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Synthesis and characterizations of nZVI-AC composites from coconut shells and its application for the adsorption of Pb(II) and Cr(VI) ions

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Abstract. The nanotechnology development has spread not only in developed country but also in developing country such as Indonesia. This technology can be used in the management of sustainable and environment friendly of soil water resources. The nanoparticle which has particle size in the magnitude of nanometer exhibit a great potent in the treatment of water, wastes and pollution. Nano zero valent iron (nZVI) although is a promising material for such application, suffer from drawback of easily forms aggregate which decrease its mobility and reactivity towards degrading contaminant. To overcome this disadvantage property, synthesis of composite containing nZVI and activated carbon from coconut shell was conducted. Among supporting materials which added to improve stability, reactivity and mobility of nZVI, activated carbon is the most feasible choice due to its high adsorption capacity, large surface area, porous structure and abundantly available. Composite of nZVI and activated carbon is expected to possess combined property i.e. high adsorption capacity and the ability of nZVI to degrade contaminant. Preparation was conducted via sulphate method using NaBH₄ reductor and FeSO₄ as Fe²⁺ source. The ratio of nZVI and activated carbon was made by 1:1, 1:2 and 1:3. Particle size of the composite was reduced to 200 mesh and shows surface area of 398.721 m²/g. Characterization methods was carried out by using gas sorption analyser, XRD, SEM/EDS and FTIR. The composite made with 1:3 ratio was used to adsorb Pb(II) and Cr(VI). Characterization result shows that nZVI-activated carbon was formed as confirm by XRD and SEM/EDS. The reduction percentage against Pb(II) and Cr(VI) are 99.7% and 99.6% and the adsorption capacity according to these metal ions are 124.6 mg/g and 124.55 mg/g respectively.

Keywords: nZVI, Activated Carbon, Composite

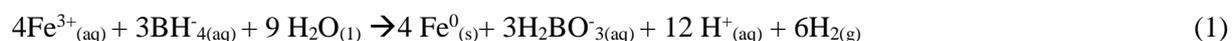
1. Introduction

Nano technology development has been spread widely to many countries not only to the developed country but also to the developing country such Indonesia. This technology can be utilized for a sustainable management of groundwater resources which is environmentally friendly [1]. The utilization of nanoparticles has been introduced widely by Nowack and Bucheli [2]. Nano material has different



chemical properties, molecular structure and size to a common material, due to large surface area. These properties may increase a chemical reactivity and improve the electronic ability of the material, besides a quantum effects such as optical and magnetic properties that dominate the material [3]. The applications of nanomaterial may have subjected to many fields such as in machinery, electronics, medical, energy and environmental remediation. Nanoparticle material has a large potential in water and wastewater treatment and air pollution control [4]. A research result from other scientist [5] that using a nano Zero Valent Iron (nZVI) to reduce the organics contaminant showed that not only the reactivity of nZVI increased due to improvement of surface area (33,5 m²/g for nZVI and 0,9 m²/g for micro-sized zero valent iron) but also reaction rate increased. This scientist result showed that nZVI is more reactive and effective as compared to micro-sized zero valent iron.

According to Muller and Nowack [6], there are many methods to synthesize nZVI particles. One of them is by reacting iron chloride with sodium borohydride in water, named as chloride method. The chloride method to synthesize nano zero valent iron had been mentioned as the first generation method to get nano - sized of iron [7]. In this method, 0.25 M sodium borohydride was slowly added to 0.045 M iron chloride hexahydrate in water, with volume ratio of 1 to 1 in an hour. The reaction occurs as follows:



