PAPER • OPEN ACCESS

Removal of Hexavalent Chromium from Raw Drinking Water by Zeolite-FeO Composite Supported Carbon: Case Study Citarum River

Removal of Hexavalent Chromium from Raw Drinking Water by Zeolite-FeO Composite Supported Carbon: Case Study Citarum River

YR Widyawati[1], S Notodarmojo[1,2], S Hidayat[1,2,3], Q Helmy[1,2,3*]

[1]Environmental Engineering Department, Institute of Technology Bandung, Indonesia
[2]Water and Wastewater Engineering Research Group, Institute of Technology Bandung, Indonesia
[3]Bioscience and Biotechnology Research Center, Institute of Technology Bandung, Indonesia

*E-mail: helmy@tl.itb.ac.id

Abstract. Citarum River plays an important role in various sectors both domestic and economic for residents along the Citarum River Basin. The different source of wastewater from 400 industries disposes their wastewater directly to the Citarum River, which is predominantly dominated by the textile industry. Those industrial activities generate hazardous heavy metals such as Cr(VI) which can degrade the quality of the river. In this research, we will conduct a treatment on series of Cr(VI) containing surface water to meet the drinking standard of raw water. Zeolite-FeO is synthesized from natural zeolite in Sukabumi, and then impregnated with FeO, characterized using XRD and the result shows that iron oxide precisely hematite (α-Fe_2O_3) successfully impregnated into the zeolite. The Zeolite-FeO then modified with sucrose to give positively charged on the surface by the contribution of carbon. The adsorption process is carried out in batch with artificial waste containing $Cr_2O_7^{2-}$ to obtain the optimum conditions such as the effect of time, pH and initial concentrations. From the adsorption experiment, the result shows the highest efficiency removal is 70,72% at pH 2 for 45 minutes by Zeolite-FeO-Sucrose.

1. Introduction

Nowadays economic and the population is growing rapidly, and it triggered the development of industries that focused to fulfill the needs and economic factors. However, it is not only giving the benefits in the economic field but also cause environmental degradation due to the waste which an industry has generated. According to BPLHD West Java, there are more than 400 industries are dispose their wastewater directly to the Citarum River, it has been dominated by textile, pulp and paper, and electroplating industry [1]. The textile industries consume large quantities of water and produces a large volume of wastewater containing various chemicals such as dyestuff, bleaching agents, finishing chemicals, and inorganics including metals [2]. Industrial activities mostly generate chemical and hazardous waste that contains heavy metals such as Cadmium (Cd), Lead (Pb), Mercury (Hg) or Chromium (Cr). Based on The West Java Regulation No 39/2000 standard for water quality at upper Citarum has been classified as type B, C, and D, and the threshold of chromium hexavalent

concentration is 0.05 mg/L. However, in previous research, it was found the concentration of chromium in Sapan and Cisirung relatively high, it was approximately 0.157 mg/L in water and 103.925 mg/kg accumulated in catfish [3].

Chromium (Cr) is one of the heavy metals with high toxicity, according to the valence of the ion. The present of Chromium (Cr) in the environment naturally is Cr(III) and Cr(VI). Compared to Cr(III), Cr(VI) has higher toxicity, corrosive and carcinogenic characteristic. Based on their characteristic, heavy metals are not biodegradable and easily accumulate in organisms and might cause several disease and disorder. However, Cr(III) present with less solubility, mobility, and toxicity for the organism [4].

Various materials have been studied or used as an adsorbent of pollutant in water or wastewater. One of natural mineral that very abundant in nature and potential to be used as a source of adsorbent is the zeolite. Natural zeolite (NZ) has a porous structure and tends to be used widely as an adsorbent for metal ions. The other advantages of zeolite, it has high cation exchange capacity (CEC) and large surface area to be used as a substrate to remove heavy metal cations [5]. Not only its ability to remove heavy metals, but adsorption method is also common to be used as a water treatment method due to easy and inexpensive implementation, however it has a poor capacity for some contaminants. Thus, to improve its effectiveness, surface modification is required.

