

Removal of Hexacyanoferrate(II) Using Zn-Al-OAc Hydrotalcite as an Anion Exchanger

Roto Roto*, Fitriana Nindiyasari and Iqmal Tahir

Department of Chemistry,
Faculty of Mathematics and Natural Sciences,
Gadjah Mada University, Sekip Utara, Yogyakarta 55281, Indonesia

*Corresponding author: roto05@ugm.ac.id

Abstract: Cyanide is a highly toxic anion and ingestion exposure can be fatal. Cyanide can be removed from water systems using Zn-Al-OAc hydrotalcite (OAc⁻=acetate) as an ion exchanger. A synthesis of Zn-Al-OAc hydrotalcite has been performed and it was used as an anion exchanger to reduce the concentration of cyanide in the form of $[Fe(CN)_6]^{4-}$. Zn-Al-OAc hydrotalcite was prepared using a stoichiometric method followed by hydrothermal treatment. The chemical composition of Zn-Al-OAc hydrotalcite was found to be $Zn_{0.73}Al_{0.27}(OH)_2(OAc)_{0.27} \cdot 0.95H_2O$. The anion exchange reaction of OAc⁻ by $[Fe(CN)_6]^{4-}$ was fit to yield a second order reaction rate constant of $k = 0.215 M^{-1}s^{-1}$ with $R^2=0.996$. The anion exchange capacity (AEC) was found to be 219 meq $[Fe(CN)_6]^{4-}/100$ g hydrotalcite. It was found that Zn-Al-Fe(CN)₆ hydrotalcite could not be regenerated by OAc⁻.

Keywords: hydrotalcite, acetate, anion exchange capacity, hexacyanoferrate(II), regeneration

Abstrak: Sianida merupakan anion yang sangat toksik, dan jika tertelan boleh membawa maut. Sianida boleh dikeluarkan dari sistem air menggunakan Zn-Al-OAc hidrotalsit (OAc⁻=asetat) sebagai penukar ion. Sintesis terhadap Zn-Al-OAc hidrotalsit telah dijalankan dan telah digunakan sebagai penukar anion untuk mengurangkan penumpuan sianida dalam bentuk $[Fe(CN)_6]^{4-}$. Zn-Al-OAc hidrotalsit telah disediakan menggunakan kaedah stoichiometric diikuti dengan rawatan hidrotermal. Komposisi kimia Zn-Al-OAc hidrotalsit telah ditemukan menjadi $Zn_{0.73}Al_{0.27}(OH)_2(OAc)_{0.27} \cdot 0.95H_2O$. Tindakbalas penukaran anion daripada OAc⁻ dengan $[Fe(CN)_6]^{4-}$ telah menghasilkan kadar tetap laju reaksi tahap kedua, $k = 0.215 M^{-1}s^{-1}$ dengan $R^2=0.996$. Kapasiti penukaran anion (AEC) telah ditemukan menjadi 219 meq $[Fe(CN)_6]^{4-}/100$ g hidrotalsit. Zn-Al-Fe(CN)₆ hidrotalsit telah ditemukan bahawa ia tidak boleh digunakan semula oleh OAc⁻.

Kata kunci: hidrotalsit, asetrat, kapasiti penukaran anion, heksasianoferrat (II), penjanaan semula.

1. INTRODUCTION

Cyanide is widely used in industry, especially for cleaning metals and electroplating. It is one of the main effluent pollutants produced by gas works and coke ovens. It is also used in certain mineral-processing operations. Silver and gold mining operations, chemical processing facilities, steel and iron industries, metallurgical industries, metal plating and finishing facilities and petroleum refineries are the largest sources for cyanide release into the water or air. The maximum legal limit of cyanide in fresh water is 0.08 mg/L.¹

Cyanide has high acute (short-term) toxicity to aquatic life, birds, and animals. Cyanide also has high chronic (long-term) toxicity to aquatic life, but it is not expected to bio-accumulate. Cyanide compounds may exist in the atmosphere as gases or small particles, where they are dispersed by air currents and may settle into the soil or water. Most cyanide compounds are water-soluble and can contaminate ground water. Both natural and human processes are responsible for cyanide in the environment. In the air, it is mainly found as gaseous hydrogen cyanide, although a small amount is present in fine dust particles. Most of the cyanide dissolved in surface water will form hydrogen cyanide and evaporate. It takes years for cyanide to break down from the air.

