



Adsorption of mercury(II) on dithizone-immobilized natural zeolite



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ABSTRACT

Adsorption of Hg(II) ions onto selective adsorbent of dithizone-immobilized natural zeolite (DIZ) from Wonosari, Yogyakarta, Indonesia has been investigated in batch mode. Some parameters influencing immobilization of dithizone and adsorption of Hg(II) were optimized including effect of temperature and reaction time on the effectiveness of dithizone immobilization as well as effect of pH, contact time and initial concentration of Hg(II) ion on the efficiency of the Hg(II) adsorption. Preliminary application of the adsorbent in the removal of Hg(II) ion in river water spiked with Hg(II) was also studied. The FT-IR and XRD analytical results show that the surface of natural zeolite can be modified by immobilization of selective organic ligand towards Hg(II) ions. The optimum conditions for the adsorption of Hg(II) is achieved at pH 5 and 90 min of contact time. Kinetics and adsorption isotherm studies suggest that the capacity, affinity and selectivity of the DIZ in adsorbing hazardous metal ions such as Hg(II) is significantly improved compared to those of non-immobilized activated natural zeolite (AZ). The Hg(II) adsorption capacity for AZ and DIZ at optimum condition is 8.0 and 13.1 $\mu\text{mol/g}$, respectively and the both adsorption follows first-order reaction. It has also been demonstrated that the DIZ adsorbent may be applied in the removal of Hg(II) ion in the river water spiked with Hg(II) ion up to 99.36% from the initial concentration of 8 mg L^{-1} in two serial batch adsorptions.

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1. Introduction

Many toxic heavy metal ions have been discharged into the environment as industrial wastes, causing serious soil and water pollution [1]. Mercury (Hg), lead (Pb), copper (Cu), iron (Fe), and chromium (Cr) are common metals that tend to accumulate in organisms, causing numerous diseases and disorders [2]. Hg(II) has especially received increasing attention as a serious pollutant due to its toxicity and bio-accumulative properties. In aquatic system, mercury can be converted by bacteria to methyl mercury, which can be magnified hundreds of thousands of times through aquatic food chain, posing a potential risk to humans and wildlife in the aquatic that consume fish. The major resources of mercury pollution in the aquatic are industries including electrical and medical equipment (batteries and thermometers), paint and color industries, catalyst, fungicides or pesticides. In addition, coal combustion, geothermal gas and waste incineration emit large quantities of mercury into the atmosphere [3]. Numerous processes exist for removing dissolved heavy metals, including ion exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis, and electro dialysis [4]. However, these methods

generally require high cost and technology, thus making it not suitable for developing countries like Indonesia. Therefore, the use of alternative low-cost materials as potential sorbents for the removal of heavy metals has been increasing recently [5,6].

Zeolites are naturally occurring hydrated aluminosilicate minerals. They belong to the class of minerals known as “tectosilicates”. Most common natural zeolites are formed by alteration of glass-rich volcanic rocks (tuff) with fresh water in playa lakes or by seawater [7]. The structures of zeolites consist of three-dimensional frameworks of SiO_4 and AlO_4 tetrahedra. The aluminum ion is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms, and the isomorphous replacement of Si^{4+} by Al^{3+} produces a negative charge in the lattice. The net negative charge is balanced by the exchangeable cation (sodium, potassium, or calcium). These cations are exchangeable with certain cations in solutions such as lead, cadmium, zinc, and manganese [8,9]. The fact that zeolite exchangeable ions are relatively innocuous (sodium, calcium, and potassium ions) makes them particularly suitable for removing undesirable heavy metal ions from industrial effluent waters. However, like many other natural adsorbents, the adsorption of zeolite towards metal ions is not selective, especially when alkaline and alkaline-earth metal ions are also available in the solution in high level of concentrations. Therefore, modification of the surface of natural adsorbents including zeolite is

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frequently done using a specific and sensitive ligand for heavy metal ions to enhance the capacity and selectivity of the adsorbents [10,11]. For example, some host materials has been used for immobilization of sugarcane bagasse waste biomass for biosorption of chromium [12] and *Mangifera indica* waste biomass for biosorption of Pb(II) [13]. Moreover, pre-treated biomaterials such as *rosa bourbonia* phyto-biomass for removal of Pb (II) and Cu (II) [14], groundnut (*Arachis hypogaea*) shell for divalent ions [15] as well as lemon grass (*Cymbopogon citratus*) for Pb(II), Cd(II) and Zn (II) ions [16] also has been reported as promising adsorbents of heavy metal ions. Meanwhile, Asasian et al. has reported elimination of mercury by adsorption onto activated carbon prepared from the biomass material [17].

Dithizone (diphenylthiocarbazone) is a suitable ligand for such purposes because it contains several *N*-donor atoms, —NH as well as —SH groups which is excellent for analytical and spectroscopic applications. This compound is also very specific for chelating heavy metal ions such as Pb(II), Cd(II), Cu(II) and Hg(II) [18,19]. Therefore, it is quite reasonable to use this chelating compound as modifying agent in the surface of various adsorbent materials such as alumina [20], polymer poly (EGDMA-HEMA) microbeads [10] and silica gel [11,21,22]. The immobilization of dithizone onto the surface of the above polymer as well as silica gel has been reported to be successfully used for the removal and selective pre-concentration of heavy metals.

