

The removal of copper (II) and lead (II) from aqueous solution using Fuller's earth and Fuller's earth-immobilized nanoscale zero valent iron (FE-NZVI) by adsorption

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Abstract. The present study investigates the propensity of Fuller's Earth, a diatomaceous earth that is cheap and abundant in several locations whose application is yet to be fully ventured, and Fuller's Earth-Immobilized Nanoscale Zero Valent Iron in removing heavy metal contaminants, particularly Pb^{2+} and Cu^{2+} , from aqueous solutions through adsorption method. FE-nZVI were synthesized through the borohydride reduction method and subsequently characterized through SEM, FTIR, and XRD. The SEM analysis shows an increase in the agglomeration of the nZVI on the immobilized Fullers' Earth with an increase in the loading of Fe⁰. Tests were conducted on various samples in order to determine the effect of three parameters on the efficiency of the adsorbent which includes the initial concentration of the heavy metal, adsorbent dosage and pH with respect to time. The results show that the FE-nZVI can be used as a new adsorbent for the sole application of heavy metal remediation in aqueous systems due to its efficiency in removing the contaminants that would allow individuals to conform to the stringent requirements dictated by environmental laws.

1 Introduction

According to Irina Bokova, the Director-General of UNESCO, in the United Nations World Water Development Report 2017, nearly 80% of the wastewaters accumulated throughout the globe are released to the environment without going any form of treatment which has caused multitude complications such as de-oxygenated dead zones in certain parts of the ocean that affects the marine ecosystem and livelihood of fishermen and even deaths that are ascribed to contaminated water due to inadequate treatment. This lack of attention to wastewater is often pointed out to lack of data availability which shows that only 55/181 countries throughout the globe have the knowledge regarding the treatment and usage of wastewater but such data are already outdated [1].

Through recent years, heavy metal ion, such as copper, present in the environment, particularly in water resources, was becoming as one of the major concerns because of their toxicity, tendency to accumulate in living organisms, wide spread presence and non-biodegradability [2], [3]. Heavy metals as distinguished as carcinogens that are effective towards humans by the International Agency for Research in Cancer and the U.S. Environmental Protection Agency can easily enter the food chain in so many ways that can cause harmful

effects over their life span with gradual accumulation in living organisms [4]. In particular, lead pollution can cause anemia, chronic headaches, diarrhea, cancer, mental retardation, kidney diseases and can damage the nervous system and reproductive. Also, the excess amount of copper intake will result to growth in the liver and will create gastro-intestinal [5]. Therefore, before disposing the heavy metals in aquatic environments, it is necessary to remove it first [4].

One of the good alternatives in removing the heavy metal ions in water is the nZVI because of its high reaction rate, high reactivity and large surface area [6]. The effectiveness of nZVI was heavily influenced by the parameters affecting the system including the adsorbent dosage, initial concentration of contaminants and pH. Zero valent iron (Fe^0) upon undergoing redox reaction, oxidizes into Ferrous Iron (Fe^{2+}) wherein the electrons released are utilized by other compounds in order to be reduced. In an actual situation, the zero valent iron would react with dissolved oxygen and water in order to undergo electrochemical reactions. Through the usage of nZVI, particles, contaminants can be removed through either reduction or adsorption. However, nZVI is not stable to air and water and undergoes aggregation because of their high intrinsic magnetic reaction and surface energy forming a larger size of particle and decreases its surface area that limits the sorption capacity [7], [8]. To address these

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issues, immobilizers, particularly clay adsorbents, were developed to reduce aggregation of nZVI and improve its dispersivity [9]. In particular, fuller's earth is a steady, relatively cheap clay mineral and an effective material to serve as a support for nZVI, that can be used for heavy metal remediation [10]. It is said to be effective adsorbent because of the hydrous alumina silicate it contains [11].

The objectives of this study are to remove Cu^{2+} and Pb^{2+} contaminants from aqueous solution using fuller's earth and fuller's earth-immobilized nZVI by adsorption, to test the effects of different parameters such as pH, initial concentration of heavy metals and adsorbent dosage on the adsorption capacity of FE and FE-nZVI and to determine their relationship with respect to time.