Removal of CN^- by adsorption is commonly performed using adsorbents such as active carbon, impregnated carbon and bentonite-loaded fabric strips.² However, activated carbon is expensive and impractical to prepare. Cyanide is also slowly degraded to carbon dioxide and nitrous oxide by hydrogen peroxide.³ Treatment of a 100 mg/L solution of cyanide with 3000 mg/L of hydrogen peroxide will only degrade 80% after 4 h and 90% after 24 h. In the presence of UV irradiation from a 25-W mercury lamp and 1200 mg/L of hydrogen peroxide, complete degradation of a 100 mg/L solution was observed in 40 min.³

Hydrotalcite-like compounds, also known as layered double hydroxides (LDH), or anionic clays, are a class of lamellar compounds that consist of positively charged brucite-like host layers that are charge balanced by hydrated, exchangeable anions in the interlayer regions. The brucite-like layers are charged due to isomorphous substitution of divalent metal ions with trivalent ones. The chemical compositions of LDHs are expressed by the general formula $[\text{M(II)}_1-x\text{M(III)}_x(\text{OH})_2][\text{A}^{n-}{}_{x/n}\cdot m\text{H}_2\text{O}]$, where M(II) and M(III) represent divalent and trivalent metal ions within the brucite-like layers, and A^{n-} is an interlayer anion.^{4,5} Such A^{n-} anions may be polymers, organic dyes, surfactants or organic acids including anionic pesticides.^{6,7} The ratio x , which is defined as $\text{M(III)}/\text{M(II)}+\text{M(III)}$, ranges from 0.20 to 0.33. The best known of these materials is hydrotalcite, $\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$, whose structure is derived from brucite, $\text{Mg}(\text{OH})_2$ and is similar to cadmium iodide in structure. It consists of

hexagonally close-packed layers of anions with 100% of the octahedral sites occupied by magnesium cations in every two hydroxyl layers. This is termed a layered structure, as it is composed of repeating OH-Mg-OH--OH-Mg-OH--OH-Mg-OH units, where the OH--OH interaction is mainly of the Van der Waals type. If cations with a higher charge but similar radius are isomorphically substituted for Mg^{2+} , the brucite-like layers become positively charged. This charge excess is balanced by anions in the non-metallic layers, along with water molecules. In the case of natural hydrotalcite, two of every eight Mg^{2+} cations are substituted by trivalent ions (e.g. Al^{3+} , Fe^{3+}).⁸

Hydrotalcite-like compounds are widely investigated for their potential applications in research and industrial processes as catalysts, catalyst precursors, anion exchangers, medicines, nanometer-sized composite materials, and electrode modifying materials. The utility of these compounds, including the acetate-containing ones, is due to their inorganic and organic anion exchange capabilities.⁹⁻²⁰ Of special note are the layered organic/inorganic hybrid materials, which can easily be synthesized by an ion-exchange reaction that substitutes interlayer ions with organic guest anions.²¹

Hydrotalcite-like compounds undergo ion-exchange reactions with unhydrated anions. The ion-exchange equilibrium constants for hydrotalcite appear in the order $OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-$ for monovalent anions, and $CO_3^{2-} > C_{10}H_4N_2O_8S^{2-} > SO_4^{2-}$ for divalent anions²². For oxoanions, the order is $HPO_4^{2-} > HAsO_4^{2-} > CrO_4^{2-} > SO_4^{2-} > MoO_4^{2-}$. Hydrotalcites can be used as anion exchangers. By utilising their characteristic ion selectivities, hydrotalcites are expected to find applications in the removal of anion pollutants from liquids, which are difficult to handle and process because of the difficulty in precipitation. Treatment with an anion exchanger is a common process, yet it is usually more expensive.