Many studies were conducted to reduce Cr(VI) to Cr(III) using a reducing agent such as ferrous salt, sulphite, and thiosulfate [4]. Beside by reducing Cr(VI) to become Cr(III), it is possible to use iron oxide to modified the zeolite as an adsorbent for heavy metals removal. Iron oxide has an active sorbent and involved in the reaction behavior of many ions [6]. The main advantages of iron among other nanomaterials are relatively low toxicity and biodegradability. In addition, iron is a relatively cheap and a widespread material. Iron typically exist in the environment as iron(II) and iron(III) oxides but also for hydroxides, oxy-hydroxides (e.g Fe_3O_4, FeO, γ-Fe_2O_3, α-Fe_2O_3, $Fe(OH)_3$). Among iron oxides, magnetite (Fe_3O4) and maghemite (Fe_2O_3) are common and easy to synthesize [7].

Consequently, the aim of this study is to conduct the effect of Iron oxide coated on zeolite surface as an adsorbent for Cr(VI) removal from water, also the kinetics and its possible isotherm. The effects of several variations are considered including solution pH, contact time and concentration of Cr(VI).

2. Experimental

2.1. Synthesis of Zeolite-FeO Composites

The zeolite used in this experiment was natural zeolite from Sukabumi. Natural Zeolite (NZ) was crushed and sieved until getting sized 30 mesh, NZ was washed by distilled water to remove dust and then oven dried at 110°C for 3 hours. Dried NZ was collected and activated HCl, 50 g NZ put to 100mL HCl1M under stirring for 2 hours. Activated NZ was filtered and washes by distilled water then oven at 110°C and calcined in the furnace at 300°C for 4 hours preparing for surface coating.

To start surface coating the zeolite with iron oxide, firstly mixed 50g activated zeolite to 25mL 1M $FeCl_3.6H_2O$ and stirred until contacted sufficiently. The mixture kept at 80°C, under the stirring condition and 75mL sodium hydroxide 1M slowly poured into the mixture. After stirring 1-2 hours, then the mixture dried in the oven overnight to remove the water and calcined in the furnace at 500°C for 4 hours. Next, the synthesized zeolite-FeO was washed using distilled water to remove iron oxide uncoated to zeolite, finally, the composite Zeolite-FeO dried at 110°C in the oven. In the second step, zeolite coated with FeO was carried out on the prepared using sucrose because after dehydration the resulting carbon possesses excellent binding capacity. Zeolite-FeO were dissolved in 10% sucrose and stirred up to solidification about 2h at 65°C using magnetic stirrer. Then after treatment with sucrose, the material was put in the oven for 30 min at 100°C and calcined at 150-200°C for 30 minutes [8]. During thermal treatment, water molecules are removed from sucrose and resulting carbon atoms remains which are deposited as 2D layers over the iron oxide particles and give a positive charge on zeolite surface [9].

2.2. Characterization of Zeolite-FeO Composite

NZ and zeolite-FeO composite were characterized by X-ray Diffraction (XRD) in Puslitbang Teknologi Mineral dan Batu Bara Bandung.

2.3. Batch adsorption experiments

2.3.1. Chromium adsorption experiments

Adsorption experiment started by prepared a stock solution of $K_2Cr_2O_7$ 1000 ppm. The initial concentration of the solution was varied from 0,5;1 and 2 ppm but the pH controlled the same at 2 with sulfuric acid. 20 g of each NZ or zeolite-FeO was added to 250mL Cr(VI) solution, then the mixture was stirred using jar test at room temperature for 1 hour at 180 rpm, a small number of samples was taken in several ranges of times. After the optimum concentration was obtained, the next step was the determination of pH optimum, the optimal concentration was used but the pH was varied 2, 4 and 6.

Liquid samples were analyzed by colorimetric method using a UV-Vis spectrophotometer (Genesys 10S UV-Vis, Thermo Scientific). Firstly, the sample filtered to remove solid particles, 10mL samples from supernatant were placed in a reaction tube and added complexion agent. The complexion agent used here was 1,5-diphenylcarbazide in acid condition by adding phosphoric acid and let stand for 5 to 10 minutes for full-color development of pink compound, the absorbance measured at 530nm using water as a blank [10].

3. Results and Discussion

3.1. Characterization of NZ and Zeolite-FeO Composite

Before both of zeolites were characterized by XRD, firstly those zeolites have to be activated. Common activation treatment is using strong acid or base. Activation with acid cause dealumination and decationation in zeolite structure. Zeolites simply can dealuminated and decationed with a strong acid (HCl) at concentration 0,1N till 11N. Dealumination process will increase surface area due to reducing some impurities that cover the zeolite pores.

