Synthesis of composite nanostructure natural ZrO$_2$ and magnetite particles (Fe$_3$O$_4$@ZrO$_2$) and study of its lead ion adsorption efficiency

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Abstract. The potential of zircon minerals in Indonesia, especially in Central Kalimantan, has not been adequately explored and developed into valuable materials with high technical and economic value and environmentally friendly. This research has the potential to be processed and formed into advanced materials, seeing its high potential as an excellent adsorbent for anions/cations in water treatment and industrial wastewater. This research aims to develop raw zircon minerals into zircon oxides, which will later be composited with magnetic nanoparticles. The zircon mineral processing is carried out using hydrothermal methods. It is known that the physical and mechanical characteristics are suitable to be developed by having good reusability and durability as advanced materials. The adsorbent characterizations of FTIR, SEM, and XRF analysis showed that the Fe$_3$O$_4$@ZrO$_2$ had many different functional groups and a high specific surface area for adsorption processes. The Fe$_3$O$_4$@ZrO$_2$ showed high adsorption uptake capacity and selectivity for the lead in the Sasirangan textiles wastewater. Therefore, the Fe$_3$O$_4$@ZrO$_2$ have the potential to be used as an adsorbent in water and wastewater treatment.

1. Introduction

In Indonesia, zircon minerals are often found on land, oceans, coastlines, and rivers. These zircon minerals are found together with calciterite, electro minerals such as gold and silver, and others minerals like ilmenite, magnetic, monalacite, xenotime, pyrite, sulfide and silica. Economically, zircon minerals are found in granules, which are breakdown of acid and metamorphic igneous rocks that are then transported, concentrated and sedimentated together with zircon grains including calciterite (the main mineral of tin), rutile, ilminite, pyrite, magnetic, gold and iron oxide. Zircon minerals have great potential to be used and developed in various applications, for example: fuel cells, electro and energy catalysis, protective coatings for optical glass and filters, nano-electronics, microelectronics, ceramic biomaterials, thermo-luminescence UV dosimeters, piezoelectric manufacturing, electro-optic, dielectric, nano-composites and nanocapping materials and other industrial applications [1, 2].

Currently, zirconium and its oxides are widely used in water treatment and purification applications using various methods to synthesize ZrO$_2$-based nanostructures with different physicochemical
properties [3-5]. Ehrlich et al. synthesized zirconium dioxide nanostructures with a hydrothermal template of chitin and had good potential from these zirconium-chitin composites for different applications. However, one of the factors limiting the use of pure chitin is its relatively low mechanical strength [6]. Ciesielczyk et al. synthesized micrometric ZrO$_2$@SiO$_2$ binary oxide through the sol-gel method [7]. The results showed that the adsorption and release capabilities of the synthesized material were significantly influenced by the number of surface functional groups and the porosity of the material. In another recent study, MgO@ZrO$_2$ oxide material was synthesized via the sol-gel method, which showed good adsorption due to the high surface area of the synthesized material. Wang et al., conducted research on the synthesis of a nano-zero-iron-reduced-zero graphite oxide composite and hydrated zirconium-oxide nanocomposite using a graphene oxide (GO) template due to its superior mechanical properties and high surface area [1, 8]. ZrO$_2$ nanosheets have a higher surface area, more active sites and a porous structure for better adsorption applications.

In addition, magnetic nanoparticles have attracted great interest research in recent years as adsorbents to remove and recover pollutants from water because the use of magnets provides a very simple and effective method of separating particles from water. But because of the possible oxidation of Fe$^{2+}$ in the structure of magnetite in air, the limited types of pollutants that have magnetite, and a relatively low adsorption capacity, the modification of the surface of magnetite for use as magnetic adsorbent for attraction is investigated intensively [9-11]. This research conducted similarly with our previous work using the one-step synthesis hydrothermal and application of magnetic adsorbents which have the advantage of not being easily oxidized, magnetic composite nanoparticles with biomass fibers and chitosan to remove and recover anions from Municipal Water Work water sources, artificial and industrial wastewater with relatively high concentrations [12-14]. The results obtained indicate that the resulting material has a high adsorption performance for pollutants (anions and cations in terms of adsorption capacity, selectivity, and kinetics. However, the mechanism is still poorly understood and its potential applications in natural water and industrial wastewater with relatively low anion concentrations. It is hoped that the zircon oxide composite with magnetic nanoparticles (Fe$_3$O$_4$@ZrO$_2$) using in this research which is applied to drinking water treatment can provide a real contribution to the treatment of household or industrial wastewater containing other ions and dissolved species.