Reaction above occurs as electron transferred from reducing agent to metal ion. To synthesize iron nanoparticle some factors may influence such as reactant concentration, capping agent, temperature and mixing. A chloride method is implementable in laboratory where fume hood is available to remove hydrogen gas produced during reaction. nZVI produced from this method is 10-100 nm in sized with specific surface area of 10-50 m²/g. In a dry state, nZVI is unstable and air-sensitive, so it need to store in an inert atmosphere. The effectivity and mobility of nZVI are the important factors. Reduction process in nZVI system is an oxidation-reduction reaction, where metal ion acts as an electron donor to reduce some contaminants to not harmful forms. As mentioned by Müller and Nowack [6], heavy metal will react into the initial state or to salt solution. If nZVI reacted to heavy metal of Pb, the reaction will occur as follows:



The ability of nZVI in reducing pollutant has been tested. The relatively unstable character of nZVI and its tendency to coagulate, decrease nZVI reactivity and mobility. Efforts had been carried out by several researchers to overcome this weakness. These efforts include combining nZVI with other metal (nZVI bimetal) or impregnating the material in an organic membrane. Activated carbon is an adsorbent with the advantage of high surface area, while nZVI shows high reactivity which make it a reductive adsorbent. Activated carbon can be used as supporting material with the ability to enhance nZVI stability, reactivity and mobility. It also has high adsorption capacity, large surface area, porous structure and can be obtained in low cost due to abundant raw material availability. Composite prepared from activated carbon and nZVI will produce combined property of high adsorption capacity and contaminant degradation ability which originates from activated carbon and nZVI respectively.

Synthesis of granular activated carbon and nZVI composite and its application on trichloroethylene degradation was reported by Tseng *et al.* [8]. Another author [9] reported using colloidal composite made from activated carbon with nZVI for in-situ remediation of soil water. Here, we reported synthesis of composite made from nZVI and activated carbon prepared from coconut shell by using sulphate method. This method required less borohydride compare to chloride method [5]. The activated carbon particle size used was 200 mesh whereas Tseng used granular activated carbon [10]. Synthesis of nZVI - activated carbon to form composite was carried out to make nZVI has large surface area by using the surface of activated carbon in addition to reductive property of nZVI which was used in contaminant degradation. The composite form will reduce nZVI drawback i.e. agglomerate easily which decrease its mobility and reactivity.

2. Materials and methods

2.1. Synthesis of nZVI-Activated carbon

Nano zero valent iron (nZVI) can be synthesized by reducing Fe^{2+} or Fe^{3+} using NaBH_4 reductor [5, 10, 11]. Here, we used FeSO_4 as Fe^{2+} source and NaBH_4 as reductor agent. The precursor materials were made in 1:1; 1:2 and 1:3 ratio. The particle size of activated carbon was 200 mesh possessing surface area $398.721 \text{ m}^2/\text{g}$ as reported in previous article [12]. 20 g FeSO_4 was dissolved in 500 mL distilled water mixed with ethanol in 3:2 ratio. The mixture of distilled water and ethanol was flowed with nitrogen for 30 minutes to remove oxygen dissolved prior used in the synthesis procedure. The FeSO_4 suspension was stirred by using magnetic stirrer at 650 rpm. The activated carbon which has been prepared was poured into FeSO_4 suspension while maintain stirring process and then oxygen was flowed for 15 minutes. Sodium borohydride was added stepwise (2 g of sodium borohydride in 50 mL distilled water) and stirred for several minutes. The resulting composite was washed using distilled water until neutralized and then washed using ethanol to flush the remaining distilled water within the composite. The characterization of composite was conducted by using AAS, XRD, SEM/EDS and FTIR spectrophotometer.

2.2. nZVI-activated carbon composite application to Pb(II) and Cr(VI) solution

nZVI-activated carbon composite used in this research is one with largest surface area. Artificial solution of Pb(II) and Cr(VI) at concentration 50 mg/L were placed into 5 separate 100 mL flasks and then added with the composite each by 10, 20, 30, 40 and 50 mg. The suspension was stirred at 130 rpm for 75 minutes then the composite was separated magnetically. Remaining Pb(II) and Cr(VI) in the solution was determined using AAS.