As illustrated in Fig. 1 below, the changes colour of zeolite from teal to brown indicates that the iron oxide was successfully attached in the surface of zeolite, however on Zeolite-FeO coated with sucrose the colour changed to dark brown, it might due to carbon forming on the surface. Doping carbon on zeolite surface has a role to give a positive charge on the surface of the zeolite.

Fig. 1 (A) Natural Zeolite (B) Zeolite-FeO (C) Zeolite-FeO-Sucrose

It was confirmed by the result of XRD, which showed characteristic peaks of iron after coating in thezeolite. XRD spectra showed (Fig. 2) obvious new pattern in NZ material before and after coating.

The characteristic peaks at 2θ 33.09°, 35.86° proved the existence of hematite (α-Fe_2O_3) [11]. Meanwhile, NZ composition was reported dominantly mordenite, quartz, albite, and illite.
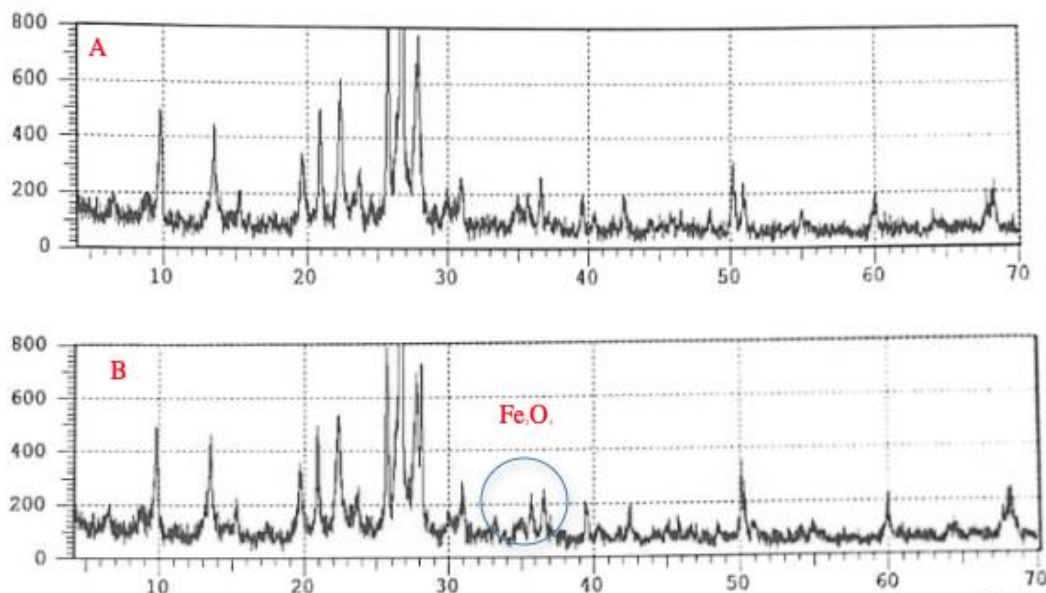

Fig. 2 XRD spectra of (A) Natural Zeolite; (B) Zeolite-FeO

Basically, zeolites are divided into seven main groups according to their crystal structure, zeolite used here has a mordenite structure. Based on the physical characteristic of some natural zeolitesmordenite has porosity about 28%, it is lower than other common natural zeolites which clinoptilolite has porosity about 47%. It was required activation with acid to remove contain amounts of impurities [12].