High anion exchange capacity and the ability to be regenerated are important factors governing the utility of hydrotalcite as an anion exchanger. In our previous publications, we have reported that Zn-Al- NO_3 hydrotalcite can be used in the removal of hexacyanoferrate(II) as well as dichromate.^{23,24} Likewise, Zn-Al- SO_4 hydrotalcite is also a good anion exchanger for absorption of aqueous hexacyanoferrate(II).²⁵ In this study, we report on the use of Zn-Al-OAc hydrotalcite as ion exchanger to remove $[Fe(CN)_6]^{4-}$ from solutions. Zn-Al-OAc hydrotalcite is easy to prepare and is not toxic. Hexacyanoferrate(II), a common cyanide complex in water, is expected to exchange the acetate ion in the interlayer space of Zn-Al-OAc hydrotalcite. This study focuses on characterising the anion exchange capacity, kinetics, and regeneration of this reaction.

2. EXPERIMENTAL

2.1 Synthesis and Characterisation of Hydrotalcite Zn-Al-NO₃

A 100 mL solution of 0.30 M Zn(NO₃)₂ and a 100 mL solution of 0.10 M Al(NO₃)₃ were prepared. Next, the aqueous solution was titrated with a 100 mL of 0.50 M NaOH under vigorous stirring. The mixture was purged with nitrogen gas to reduce the incorporation of carbonate and the pH of the solution was maintained at 8 using NaOH. After 2 h of stirring, hydrothermal treatment at 100°C was performed. The product was centrifuged, filtrated and washed. The product was then dried at 100°C for 24 h, and crushed. This product is hereto referred as Zn-Al-NO₃ hydrotalcite.²⁶

Powder X-ray diffraction (PXRD) patterns of the samples were acquired with a Shimadzu Diffractometer XRD-6000. Fourier transform Infrared Spectroscopy (FTIR) spectra were recorded using a Shimadzu FT-IR-820 IPC. The Zn/Al ratio and AEC was determined using a Perkin Elmer 3110 AAS.

2.2 Synthesis and Characterisation of Hydrotalcite Zn-Al-OAc

A 4.80 g portion of NaOAc was suspended in 50 mL of deionised water under a nitrogen atmosphere for 30 min. Zn-Al-NO₃ hydrotalcite was then introduced to the NaOAc solution, under nitrogen atmosphere, for 2 h. After 2 h of stirring, the solution was subjected to hydrothermal treatment at 90°C. The product was centrifuged, filtrated and washed. The product was then dried at 80°C for 20 h and crushed. This product is hereto referred as Zn-Al-OAc hydrotalcite.

2.3 Intercalation of [Fe(CN)₆]⁴⁻ in Zn-Al-OAc Hydrotalcite

A 0.10 g portion of the Zn-Al-OAc hydrotalcite was suspended in 10 mL of deionised water under nitrogen atmosphere for 30 min. 0.0233 g of K₄[Fe(CN)₆] was suspended in 10 mL of deionised water and added to the Zn-Al-OAc hydrotalcite slurry, under nitrogen atmosphere for 2 h, where the molar ratio of OAc⁻ to [Fe(CN)₆]⁴⁻ was adjusted to 1:4. The mixture was allowed to sit for 24 h at 100°C. The solid was then centrifuged, filtered, washed, and dried at 75°C for 20 h. The ion exchanged product was assumed to be Zn-Al-Fe(CN)₆ hydrotalcite and was characterised using XRD and FTIR.