2 Materials and methods

2.1 Materials and reagents

Fuller's earth, hydrochloric acid (HCl), sodium borohydride (NaBH_4), polyethylene glycol, anhydrous ferric chloride (FeCl_3), methanol (CH_3OH), sodium hydroxide (NaOH), Cu^{2+} sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and lead nitrate $\text{Pb}(\text{NO}_3)_2$ will be used for the entirety of the experiment.

Atomic Absorption Spectroscopy (AAS), Fourier Transform Infra-red (FTIR) spectrometer and Scanning Electron Microscope (SEM) will be the apparatuses to be used in the characterization.

2.2 Preparation of chemicals

Fuller's earth, together with iron (III) hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and Sodium borohydride (NaBH_4) will be purchased. Synthesizing of FE-nZVI will be attained by mixing a 2% of polyethylene glycol aqueous solution that is obtained by dissolving 10 grams of polyethylene glycol in a 500 mL distilled water, and a 10% NaBH_4 solution that is obtained by dissolving 10 grams of NaBH_4 in a 100 mL deionized distilled water.

2.3 Preparation of stock solution

Stock solution of copper will be prepared by dissolving 3930 mg of Cu^{2+} sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in 1000mL of distilled water in a 1000 mL beaker to make 1000 mL of 1000 ppm copper stock solution.

Stock solution of lead will be prepared by dissolving 1598 mg of lead nitrate $\text{Pb}(\text{NO}_3)_2$ in 1000mL of distilled water in a 1000 mL beaker to make 1000 mL of 1000 ppm lead stock solution.

2.4 Synthesis of FE-nZVI

The iron nanoparticles will be immobilized using fuller's earth in a flask reactor with three open necks. Ferric Chloride will be added to a suspension of fuller's earth (36g) in 2% aqueous polyethylene glycol solution (500mL) and will be stirred for 30 minutes. 10% Sodium

borohydride solution will be poured in a burette and will be added 1 drop per 2 seconds with a continuous stirring using mechanical stirrer with a speed of 300 rpm. The completion of reaction should be characterized by the colorless solution and black colored suspension should settle to the bottom. The black colored precipitate will be separated by Buchner filtration. By the use of excess methanol, the residue will be washed in order to take off some borohydride impurities and moisture that is left at the outer layer of the substance. The resulting black solid will be stored in a tight capped container to prevent aerial oxidation prior to characterization and adsorption experiment.

2.5 Characterization of Fuller's earth and FE-nZVI

Elemental analysis of fuller's earth will be observed under XRD. Meanwhile, the morphological analysis of FE-nZVI will be observed under the SEM.

2.6 Adsorption and treatment process

A preparation of 1000ppm stock solutions of Cu^{2+} and Pb^{2+} will stand by for its dilution to produce the desired concentration of Cu^{2+} and Pb^{2+} solutions. Adsorption studies proceed by starting at the preparation of 50mL pure Cu (II) aqueous solution and 50mL pure Pb^{2+} aqueous solution, followed by adjusting of pH between 2 and 6 using NaOH and HCl, then addition of different dosages of adsorbents. The flasks will be maintained at constant room temperature under shaking at 150rpm using an incubator shaker. The solutions will be filtered after a given time using a Whatman filter paper and will be analyzed AAS. The filtrate will also be analyzed using FTIR spectrometer.

3 Results and discussion

3.1 SEM result

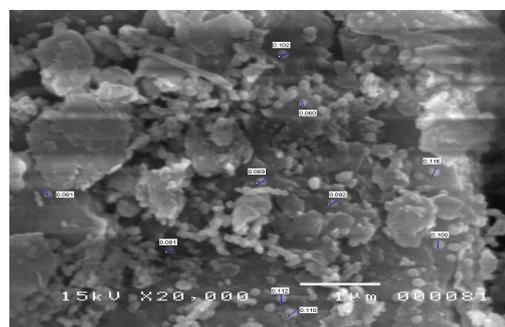


Fig. 1. SEM Image of FE-nZVI

Fig. 1 shows the surface morphology of the FE-nZVI. The morphology shows that FE-nZVI has a uniform particle size varying from 80-120 nm. It also shows that the nZVI was being formed and dispersed in the surface of the fuller's earth. This aggregation is due to the magnetic interactions of the primary iron particles.