3.2. Result of adsorption studies

3.2.1. Effect of pH and concentration

The effect of pH in chromium solution was investigated, depends on the pH of the solution the oxidation states of chromium ranging from +2 to +6 with different stability. Adsorption of metals ion here is $Cr_2O_7^-$ depends upon pH in solution, it also controlled the presence ionic species in the solution. In this study, the range of pH used was from 2 to 6, the results shown in Fig 3. The result from the experiment obtained that the adsorption efficiency of Cr(VI) increases when the pH decreases from 6 to 2. Consequently, optimum adsorption is seen at pH 2, while at higher pH than 2 the removal of metals ion decrease [13]. Adsorption process of metals ion is optimum in the acid condition, this might be due to in the acid condition the chromium ions are present in the form of $HCrO_4^-$ ions. Whereas, in alkaline condition chromium present as CrO_4^- and $Cr_2O_7^{2-}$ ion which competes with OH^- to adsorbed on the surface of zeolite through hydrogen bonding [14]. If compared among three kinds of adsorbents, Zeolite-FeO-Sucrose has the highest efficiency on chromium removal, this illustrates in Fig 4.
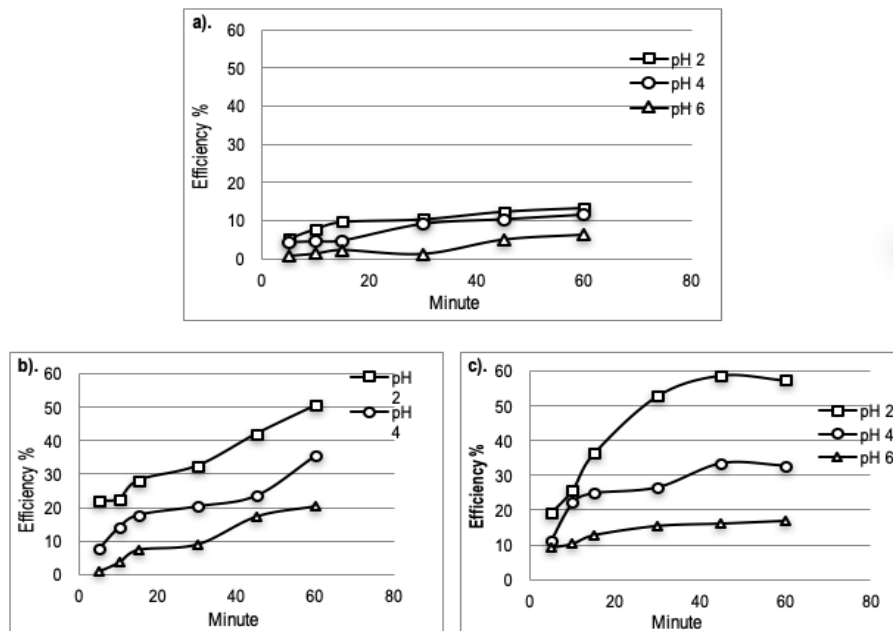
Fig. 3 Optimum pH at different adsorbent (A) Natural Zeolite (B) Zeolite-FeO (C) Zeolite-FeO-Sucrose
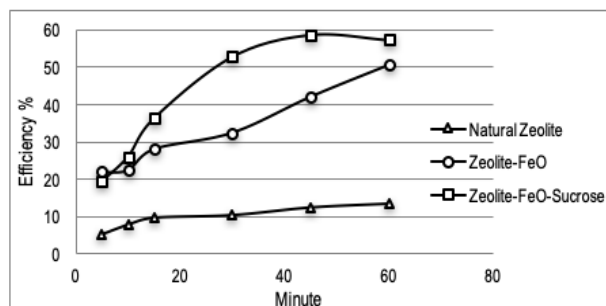

Fig. 4 Optimum pH at different kind of adsorbents

In this study, Cr(VI) removal experiments were carried out and put in different concentration 0.5; 1 and 2 ppm. The result is shown in Fig. 5 which reveal that the highest removal efficiency up to 70,72%. It was achieved by Zeolite-FeO-Sucrose at pH 2 in 45 minutes with concentration 0.5 ppm. Zeolite-FeO-Sucrose gave higher efficiency due to the availability of active binding sites.
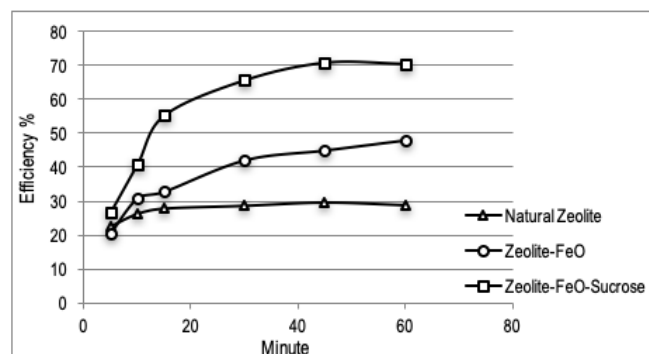

Fig. 5 Optimum concentration at different kind of adsorbents

There are two mechanisms for adsorption of Cr(VI) ions in solution, first direct reduction and second one indirect reduction. Ion chromium involved many protons and electrons to get reduce into Cr(III). In the second mechanism, firstly it happened interaction of negatively charged Cr(VI) ionic species with positively charged on the zeolite-FeO due to the addition of sucrose surface on Zeolite-FeO occurs by forming from carbon while H^+ ion in strong acid also contributed.