The aim of this study is to prepare a mercury-selective adsorbent by immobilization of dithizone onto the surface of zeolite and to study its adsorption characteristics towards mercury (II) ion. The modified adsorbent is intended to be used for the adsorption of mercury pollutant in industrial liquid waste as well as the supporting material in the solid-phase extraction process for pre-concentration of mercury ion. Dithizone has been selected as the organic ligand in this study because this ligand is very selective for Hg, Cd and Pb. In this study, we use natural zeolite from Wonosari, Yogyakarta, Indonesia as a supporting material for the immobilization of dithizone because it is easily obtained in Indonesia and its price is cheaper than the synthetic polymer or silica gel.

2. Materials and methods

2.1. Materials

Mercury(II) chloride salts (HgCl_2) and dithizone (1,5-diphenylthiocarbazone) were purchased from Merck, Germany. Natural zeolite was obtained from Wonosari, Yogyakarta, Indonesia. Zeolite activation and dithizone immobilization were prepared and characterized according to previously reported procedure [23,24]. Organic solvents were of reagent grade and used as received. For all solutions, double distilled water was used and the buffer solutions were prepared by mixing citric acid and sodium citrate for $\text{pH} < 7$ and sodium dihydrogen phosphate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$) and sodium hydrogen phosphate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$) for $\text{pH}: 7-9$ and the pH -value of the resulting solution was checked by pH -meter.

2.2. Instrumentations

The pH measurements were conducted by a TOA pH meter model HM5B calibrated against two standard buffer solutions of pH 4.0 and 9.2. Infrared spectra of natural zeolite and dithizone-immobilized zeolite were measured from KBr pellets by a Shimadzu FT-IR/8201 PC spectrophotometer. Mercury(II) determination was performed by a GBC 932 AA atomic absorption spectrophotometer equipped with GBC HG-3000 vapour generation accessory at Laboratory of Analytical Chemistry, Chemistry

Department, Gadjah Mada University, Yogyakarta, Indonesia. X-ray diffraction (XRD) spectra of natural zeolite and dithizone-loaded natural zeolite were recorded on Phillips model PW 3710 BASED XRD spectrophotometer (Shimadzu 6000X, radiation source: Cu, $\text{K}\text{-}\lambda$ 1.5402 nm).

2.3. Dithizone immobilization on zeolite

The following procedure which is analog to the previously reported procedure [22–24] was applied for immobilization of dithizone on the surface of zeolite. Zeolite (4.0 g) was added to 80 mL toluene and mixed with 1.0311 g dithizone in a 500 mL flask. The mixture was heated and stirred for 4 h and the temperature of the mixture was varied at 50, 70, 90 and 110 °C. The product was filtered and washed consecutively with toluene, ethanol and water several times until the filtrate showed no characteristic color of dithizone. The dithizone-immobilized zeolite (DIZ) was then dried in an oven at 70 °C for 6 h and filtered through 200-mesh filter. The obtained DIZ was then characterized and used for adsorption study.

2.4. Adsorption study

2.4.1. Effect of pH on the Hg(II) adsorption

The experiment was done by batch system. The adsorbent (20 mg, 200 mesh) was interacted with 10 mL of Hg(II) ion (5 mg/L) solution and the pH of the solution was varied from 3.0 to 9.0 using buffer solution. The mixture was stirred using horizontal shaker for 60 min. The mixtures was then filtered and the concentration of Hg (II) ion in the filtrate was determined by cold-vapor (CV) AAS. For a control solution, the same concentration of Hg(II) solution at corresponding evaluated pH was treated in the similar procedure but without the addition of adsorbent.

2.4.2. Effect of contact time on the Hg(II) adsorption

This experiment was carried out to evaluate kinetic aspects of Hg(II) ion adsorption on the DIZ adsorbent. A similar procedure to that described in the previous section (effect of pH) was applied but the stirring/contact time was varied from 5 to 180 min. The obtained data were then evaluated by modified Langmuir-Hinshelwood equation [16]:

$$\frac{\ln(C_0/C_A)}{C_A} = k_1(t/C_A) + K \quad (1)$$

where C_0 is initial concentration of metal ion and C_A is concentration of metal ion at equilibrium. Plot of $\ln(C_0/C_A)/C_A$ versus t/C_A gives the slope and *Y*-intercept equal to first-order adsorption rate (k_1) and adsorption equilibrium constants (K), respectively.

2.4.3. Effect of initial concentration of metal ions on the adsorption capacity

The effect of initial concentration of Hg(II) ions on the adsorption capacity of DIZ adsorbent was examined by conducting adsorption experiment in various concentration of Hg(II) ion. The similar procedure to pH effect study was applied but the concentration of Hg(II) was varied in the range of 0–10 mg/L. The obtained data were evaluated by Langmuir isotherm adsorption model (Eq. (2)) to determine adsorption capacity (*b*) and equilibrium constant (*K*).

$$\frac{C}{m} = \frac{1}{bK} + \frac{1}{b}C \quad (2)$$

where *C* is concentration of Hg(II) ion at equilibrium and *m* is mole of Hg(II) ion adsorbed by 1.0 g of adsorbent. The value of *K* was then

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