3.2 XRD result

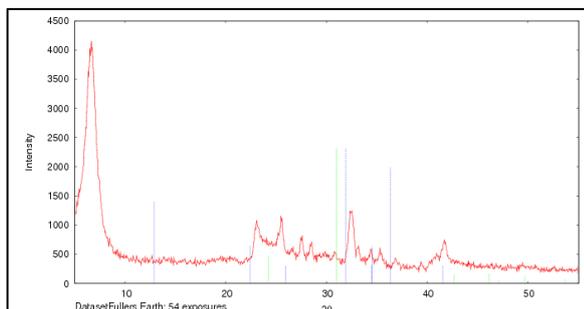


Fig. 2. XRD Pattern of FE-nZVI.

Fig. 2 shows the major peaks in the XRD pattern of fullers' earth and its corresponding characteristics. The XRD result revealed a characteristic peak at 2θ of 23.1 which is attributed to TiO_2 . The peak at 2θ of 25.6 corresponds to the characteristics of quartz. The characteristics of montmorillonite and Al_2O_3 was also observed at the peak 2θ of 32.45 and 41.8, respectively. This pattern suggests the presence of montmorillonite which is the common composition of FE [12].

3.3 AAS result

The data gathered for this research were treated using ANOVA for the selected factorial model in order to determine how well the data fits the model and which parameters considered in this research were actually significant. In the case of Pb^{2+} adsorbed by FE, the R^2 is equal to 0.8738. Based on α value of 0.0500, the model has a p-value of 0.0366 deeming it to be significant. For the data regarding the Cu^{2+} adsorbed by FE, the R^2 is equal to 0.9690. On the basis of α value of 0.0500, the model obtained a p-value of 0.0001, thus making it significant. For the data regarding the Pb^{2+} adsorbed using FE-nZVI, the R^2 obtained is equivalent to 0.9746. Based on α value of 0.0500, both the model and the pH parameter obtained a p-value < 0.0001 , thus both are significant. For the Cu^{2+} that was adsorbed using FE-nZVI, the data obtained has an R^2 of 0.9734. The α value was set to 0.0500 wherein the model, the pH and the initial concentration are all significant with a p-value of 0.0002, < 0.0001 , and 0.0032 respectively.

3.4 Effect of pH

Based on **Fig. 3.a**, the amount of Cu^{2+} adsorbed on Fuller's Earth is directly proportional to the pH of the aqueous solution. The % adsorption tends to increase from pH 2 to 6. The highest % adsorption was at pH 6 for a contact time of 60 minutes which amounted to 75.82%.

Based on **Fig. 3.b**, the amount of Cu^{2+} adsorbed by the FE-nZVI tends to increase as the pH of the solution also increases. As the pH of the aqueous solution increased, more of the Cu^{2+} was removed from the aqueous solution wherein the largest % adsorption was obtained at 98.84 % for pH 4 for a contact time of 60 minutes.