3. Results

Surface area of nZVI-activated carbon composite was calculated according to BET adsorption isotherm data which measured by Nova Instruments using nitrogen adsorbate. The composite with 1:1 ratio shows surface area $153.094 \text{ m}^2/\text{g}$; while 1:2 and 1:3 ratio has $254.363 \text{ m}^2/\text{g}$ and $270.846 \text{ m}^2/\text{g}$ surface area respectively. The composite at all nZVI to activated carbon ratio has larger surface area compare to nZVI alone as reported by Yusmartini and Setiabudidaya [11] i.e. $17.229 \text{ m}^2/\text{g}$. The increase of surface area represents porosity change within activated carbon inner structure. As amount of nZVI impregnation increased, the activated carbon surface area is decreased proportionally. The change in surface area confirms the impregnation of Fe^{2+} into activated carbon pore and reduction by NaBH_4 which caused pore blocking and surface area to decrease [8]. The surface area of activated carbon after being composite with nZVI is decreased. The particles of nZVI on the other hand is being spread on activated carbon surface and pores hence enhancing its area. Overall, the amount of adsorbed species is increased in larger surface area whilst the reductive character of nZVI is enhanced after being composite with activated carbon. Sun *et al.* [10] obtained surface area of nZVI $14.5 \text{ m}^2/\text{g}$ which is similar to what had been reported by Crane *et al.* [13]. Based on this result, it is can be concluded that the surface area of composite is larger than nZVI alone. The composite has surface area at interval $153.094\text{-}270.846 \text{ m}^2/\text{g}$.

XRD measurement on the nZVI-activated carbon composite was conducted to identify crystalline phase of the material. The diffractogram of composite is shown on Fig. 1. All composite of difference ratio shows characteristic 2θ at 46.4° which correspond to 110 reflection. The correspond 2θ reflection indicates the existence of nZVI phase within nZVI-activated carbon composite. The composite made with 1:3 ratio shows highest intensity on this 2θ reflection. All composite made with all ratios also shows 2θ reflection at 24° and 36° [13, 14] which is not appears on nZVI. Both reflection at these 2θ is intense and confirm by JCPDS 74-2330 data reference [14]. The XRD diffractogram of composite result proved the formation of nZVI phase and activated carbon phase.

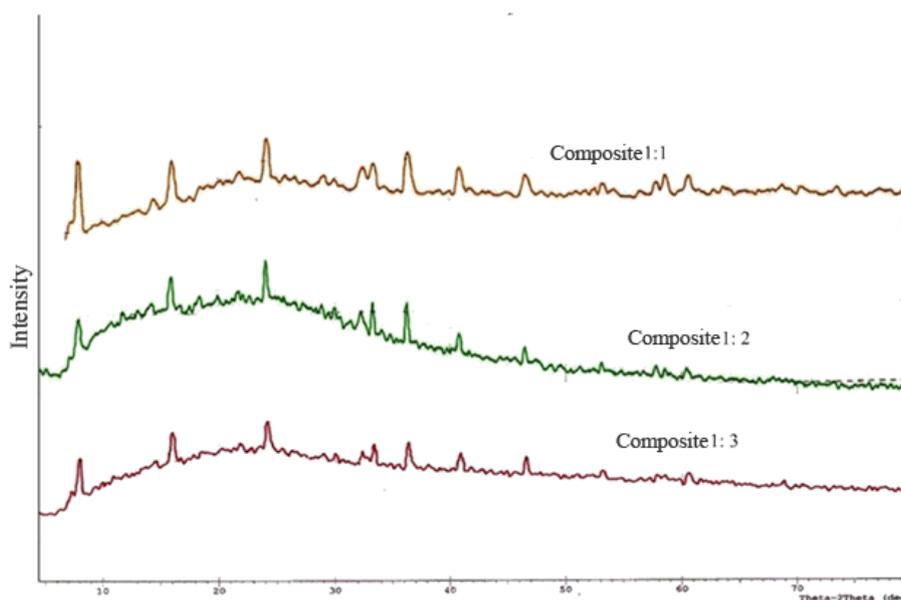


Figure 1. XRD patterns of nZVI and nZVI-activated carbon composites.

