cell production, and anemia. However, excessive cobalt intake causes serious problems such as asthma, allergies, heart damage, heart failure, and thyroid and liver damage (Briffa et al., 2020; Das et al., 2023; Shafaei et al., 2011). Therefore, the cobalt content must be reduced or eliminated before the effluent of industrial wastewater is released into the environment.

In aqueous solutions, cobalt is present in the form of Co(II). Many methods have been used for the removal of Co(II) from aqueous solutions, like membran separation, ion exchange, chemical precipitation, electrocoagulation, bioremediation, and adsorption (Kulkarni, 2016; Luo et al., 2018; Shafaei et al., 2011; G. Wang et al., 2020). Adsorption is a way to get rid of heavy metal

ions by using an adsorbent surface with lots of functional groups, well-developed pores, or a high specific surface area (Abbou et al., 2021; Briffa et al., 2020; Das et al., 2023; G. Wang et al., 2020). It is an efficient, operable, and economical method for removing Co(II) (Siddiqui et al., 2021).

Researchers have investigated the adsorption of Co(II) from aqueous solutions using porous materials as adsorbent (Hernández-Ramírez et al., 2007; Siddiqui et al., 2021; Yang et al., 2022). Among the porous adsorbents, mesoporous has interested researchers to study its use as adsorbent for heavy metals (Bernabé et al., 2019; Salmani et al., 2020; Siddiqui et al., 2021). Silica-based mesoporous are one of the most widely used adsorbents in recent years (Cashin et al., 2018; Salmani et al., 2020).

MCM-41 is one of mesoporous silica-based with great thermal stability, having honeycomb-like pores with a diameter of about 15-100 Å and a specific surface area of ~1,000 m^2/g. (Alardhi et al., 2020; Albayati, 2019). MCM-41 application as an adsorbent is limited to the adsorption of gases and organic compounds (Cheng et al., 2020; Santos et al., 2019; Shen et al., 2021; Zhao et al., 2022). Among them is by inserting trivalent elements, such as Al or Fe, into the silicate framework, leading the originally neutral MCM-41 framework to become negatively charged due to the presence of Brønsted acid sites (Bedoya et al., 2022; Hung et al., 2024).

Some authors reported successfully inserting Al(III) into the MCM-41 silicate matrix hydrothermally (Bedoya et al., 2022; Hung et al., 2024; Vu et al., 2020). Al-MCM-41 products were found to be good for adsorption of metal ions, including Pb(II), Cu(II), and Cd(II). Parida and Dash (2010) and Ngcobo and coworkers (2023) also reported the successful hydrothermal insertion of Fe(III) into the MCM-41 framework and the Fe-MCM-41 product has the ability to adsorb Cu(II) metal ions.

Therefore, in this works is necessary to modify MCM-41 to improve its performance, in this study, MCM-41 was modified to Fe-MCM-41 by using sonochemical method, which was used to remove Co(II) ions in aqueous solutions.

MATERIALS AND METHODS

Materials and Tools

This study used materials manufactured by Merck including sodium silicate solution (SSc), cethyltrimethylammonium bromide (CTAB), iron(III) nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$), ethyl acetate (EAc), and cobalt(II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$). Distilled water was purchased from CV. General Labora (Yogyakarta, Indonesia).

The tools used were laboratory standard glassware and porcelain, vacuum pump, digital oven (Fischer Scientific 655K), analytical balance (AND G20), hotplate stirrer (IKA C-MAG HS7), ultrasonic bath (Bransonic 220, 48 kHz), and furnace (FB 131OM-33).

Fe-MCM-41 synthesis

Fe-MCM-41 synthesis modified the procedure of Syamsuri et al. (2017). The materials with a molar ratio of 0.33 CTAB: 0.1 Si: 0.011 Fe: 1.86 EAc: 450 H_2O were mixed. The mixture was stirred until a white slurry was formed and sonicated for 90 minutes. The precipitate was filtered, washed to neutral, and dried at 110°C for 6 hours. Finally, it was calcined at 550°C for 6 hours. Fe-MCM-41 was characterized by XDR (Shimadzu 6000) and FTIR (Shimadzu Prestige 21).