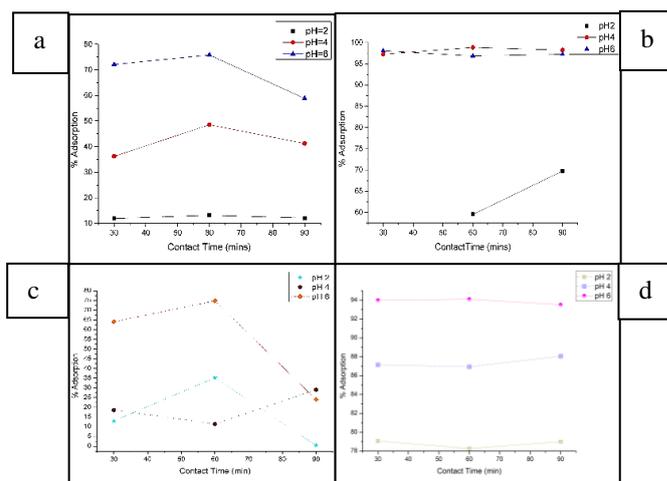


Fig. 3: Effect of pH on the Adsorption Capacity of a) Cu^{2+} using FE, b) Cu^{2+} using FE-nZVI, c) Pb^{2+} using FE and d) Pb^{2+} using FE-nZVI.

Based on **Fig. 3.c**, the amount of Pb^{2+} adsorbed by the FE tends to increase as the pH was increased from 2 to 6. The highest % adsorption from the figure is 74.86% wherein the samples conducted here occurred at pH 6 for an initial concentration of 20 ppm and an adsorbent dosage of 40 mg.

From **Fig. 3.d**, it can be observed that the amount of Pb^{2+} adsorbed by the FE-nZVI tends to increase as the pH of the aqueous solution increased from 2 to 6. The highest amount of Pb^{2+} adsorbed was at pH 6 with 94.11

From the data gathered, the % adsorption of both the FE and FE-nZVI tend to increase as the pH of the solution increases. It occurred for both the remediation of the aqueous solution of Cu^{2+} and Pb^{2+} . In regards to the experiments conducted, the highest % adsorption occurred at pH 6 which is in accordance to most of the journals gathered regarding the topic at hand.

The diatomaceous earth utilized for this research has a close resemblance to that of montmorillonite which has been the subject of various journals, wherein it mostly stated that the adsorption of Cu^{2+} was possible through inner-sphere surface complexes at pH 5.90. The adsorption of Pb^{2+} is attributed to low ionic strength pH independent mechanisms that are consistent with complexation occurring in the outer sphere and high ionic-strength pH-dependent mechanisms consequent to complexes in the inner sphere where Pb^{2+} would form covalent bonds and be adsorbed at pH levels in proximity to 6.5. Their results indicate that monoatomic solutions that are acidic in nature are efficient for the adsorption of Cu^{2+} and Pb^{2+} wherein adsorption below pH 6 was dominated by precipitation which is quite common since both of the aforementioned heavy metals form oxides and hydroxides at pH levels below 5 [13].

3.5 Effect of initial concentration

Fig. 4.a shows that the lowest % adsorption is at 20 ppm under 60 minutes while the highest % adsorption lies on 10 ppm at a contact time of 10 minutes. The data revealed that the % adsorption ranges from 8 % to 65 %.

Fig. 4.b revealed that lowest % adsorption lies on 10 ppm at a contact time of 60 minutes while the highest % adsorption is on 20 ppm at 30 minutes contact time. The % adsorption is ranging from 67% to 98%.

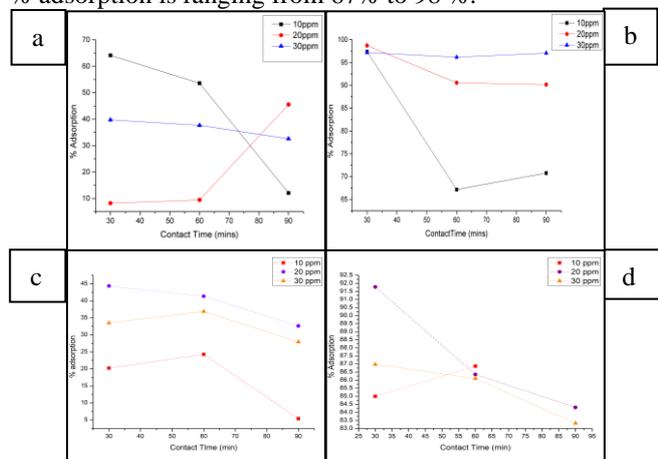


Fig. 4. Effect of Initial Concentration on the Adsorption Capacity of a) Cu²⁺ using FE, b) Cu²⁺ using FE-nZVI, c) Pb²⁺ using FE and d) Pb²⁺ using FE-nZVI

Fig. 4.c shows that the lowest % adsorption is at 20 ppm in 90 minutes of contact time while the highest % adsorption lies on 20 ppm at a contact time of 30 minutes. The data revealed that the % adsorption is ranging from 84% to 92%.