SEM figures of composite with precursor ratios of 1:1, 1:2 and 1:3 in magnification of 10.000x are shown in Fig. 2, to show the morphological structures of composites.

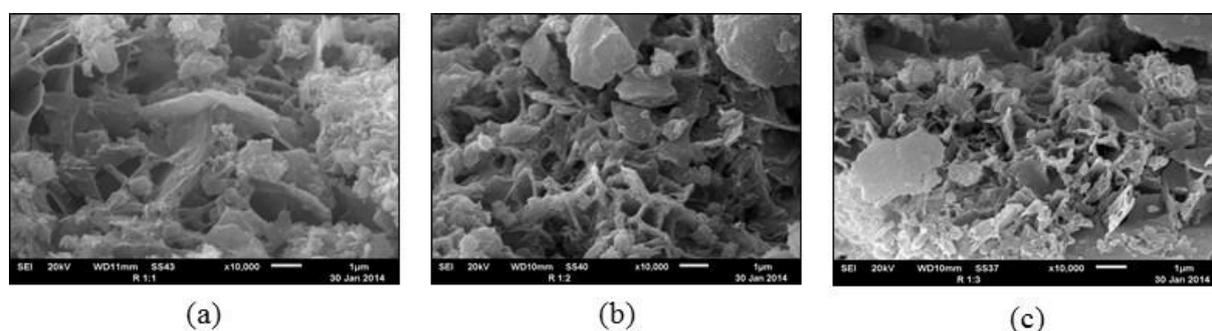


Figure 2. a) SEM figures of composites with ratios of 1:1, b) 1:2 and c) 1:3.

SEM image indicates nZVI is distributed on activated carbon surface at all composite prepared. The nZVI adhere to activated carbon surface and no aggregation appears on SEM image. The nZVI is coated by activated carbon and creates electrostatic repulsion which causes the nZVI particle to keep apart hence no aggregation is observed [15]. At higher ratio of activated carbon within composite, the amount of Fe adhere to surface becomes lower. EDS analysis provides quantitative percentage of elements comprises the composite. The results of EDS analysis for composite at all ratio is shown on Table 1.

Table 1. Percentages of constituent elements of nZVI-activated carbon.

Sample	Elements (%)		
	Fe	C	O
Composites nZVI-AC 1:1	59.7	16.4	23.9
Composites nZVI-AC 1:2	35.19	40.82	23.97
Composites nZVI-AC 1:3	19.84	55.74	24.43

Table 1 informs the composition of composite made from all variation of ratio consist of mainly C and Fe which is in accordance with XRD result. The composite of all ratio has O content at 23.9-24.43% while Fe at 59.7 – 19.84%. Other authors reported a different result [16] i.e. nZVI with 87.72% of Fe; 12.28% of O and 72.11% of Fe and 20.66% of O. The amount of Fe within activated carbon composite correspond to the variation of ratio used in the preparation step i.e. 1:1 ratio shows highest Fe content whereas at 1:3 ratio, Fe content smaller than carbon content. At 1:2 ratio, Fe and carbon appear in similar percentage. The combination of activated carbon adsorption capacity and reductive adsorbent of nZVI attain result as expected for all ratio variation as confirm by characterization result.

FTIR spectra has been done to confirm the functional groups of nZVI, activated carbon and nZVI-activated carbon composite. The FTIR characterization of carbon before and after activation, nZVI and composite with precursor ratios of 1:1, 1:2 and 1:3 has been done in wavelength range of 500-4000 cm^{-1} . FTIR spectrophotometer results are showed in Fig. 3, which is carbon without activation shows peaks at 1595.22 cm^{-1} with C-H peak at 749.14 and C=C peak at 1595.22 cm^{-1} . No bonded oxygen in carbon without activation process showed that carbonization process of coconut shells at 700°C had been completed, even though hydrogen bonded is still exist at peak 300-3500 [17].