After ion exchange, the concentration of Fe²⁺ in the filtrate was determined using Atomic (AAS) to obtain the AEC. A standard solution of Fe²⁺ was prepared by dissolving 0.0189 g of K₄[Fe(CN)₆] in 100 mL of deionised water to give 25 mg/L of Fe²⁺. The iron concentration in this stock solution was

confirmed using a primary standard solution of 1000 mg/L of iron(II) nitrate obtained from Merck. A standard curve was constructed using Fe^{2+} solutions of 2, 4, 6, 8 and 10 mg/L.

2.4 Kinetics Study of Anion Exchange and Regeneration Process

A kinetics study was carried out by preparing five solutions of 0.33 g $\text{K}_4[\text{Fe}(\text{CN})_6]$ in 25 mL of deionised water. To each solution, 0.10 g of Zn-Al-OAc hydrotalcite was added under nitrogen atmosphere and the pH was maintained at 10 using 0.10 M NaOH. Each mixture was stirred under nitrogen atmosphere for 120, 240, 360, 500, 1800 and 3600 sec. Solid hydrotalcite was separated by centrifugation and washed repeatedly with distilled water. The Fe(II) content of the solution was determined using Atomic Absorption Spectrophotometer (AAS). Subsequently, the concentration of hexacyanoferrate(II) was calculated from the concentration of Fe(II), assuming a one to one molar ratio of hexacyanoferrate(II) to Fe(II).

To regenerate hydrotalcite, 0.10 g of Zn-Al- $\text{Fe}(\text{CN})_6$ was mixed with 25 mL of 0.40 M NaOAc under nitrogen atmosphere for 2 h. This sample was subjected to a hydrothermal process at 100°C for 15 h. The resulting solid was separated and dried at 90°C for 4 h using an air oven. The solid was characterised by X-ray diffraction (XAD) and FTIR.

2.5 Determination of Anion Exchange Capacity (AEC)

A 0.10 g solid sample of Zn-Al-OAc hydrotalcite was added to a 25.0 mL, 0.010 M solution of $\text{K}_4[\text{Fe}(\text{CN})_6]$ in a closed, 50-mL beaker. The solution was stirred overnight to complete the ion exchange reaction. The resulting solid was removed by centrifugation. The concentration of Fe(II), and therefore hexacyanoferrate(II), in the supernatant was measured by AAS. The amount of Fe(II) absorbed by the ion exchanger was calculated by measuring the Fe(II) concentration before and after exchange. It is noted that while 1 mole of hexacyanoferrate(II) contains 1 mole of Fe(II), 1 equivalent of hexacyanoferrate(II), $[\text{Fe}(\text{CN})_6]^{4-}$ contains $\frac{1}{4}$ moles. The anion exchange capacity was calculated from the amount of hexacyanoferrate(II) adsorbed by a 100 g hydrotalcite ion exchanger, and is typically expressed in milliequivalent (meq) amounts of anion per 100 g of exchanger, or meq/100g.

3. RESULTS AND DISCUSSION

Figure 1 (curve a) shows the XRD pattern of Zn-Al-OAc hydrotalcite prepared using the corresponding nitrate salts and a NaOAc solution. The Zn-Al-

OAc hydrotalcite was found to have basal spacings of $d_{003} = 12.71 \text{ \AA}$, $d_{006} = 2.47 \text{ \AA}$ and $d_{009} = 4.22 \text{ \AA}$. Figure 2 (curve a) shows the presence of acetate with a broad absorption band at around 3348 cm^{-1} . The absorption band at 1766 cm^{-1} was ascribed to carbonyl group C=O stretching and a band at 1373 cm^{-1} was assigned to C-O stretching. Strong bands at 1560 and 1420 cm^{-1} were attributed to stretching modes of the carboxylate group (CO_2^-) that are characteristic of acetate.⁴ The presence of carbonate could not be measured since its vibrations overlap with acetate. A small amount of carbonate is usually present in most hydrotalcite-like compounds. Vibrations of the Zn-O-Al bonds appeared at 424 cm^{-1} . The bands in the $400 - 900 \text{ cm}^{-1}$ range provided evidence that the characteristic of LDH network had been formed.^{27,28,29}

Table 1: Chemical composition of hydrotalcite Zn-Al-OAc.