Fig. 4.d shows that lowest % adsorption is at 20 ppm in 60 minutes of contact time while the highest % adsorption lies on 10 ppm at a contact time of 10 minutes. The data revealed that the %age adsorption is ranging from 8% to 65%.

Based on the data gathered, using FE alone, as an adsorbent in removing heavy metals such as Cu²⁺ and Pb²⁺ in an aqueous solution, shows that the lowest and the highest % of adsorption lie in the same concentration. Immobilizing the FE by nZVI as adsorbent make some changes in the result of % adsorption in terms of initial concentration. It shows that the relationship of initial concentration to the % adsorption is inversely proportional.

Initial concentration is one of the efficient and effective factors of adsorption process. It can be shown from the analysis results that Pb²⁺ or other heavy metals removal rate decreased with the increase of their concentration [14].

At lower concentrations, the ratio of the adsorption sites of adsorbent to the molecules of heavy metals is huge and subsequently the fractional adsorption becomes independent of initial concentration. However, at higher concentrations, the available adsorption sites become fewer, and hence the %age adsorption of the heavy metals such as Pb²⁺ which depends upon the initial concentration, decreases [14].

3.6 Effect of adsorbent dosage

Based on **Fig. 5.a**, the adsorbent dosage of 60mg at 60 minutes has the highest % adsorption of 79.62%. It was also obtained that at conditions of pH 6 and an initial

concentration of 10ppm, the amount of Cu²⁺ adsorbed is 8.85mg/g.

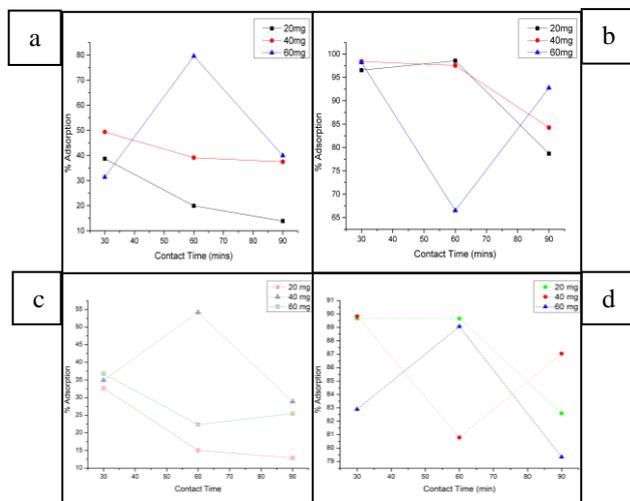


Fig. 5. Effect of Adsorbent Dosage on the Adsorption Capacity of a) Cu²⁺ using FE, b) Cu²⁺ using FE-nZVI, c) Pb²⁺ using FE and d) Pb²⁺ using FE-nZVI

Based on **Fig. 5.b**, the adsorbent dosage of 40mg at 30 minutes has the highest % adsorption of 98.41%. It was also obtained that at conditions of pH 6 and an initial concentration of 30ppm the amount of Cu²⁺ adsorbed by the FE-nZVI is equivalent to 56.77mg/g.

Based, **Fig. 5.c**, the adsorbent dosage of 40mg at 60 minutes has the highest % adsorption of 54.17%. The pH was 6 and the initial concentration was 10ppm. It was also obtained that the amount adsorbed by the Fuller's Earth is equivalent to 9.38mg/g.

Based on **Fig. 5.d**, the adsorbent dosage of 40mg at 30 minutes has the highest % adsorption which is 89.83%. It was also obtained that at conditions of pH 6 and an initial concentration of 30ppm, the amount of Pb²⁺ adsorbed is 20.6mg/g.