Adsorpsi study of Co(II)

A fixed amount of 200 mesh Fe-MCM-41 (0,01 g) was placed into 10 ml of Co(II) solutions of different concentrations in a vial bottle. The mixture was stirred for 15 minutes and filtered. The Co(II) concentration in the filtrate was analyzed by AAS (Perkin-Elmer 3110).

The amount of adsorbed Co(II) ions per unit adsorbent mass at time q_t (mg/g) was calculated by the following equation:

$$Q_t = \frac{(C_o - C_t)V}{m}$$

Co(II) removal efficiency (R%) was calculate by the following equation:

$$R\% = \frac{Q_t}{C_o} x100\%$$

where C_o is the Co(II) ions initial concentration (mg/L), C_t is the Co(II) ions concentration left in aqueous solutions at time (mg/L), V is the volume of the aqueous phase (l), and m is the bentonite amount (g).

RESULTS AND DISCUSSIONS

Characterization of Fe-MCM-41

The X-ray diffractogram in Fig. 1 shows a 2θ shift of the 100 plane to a smaller value, from about 2.39° to 2.27°. This is followed by a decrease in peak intensity in the [100] plane. The increase in d-spacing value occurs due to the isomorphic substitution of Si-O bonds by longer Fe-O bonds. The decrease in intensity is due to the irregular arrangement of atoms in the Si-O-Fe bond and the lack of uniformity of the MCM-41 mesoporous structure caused by the entry of trivalent elements into the MCM-41 framework.

The diffractogram pattern in Fig. 1 is similar to Adjdir et al. (2009) dan Boudinar et al. (2024). The direct synthesis of Al(III) resulted in a decrease in the intensity of the main peak of MCM-41 as well as a 2θ shift to a smaller value. The reduction in the intensity of the main peak is due to the isomorphic substitution of the Si-O bond (1.61 Å) by the longer Al-O bond (1.69 Å). This was also reported by Parida & Dash (2010) and Hu et al. (2024) successfully synthesized Fe-MCM-41.

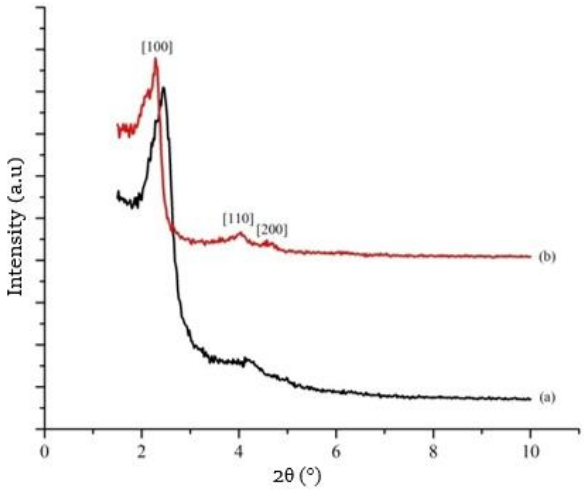

Figure 1. X-ray diffractograms of: (a) MCM-41 and (b) Fe-MCM-41

In Fig. 2, the absorption band at 1427 cm-1 is observed which indicates the presence of Fe(III) species in tetracoordinate form. This corresponds to the study of Bordiga et al. (1996) and Suyanta et al. (2023) that Fe(III) tetracoordinate absorption in the silicate framework is observed in the 1430-1380 cm^{-1} region. The figure also shows the shifting of typical MCM-41 absorption bands at 1087 cm^{-1} and 794 cm^{-1} to the smaller wave numbers, 1056 cm^{-1} and 786 cm^{-1}. This shift is due to the isomorphic substitution of the Si-O bond by the longer Fe-O bond. Based on this, it could be said that Fe(III) is incorporated into the MCM-41 framework.