Component	Composition per 100 g	
	% (w/w)	Moles
Zn	14.97	0.23
Al	2.25	0.08
H ₂ O	5	0.30
Ratio Zn/Al		2.7

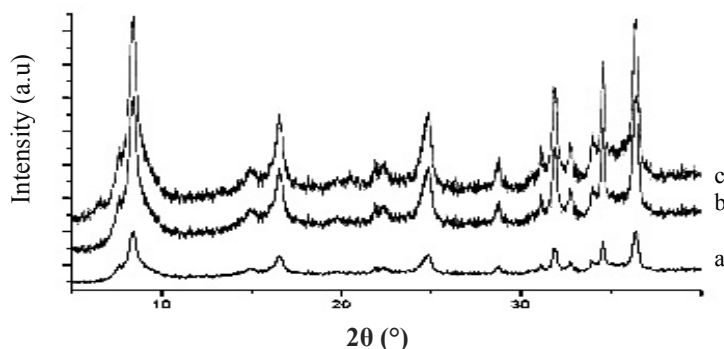


Figure 1: XRD patterns of (a) initial Zn-Al-OAc hydrotalcite, (b) Zn-Al-Fe(CN)₆, and (c) Zn-Al-OAc after regeneration.

Table 1 shows the chemical composition of Zn-Al-OAc hydrotalcite. The crystalline water content was estimated to be 0.30 moles. After fitting, the stoichiometric composition of hydrotalcite was found to be $\text{Zn}_{0.73}\text{Al}_{0.27}(\text{OH})_2(\text{OAc})_{0.27} \cdot 0.95\text{H}_2\text{O}$, in which the Zn/Al ratio was 2.7. A Zn to Al ratio close to 3:1 was expected based on the compositions of the precursor solutions of zinc nitrate and aluminium nitrate.

Figure 1 shows the XRD patterns of unexchanged Zn-Al-OAc hydrotalcite, anion exchanged Zn-Al-Fe(CN)₆ and Zn-Al-OAc hydrotalcite after regeneration. The exchanged [Fe(CN)₆]⁴⁻ anion was evidenced by the shift of d₀₀₃ from 12.71 to 10.53 Å. The XRD patterns show that the nitrate could not regenerate dichromate, as shown by the insignificant shift of 10.53 to 10.63 Å, as presented in Table 2.

Table 2: Basal spacing data of Zn-Al-OAc hydrotalcite.

	Zn-Al-OAc (initial)	Zn-Al-Fe(CN) ₆ (anion exchanged)	Zn-Al-OAc (regenerated)
d₀₀₃ (Å)	12.71	10.53	10.63
d₀₀₆ (Å)	2.42	2.47	2.47
d₀₀₉ (Å)	4.22	2.59	2.60