2. Materials and Methods

2.1. The synthesis of zircon mineral with magnetic nanoparticles composites
The synthesis of zircon mineral composites and magnetic nanoparticles was carried out by means of a one-pot solvothermal reaction (Irawan et al. 2018b). Initially anhydrous sodium acetate (1.6 g) and FeCl$_3$.6H$_2$O (0.8 g) were dissolved in ethylene glycol (24 mL), the mixture was heated at 60 oC while stirring (100 rpm) until the solution was homogeneous and colored orange. The zircon mineral (1 g) is added to the mixture and left for 20 minutes, then poured into a solvothermal reactor. The reaction lasts for 6 hours at 200 oC. After the reaction has been achieved, it is cooled down at room temperature. The resulting composites are washed with distilled water until the solution is clean from the rest of the other chemicals. Subsequent washing with ethanol (50%) for 3 times. To simplify the washing process, magnets are used to separate the composite from the mixture. The resulting composites are stored in distilled water for the next stage of use, the purpose of which is storage in distilled water is to avoid the oxidation process with air. On the other hand, to modify the amino functional group on the composite surface was added 1,6-hexanediadmine to the mixture (7 mL) before entering the reactor.
2.2. The batch adsorption experiment
The adsorption process by batch experiment was carried out by taking a sample of 50 mL of Sasirangan textile-containing lead wastewater which was placed in a 100 mL glass bottle and the pH value was adjusted to 1 M NaOH or 1 M HCl. A certain amount of adsorbent is put into the glass bottle. The mixture is then placed in a shaker with a stirring speed of 100 rpm, for a certain contact time at room temperature and then samples are taken for analysis. The adsorption experiments were done in triplicate samples and the average value was taken. The data from the experiment were fitting and figure out by Sigma Plot® version 10 of software.

3. Results and Discussion

3.1. Characterization of Fe₃O₄@ZrO₂ composites
The structure morphology properties and chemical composition properties of Zircon mineral and Fe₃O₄@ZrO₂ composites have been characterized using scanning electron microscopy (SEM, JOEL JSM-6500F) with energy-dispersive X-ray spectroscopy (EDAX) and elemental analysis by Energy Dispersive X-ray Fluorescence (XRF, PANalytical's MiniPal 4 energy-dispersive EDXRF bench-top spectrometer) to conclude the identity and quantities of the elements in samples.

Typical SEM images of a representative sample show the smooth surface of the zircon mineral (Fig. 1a). The Fe₃O₄@ZrO₂ composites revealed the round-shaped magnetic nanoparticle along zircon surface with diameter size in the range of 20–30 nm when FeCl₃·6H₂O was included in the reaction solution. In addition, due to the presence of magnetic nanoparticles that covered space layer of zircon, the color of composites is dark-brown (Fig. 1b).

![Figure 1](image)

Figure 1. SEM images of (a) Zircon mineral and (b) Fe₃O₄@ZrO₂ composites

| Sample                 | Chemical composition (Percentage of mass, %) |
|------------------------|---------------------------------------------|
|                        | SiO₂  | Fe₂O₃ | ZrO₂   | HfO₂  | Other |
| Zircon mineral         | 28.21 | 10.80 | 58.95  | 1.28  | 0.76  |
| Fe₃O₄@ZrO₂ composites | 0.5   | 66.26 | 32.0   | 0.69  | 0.55  |

Table 1. Elemental analysis of zircon mineral and Fe₃O₄@ZrO₂ composites measured by XRF
The XRF data provide evidence of the chemical composition of each the adsorbent in Table 1, respectively. It illustrates that the major component are Si, Fe, and Zr. It can only determine the total amount of chemical composition in each sample. These data show that the zircon mineral dominated by Zr, Si then Fe, while the Fe$_3$O$_4$@ZrO$_2$ composites dominated by Fe, Zr then Si that seem similar to zircon but the amount of element increased when combined each other. Therefore, these materials of the samples are identical. It illustrates that XRF cannot differentiate between the chemical compositions in the samples. Still, it can only determine the total amount of Si, Fe and Zr as a major component in the samples.