Adsorbent dosage is a significant factor affecting the adsorption capacity. The more dosage of nZVI or adsorbent added, the higher the efficiency of % removal [2], [15]. The highest % adsorption lies mostly between 40mg and 60mg using FE-nZVI on Cu²⁺, FE on Pb²⁺ and FE-nZVI on Pb²⁺ and FE for Cu²⁺ contact time of 60 minutes for FE and 30 minutes for FE-nZVI. Wherein if there is also specific contact time, there is an increase in the adsorption process [16]. 40mg and 60mg were still higher in value compared to 20mg. Also, the removal efficiency increased with the increase of material addition.

3.7 FTIR result

FTIR Spectra for the FE, FE-nZVI as well as changes after its adsorption of copper and lead were tested. Major adsorption bands for FE were observed to be at 3425.91cm⁻¹ and 1038.38cm⁻¹ indicating presence of Si-O-H and Si-O. Loading of nZVI on the surface of the clay weakened the adsorption band at 3426.16cm⁻¹. This suggests breaking of O-H bonds due to the presence of iron on its surface.

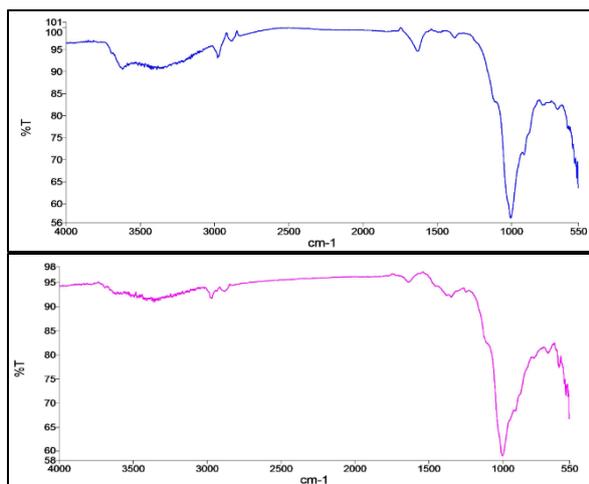


Figure 6: FTIR Spectra of FE(up) and FE-nZVI(down)

4 Conclusion

The SEM results show that the FE-nZVI were in the range of 80 – 120 nm, proving that it is classified as a nanoparticle while the XRD pattern obtained indicated that it is of close resemblance to another diatomaceous earth, Montmorillonite, for a peak of 41.8. The effect of three parameters, the pH, initial concentration of the heavy metal, and the adsorbent dosage, to the % adsorption was observed through the data gathered from the AAS. The results show that the pH is the most significant parameter that has the greatest effect on the % adsorption of both the FE and that of the FE-nZVI. Alongside with it is the interaction between the pH and that of the initial concentration which also greatly effects the adsorption of the concerned heavy metals. According to the results the greatest % adsorption is obtained at pH levels equivalent to 6 despite high initial concentrations. Between the two adsorbents used, FE-nZVI was able to adsorb more of the heavy metal than the FE alone. In terms of Pb²⁺, FE-nZVI was able to adsorb 20.6mg/g, which is almost three times more than that for FE can adsorb where to as for Cu²⁺, FE-nZVI was able to adsorb 56.77mg/g, which is approximately seven times more than that obtained by the FE. FTIR results indicate the presence of Si-O-H and Si-O on the FE as well as the presence of nZVI on the FE indicated by the weakened adsorption band at 3426.16cm⁻¹ which suggests the breakage of O-H bonds. The results also show the presence of the heavy metals after the adsorbents were utilized indicating that they were adsorbed on their surface. Peaks between the wavelengths of 3400cm⁻¹ to 3700cm⁻¹, indicate that the interactions involved in the adsorption process include alcohols and the siloxane groups. Based on the results, FE-nZVI has the capacity to be utilized as an adsorbent for Cu²⁺ and Pb²⁺ that would yield efficient results and is viable for further research into its properties.

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