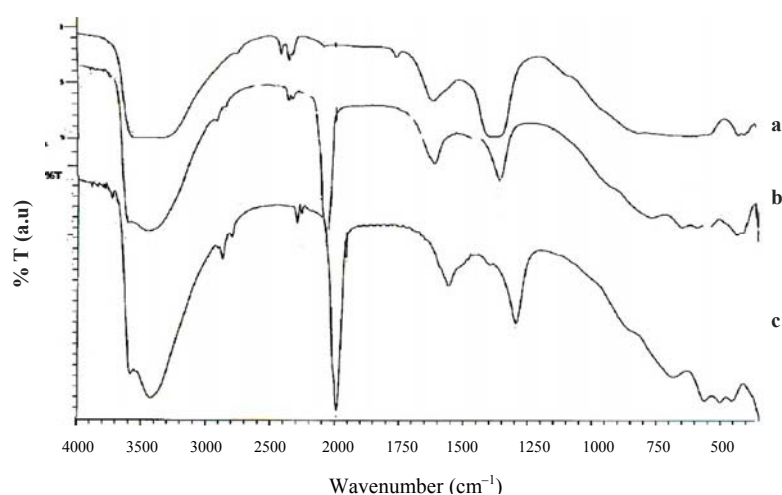


Figure 2: FTIR spectra (a) unexchanged Zn-Al-OAc hydrotalcite (b) Zn-Al-Fe(CN)₆, and (c) Zn-Al-OAc after regeneration.

The FTIR spectra are shown for unexchanged Zn-Al-OAc hydrotalcite, anion exchanged Zn-Al-Fe(CN)₆ and Zn-Al-OAc hydrotalcite after regeneration (Fig. 2). The characteristic vibration of [Fe(CN)₆]⁴⁻ is the 2067 cm⁻¹ stretching vibration of the nitrate. The anion exchanged spectra also showed a shift from 3348 to 3448 due to the OH stretching modes of water molecules and hydroxyl groups in the brucite layers. A shift of the 1776 cm⁻¹ carbonyl C=O stretch was not observed in the spectra of anion exchanged hydrotalcite, indicating that the [Fe(CN)₆]⁴⁻ anion can exchange OAc⁻ in the interlayer region of hydrotalcite. FTIR spectra from the regenerated sample did not show any significant shifts.

Characteristic modes of acetate in the interlayer regions of hydrotalcite did not reappear. Based on this result, we found that OAc^- could not regenerate Zn-Al-Fe(CN)_6 hydrotalcite, due to steric effects for acetate. Figure 3 presents models for the spatial orientation of the $[\text{Fe(CN)}_6]^{4-}$ anion, intercalated in the LDH.

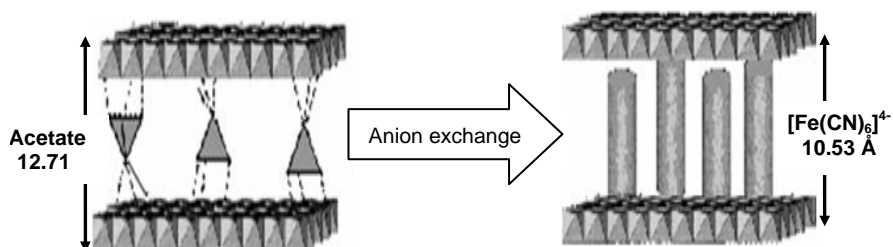


Figure 3: Models for the spatial orientation of $[\text{Fe(CN)}_6]^{4-}$ intercalated into the LDH.

The anion exchange kinetics of Zn-Al-OAc hydrotalcite with $[\text{Fe(CN)}_6]^{4-}$ were studied by measuring the Fe^{2+} content using atomic absorption spectroscopy. Figure 4 shows the concentration of $[\text{Fe(CN)}_6]^{4-}$ in solution versus time. A linear dependence was found for $1/C$ versus time, where C is the molar concentration of Fe^{2+} (Fig. 5). The reaction was well described by a second order rate constant of $k = 0.215 \text{ M}^{-1}\text{s}^{-1}$, with $R^2 = 0.996$.