3.2. Batch Adsorption Studies

The effect of contact time on the adsorption of lead onto Fe$_3$O$_4$@ZrO$_2$ composites as adsorbent was examined by conducting an experiment at room temperature, initial lead concentration of ca. 60 mg/L, adsorbent dose of 0.5 g/L, and shaking rate of 100 rpm. Fig. 1a shows that during the first 60 minutes, lead uptake capacity increased significantly from 0 mg/g to 108 mg/g, which was probably due to the diffusion taking place into the pores and or adsorption onto the surface of the adsorbent. Initially, the lead concentration gradient was relatively high diffusing into and through the pore of the adsorbent. Afterward, the lead uptake capacity slightly increased to lead uptake capacity of 112 mg/g and being constant until reached equilibrium condition within 6 hours. The equilibrium adsorption experiments were conducted in 6 hours of reaction time.

Figure 2. Pb adsorption capacity of (a) The effect of contact time (pH$_e$ of 7.0±0.2) (b) The effect of equilibrium pH (6 hours), at room temperature, stirring rates of 100 rpm, adsorbent dose of ca. 0.5 g/L, respectively.

Several investigators reported that lead adsorption process usually pH-dependent and found optimum pH range of lead removal on the different adsorbents such as activated carbon [15], nanozirconium silicate [16], Fe$_3$O$_4$@BDC@AGPA nanocomposites [17] and magnetic nanoparticle coated montmorillonite [14]. Fig. 2a shows that pH affected lead adsorption density over a wide pH range of 3.0 - 9.0. The uptake adsorption capacity is relatively low at lower pH. However, increasing equilibrium pH, a significant enhancement in adsorption uptake capacity, is recorded. The optimum pH for Fe$_3$O$_4$@ZrO$_2$ composites as adsorbent was found to be 7.0±0.2, with the uptake capacity of about 110 mg/L Pb(II). At lower pH, Pb(II) uptake decreased because the adsorbent’s surface area was more protonated and competitive adsorption occurred between H$^+$ protons and free Pb(II) ions and their hydroxides towards the fixation sites. Therefore, H$^+$ ions react with anionic functional groups on the surface of Fe$_3$O$_4$@ZrO$_2$ composites and results on the reduction of the number of binding sites available for the adsorption of Pb(II). The amount adsorbed increased as pH increased from 3.0 to 9.0.
This increase may be due to the presence of negative charge on the adsorbent's surface that may be responsible for metal binding. However, as the pH is lowered, the hydrogen ions compete with the metal ions for the sorption sites in the sorbent; the overall surface charge on the adsorbent becomes positive, and hinds the binding of positively charged metal ions. At pH 9.0, a decrease in Pb(II) adsorption was observed due to the formation of soluble hydroxyl complexes. It could also increase concentration of hydroxyl ion (OH\(^-\)) which intermolecular competitiveness with lead ion for the Fe\(_3\)O\(_4\)@ZrO\(_2\) composites surface site adsorption and depressed the lead uptake capacity. The excess of hydroxyl ions surrounding the adsorbent's binding sites was made the adsorption process unfavourable and leading to precipitated was observed.

Moreover, the force acting between the neutral charge of lead (Pb(OH)\(_2\)) and the surface is the weaker van der Waals interaction due to the attractive force between molecular activities with one another or with neutral molecules. The lowest of molecular interaction and these interactions appear because molecules have an unsymmetrical electronic distribution that creates small dipoles that can induce complementary dipoles in the neighboring surface, which depend on the molecule's orientation respect to the surface of the adsorbent.

4. Conclusions
The Fe\(_3\)O\(_4\)@ZrO\(_2\) was successfully synthesized using a one-pot hydrothermal process. It showed high selectivity adsorption uptake capacity up to 110 mg/g for the lead in the Sasirangan textiles wastewater at room temperature, pH\(_4\) of 7.0±0.2, stirring rates of 100 rpm, adsorbent dose of ca. 0.5 g/L. The adsorption mechanism of lead adsorption by Fe\(_3\)O\(_4\)@ZrO\(_2\) was a combination of electrostatic attraction and Van der Waals interaction, whereas at pH above 7 was precipitated. Therefore, the Fe\(_3\)O\(_4\)@ZrO\(_2\) has the potential to be used as an adsorbent in water and wastewater treatment.

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