For the activated carbon, peaks are showed from 688.11 to 1714.51 cm^{-1} . Peaks at around 1650-1500 cm^{-1} show the vibration bond of C=C from the aromatic groups in activated carbon [18]. In activated carbon spectra, C=C bond shows at 1584.13 cm^{-1} with high intensity. Peaks at around 1690-1760 cm^{-1} show C=O bond from carbonyl group such ketones in activated carbon structure, where vibration bond of C=O shows at 1714.51 cm^{-1} .

Fig. 3 showed high and broad intensity of nZVI peak at around 3200-3600 cm^{-1} with composite ratios of 1:2 and 1:3. This peak shows the vibration bond of O-H groups in nZVI and composite ratios of 1:2 and 1:3, due to air and moisture affected the samples during measurement. Meanwhile, this peak does not show up in carbon before and after activation. From the FTIR results, it can be concluded that activated carbon has been carbonized completely where during the activation process most parts of volatile matter has been disappeared at H_2SO_4 soaking, heating and washing steps [18].

FTIR spectra of nZVI in Fig. 3 shows peak at 618.29 cm^{-1} where in carbon before and after activation does not showed this peak. According to Al-Swaidan and Ahmad [17], the existence of peak around 620 - 400 cm^{-1} shows metal vibration to O groups (Fe – O). From the composite of ratios 1:2 and 1:3, metal vibration to O group shows at 618.29 cm^{-1} , while at composite ratio of 1:1 is shifted to 624.93 cm^{-1} . The vibration of Fe and O shows that nZVI has formed composite to activated carbon.

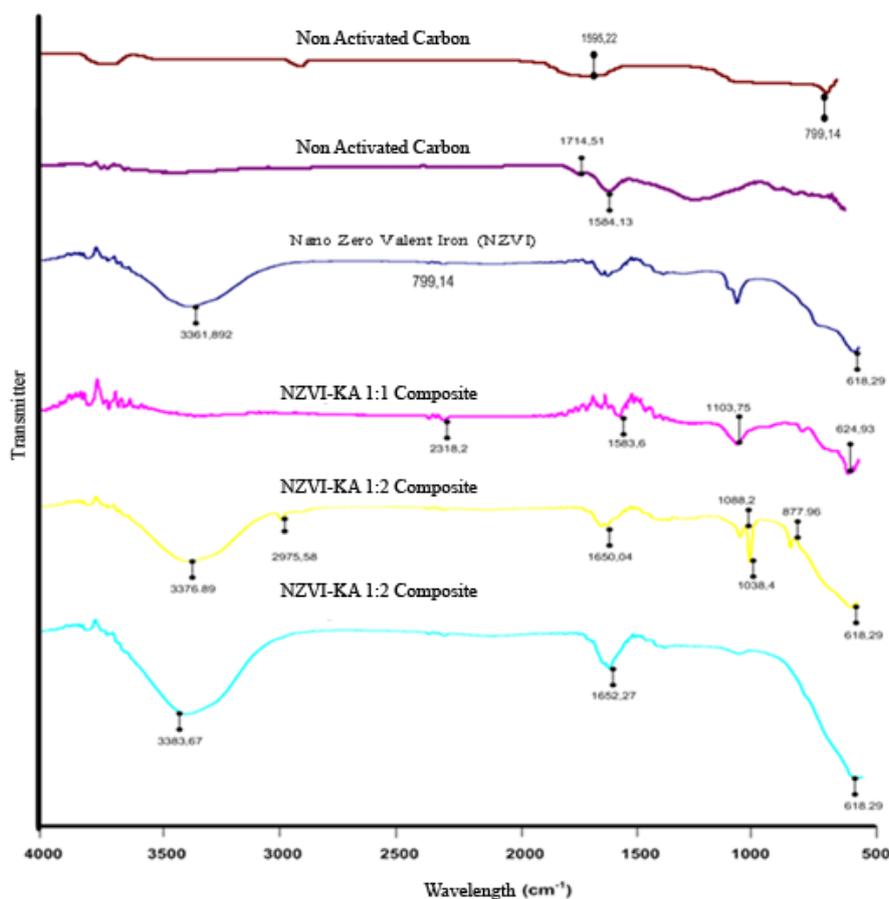


Figure 3. FTIR spectra of nZVI-activated carbon composites.