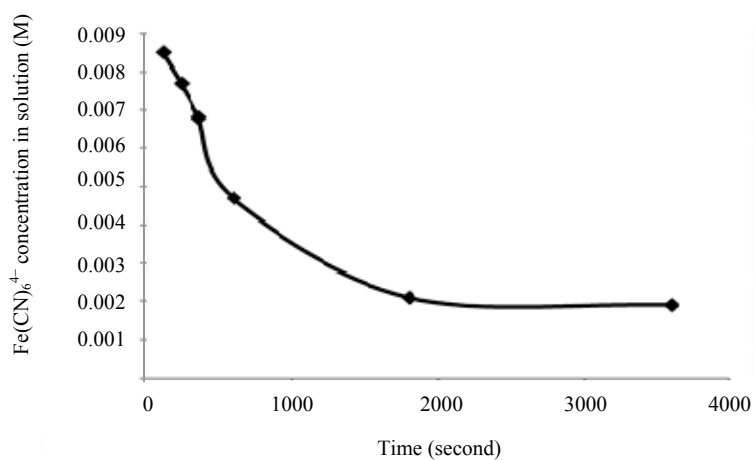


Figure 4: Time-dependent $[\text{Fe(CN)}_6]^{4-}$ concentration during ion exchange.

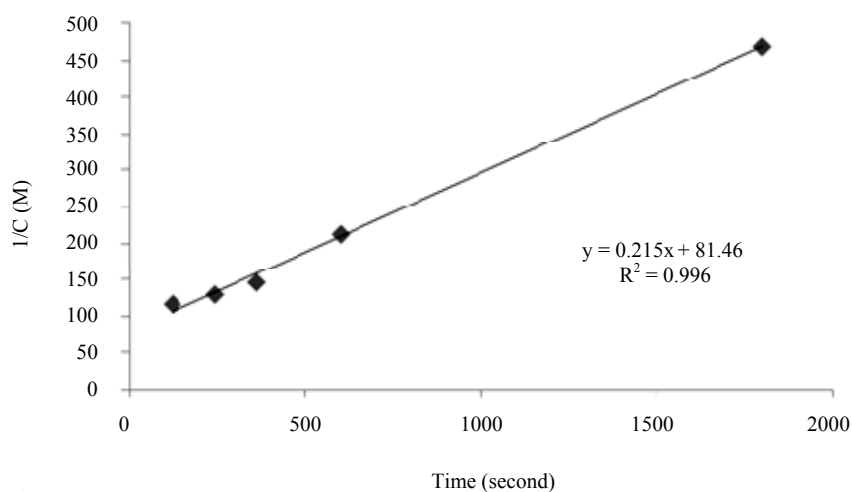


Figure 5: Plot of $1/C$ versus time for ion exchange reaction of Zn-Al-OAc by $[\text{Fe}(\text{CN})_6]^{4-}$.

The anion exchange capacity of Zn-Al-OAc hydrotalcite with $[\text{Fe}(\text{CN})_6]^{4-}$ was found to be 219 meq $[\text{Fe}(\text{CN})_6]^{4-}/100$ g. This capacity is less than that of Zn-Al- NO_3 hydrotalcite with $[\text{Fe}(\text{CN})_6]^{4-}$, which was reported as 405 meq $[\text{Fe}(\text{CN})_6]^{4-}/100$ g²³. A comparative list of ion selectivity for anion exchangers showed influence due to anion charge, electron density, and hydrogen bonding.²²

4. CONCLUSION

Zn-Al-OAc hydrotalcite was successfully synthesised and its utility as an anion exchanger was evaluated. Its chemical composition was determined to be $\text{Zn}_{0.73}\text{Al}_{0.27}(\text{OH})_2(\text{OAc})_{0.27} \cdot 0.95\text{H}_2\text{O}$ and a considerably high anion exchange capacity of 219 meq $[\text{Fe}(\text{CN})_6]^{4-}/100$ g was measured. The kinetics of anion exchange of OAc^- in Zn-Al-OAc hydrotalcite by $[\text{Fe}(\text{CN})_6]^{4-}$ were fit to a second order reaction model and a rate constant (k) of $0.215 \text{ M}^{-1}\text{s}^{-1}$ was determined with $R^2 = 0.996$. The Zn-Al- $\text{Fe}(\text{CN})_6$ hydrotalcite could not be regenerated with a solution of potassium nitrate.

5. ACKNOWLEDGEMENTS

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