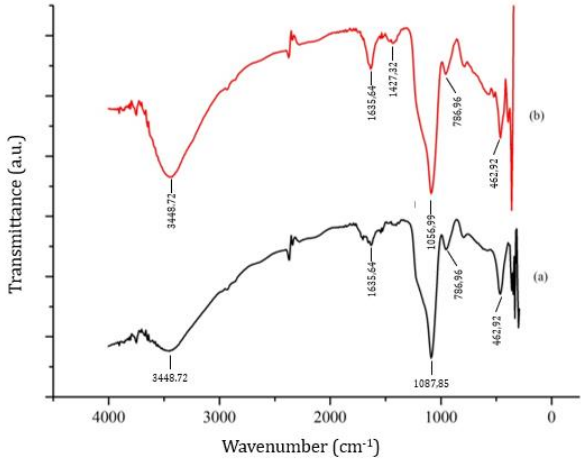

Figure 2. FTIR spectra of : (a) MCM-41 and (b) Fe-MCM-41

The performance of Fe-MCM-41 in adsorbing Co(II) ions

The performance of Fe-MCM-41 in adsorbing Co(II) ions was investigated by metal concentration. The metal concentration variations in this study were 100, 150, 200, 250, and 300 ppm. After each mixture was stirred for 15 minutes and filtered. The Co(II) concentration in the filtrate was analyzed. The results obtained from the experimental studies are shown in Fig. 3. It can be seen that the equilibrium adsorption capacity of the Fe-MCM-41, q_e increases with an increased initial concentration of Co(II) ions.

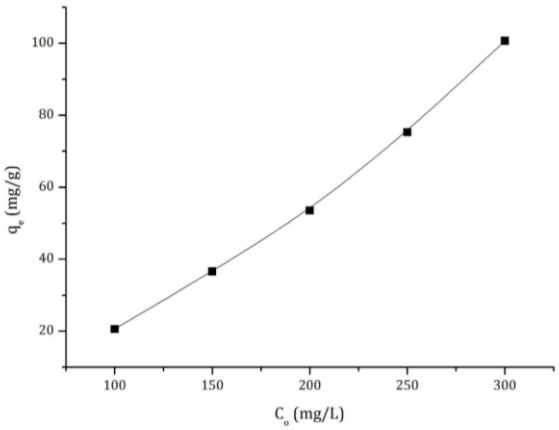

Figure 3. The dependence of the equilibrium adsorption capacity on the initial concentration of Co(II) ions

Adsorption isotherm studies were done to determine the maximum adsorption capacity of Fe-MCM-41 in adsorbing Co(II) ions. Both the Langmuir and Freundlich adsorption isotherms are widely used adsorption models. The calculated results and correlation coefficients (R^2) are listed in Table 1.

Table 1. Langmuir and Freundlich isotherms Parameters

Isotherm	Parameters	Value
Langmuir	R^2	0.997
	q_m (mg/g)	62.89
	b	3140
Freundlich	R^2	0.995
	K_f	80.97
	$1/n$	0.59

From the correlation coefficients (R^2) in Table 1, the adsorption of Co(II) metal ions on Fe-MCM-41 follows the Langmuir adsorption isotherm model. Therefore, the adsorption of Co(II) metal ions on Fe-MCM-41 is monolayer adsorption, where the active sites on the adsorbent surface have the same ability to interact with the adsorbate. Comparison of adsorption capacity of various adsorbents were illustrated in Table 2.

Table 2. Adsorption capacity of Co(II) metal ion on various adsorbents

Adsorbent	Adsorption capacity (mg/g)	Ref
MCM-41	0	(Lam et al., 2006)
SA-MCM-41	4,12	(Mathew, 2018)
RH-MCM-41	67,93	(Hatem et al., 2024)
Fe-MCM-41	62,89	This work

CONCLUSIONS

The concentration of Co(II) ions in an aqueous solution can be reduced by using Fe-MCM-41 adsorbent. The Langmuir and Freundlich models were used to fit the adsorption isotherm. The Langmuir equation indicated monolayer adsorption could be well-fitted for the adsorption isotherms. The maximum adsorption capacity of Co(II) ions on Fe-MCM-41 was 62.89 mg/g.

ACKNOWLEDGEMENTS

The authors would like to thank Universitas Islam Negeri Raden Fatah Palembang for providing the BOPTN Research Fund 2024 year for the Capacity Development Cluster.

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