Reduction percentage was effected mainly by the amount of adsorbent. The more amount of adsorbent added, the more Pb and Cr ion reduced and increased in reduction percentage. In the application, the ratio adsorbent used to volume of wastewater need to justify, to calculate the maximum reduction percentage, so by only using small amount of adsorbent may give a maximum result. To test the adsorption capacity of nZVI-activated carbon composite with ratio 1:3, metal pollutant using artificial solution of Pb(II) and Cr(VI) has been used. Composite made from 1:3 ratio was chosen base on larger surface area compare to other variation ratio i.e. 1:1 and 1:2. The diffraction intensity also shows highest count on composite from 1:3 ratio. This test is also to measure the reduction percentage of heavy metal. Reduction percentage is to show how much concentration of heavy metal adsorbed to composite per initial concentration of heavy metal. In every measurement, Pb(II) and Cr(VI) volume is 100 mL with composite amount of 10, 20, 30, 40 and 50 mg. In Fig. 4, the initial concentration of Pb(II) and Cr(VI) is 50 mg/L, respectively. A maximum reduction percentage reached by using composite amount of 40 mg, with percent reduction of Pb(II) and Cr(VI) are 99.7 % and 99.6 %, respectively. Adsorption capacity of 40 mg composite for Pb and Cr adsorption are 124.6 mg/g and 124.55 mg/g. Research of [19] using nZVI to adsorbed Cr(VI) ion has maximum reduction percentage of 50 mg/L at nZVI amount of 50 mg.

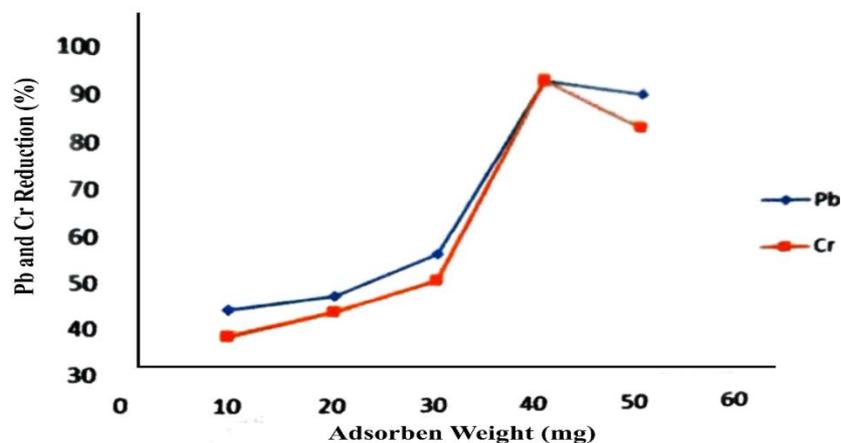


Figure 4. Effects of amount of composite to the reduction of Pb(II) and Cr(VI) solutions.

4. Conclusions

The characterization of nZVI-activated carbon composite made with 1:1, 1:2 and 1:3 ratio show that the highest diffractogram intensity of nZVI phase at $2\theta=46.4^\circ$ obtained by 1:3 ratio whereas reflection angle of 2θ for activated carbon shows intensity at 24° and 36° . SEM/EDS and FTIR support the existence of nZVI - activated carbon composite. The reduction percentage of Pb(II) and Cr(VI) are 99.7% and 99.6% and the calculated adsorption capacity for these metal ions are 124.6 mg/g and 124.55 mg/g.

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