4. Conclusion

The results presented in this study show that the synthesized of iron oxide is successful and attached in the zeolite. Adsorption experiments resulted that adsorbent Zeolite-FeO supported with carbon is more efficient as Cr(VI) removal in water with removal efficiency up to 70.72% at pH 2 in 45 minutes with concentration 0.5 ppm. The adsorption Cr(VI) process with Zeolite-FeO-Sucrose was optimum in the acid condition at pH 2. The efficiency of ion chromium removal is increasing as the solution was maintained in acid condition.

5. Acknowledgment

References

[1]   BPLHD Provinsi Jawa Barat (Badan Pengendalian Lingkungan Hidup Daerah Provinsi Jawa Barat/West Java EPA): *Pengelolaan DAS di Jawa Barat, Kasus DAS Citarum Hulu*. (2003) West Java: West Java Provincial Government More references

[2]   Suryawan I W K, Helmy Q, and Notodarmojo S 2018 *IOP Conf. Ser.: Earth Environ. Sci.* 106012102.

[3]   Septiono, M.A., and Roosmini, D., Heavy Metal Distribution In Water, Sediment, And Fish At Upper Citarum River And Its Potential Exposure Pathway To Human , The 5th Environmental Technology and Management Conference "Green Technology towards Sustainable Environment" November 23 - 24, (2015) Bandung, Indonesia. ISBN: 978-979-98278-5-2

[4]   Chong, H., Yanan, J., Qianqian, W., Wangjin, Y., He, Y., Xiangxin, X.,: Kinetics and Mechanism of Hexavalent Chromium Removal by Basic Oxygen Furnace Slag, Journal of Environmental Science 46 (2016) 63-71

[5]   Gaoxing, D., Zhaohui, L., Libing, L., Renee, H., Samantha, L., Nicole, H., Wei-Teh, J.,: Cr(VI) Retention and Transport through Fe(III)-Coated Natural Zeolite. Journal of Hazardous Materials 221-222 (2012) 118-123

[6]   Milan K, Aleksandra D, Z˘ivko S, Marina T, Marin U, Jelena P, G. Diego G, Removal of lead from aqueous solutions by using the natural and Fe(III)-modified zeolite, Applied Surface Science 258 (2012) 3667 – 3673

[7]   Boris I. Kharisov,H. V. Rasika Dias,Oxana V. Kharissova,Victor Manuel Jime ́nez-Pe ́rez, Betsabee Olvera Pe ́rezand Blanca Mun ̃oz Flores, Iron-containing nanomaterials: synthesis, properties, and environmental applications, RSC Advances 2012, 2, 9325-9358

[8]   Gupta, S.S., Sreeprasad, T.S., Maliyekkal, S.M., Das, S.K., Pradeep, T., 2012. Graphene from sugar and its application in water purification. ACS Appl. Mater. Interfaces 4, 4156–4163.

[9]   Nidhi Khare, Jaya Bajpai, A.K. Bajpai, Graphene coated iron oxide (GCIO) nanoparticles as efficient adsorbent for removal of chromium ions: Preparation, characterization and batch adsorption studies. Environmental technology, Monitorung & Management 10 (2018) 148 -

162

[10] Eaton, A. D., Clesceri, L. S., Greenberg, A. E., Franson, M. A. H., American Public Health Association., American Water Works Association., & Water Environment Federation. (1998). *Standard methods for the examination of water and wastewater*. Washington, DC: American Public Health Association.

[11] Cui, H., Liu, Y., Ren, W., 2013. Structure switch between a-Fe2O3,C - Fe2O3 and Fe3O4 during the large scale and low temperature sol–gel synthesis of nearly monodispersed iron oxide nanoparticles. Adv. Powder Technol. 24, 93–97.

[12] Aysha, A. A., Syhthesis, Characterization and Application of Magentic Adsorbent based on Sepiolite and Zeolite. Doctoral Dissertation. University of Belgrade Faculty of Technology and Metallurgy (2016).

[13] Berciaud, S., Ryu, S., Brus, L.E., Heinz, T.F., 2008. Probing the intrinsic properties of exfoliated graphene: Raman spectroscopy of free–standing monolayers. Nano Lett. 9 (1), 346–352.

[14] Babu, B.V., Gupta, S., 2008. Adsorption Of Cr(VI) Using Activated Neem Leaves: Kinetic Studies 14. pp. 85–92.