Capacity adsorbent of unmodified zeolite, zeolite@AuNPs and zeolite@AuNPs@MET against razor blade factory and wells

Nurdiani

Abstract

Many studies have been carried out to find an effective method for treating heavy metal waste, including chemical precipitation, ion exchange and reverse osmosis. These techniques are quite expensive and have several shortcomings, among others, which require a lot of reagents and produce toxic sludge or other waste products that require a separate exhaust system. The adsorption method is an easy and simple method for absorbing heavy metal ions. Zeolite can be used as an adsorbent for heavy metal ions because zeolite is a material that has a very regular crystal shape with cavities that are interconnected in all directions and makes the surface area of zeolite very large so it is very good to be used as an adsorbent. Unmodified zeolite has a low adsorption capacity. Modifying compounds which are immobilized will be better if they prefer to bond with only one or several specific metal ions so that the adsorption occurs more selectively. This study modified zeolite with gold metal ions and gold metal ions which were successfully immobilized synthesized using binahong (Anedera cordifolia) leaf extract. The selection of gold nanoparticles is based on their inert nature and is not easily oxidized. The gold nanoparticles stabilizing agent is used by mercaptoethanol ligand because it has a thiol group (RSH) which has high affinity for gold metal ions. Nurdiani et al. (2015) which successfully modified zeolite with gold nanoparticles (in situ synthesized with binahong leaf as reducing agent) and stabilized zeolite@AuNPs with organic substances mercaptoethanol acid ligands. The success of zeolite@AuNPs@MET modification needs to be tested for its adsorption power. This has been done on Mn$^{2+}$ solution and Fe$^{3+}$ solution as well as in razor blade factory and well water. Furthermore, compared to the unmodified zeolite, zeolite with modification of gold nanoparticles, and modification of zeolite@AuNPs@MET. The final step is to regenerate zeolite, zeolite@AuNPs and zeolite@AuNPs@MET by using Na-EDTA so that all adsorbents can be reused as adsorbents. The adsorption capacity of zeolite@AuNPs@MET adsorbent is better than the unmodified zeolite and zeolite@AuNPs with adsorption capacity sequence for Mn$^{2+}$ ions is zeolite@AuNPs@MET (0.664 mg/g) > unmodified zeolite (0.274 mg/g) > zeolite@AuNPs (0.229 mg/g), while for Fe$^{3+}$ ions are zeolite@AuNPs@MET (0.815 mg/g) > unmodified zeolite (0.805 mg/g) > zeolite@AuNPs (0.795 mg/g). The adsorption optimum condition of zeolite@AuNPs@MET with Mn$^{2+}$ ion adsorption capacity of 0.39 mg/g and 0.41 mg/g Fe$^{3+}$ ion was achieved in conditions of adsorbent weight of 0.10 grams, metal concentration of 5 mg/L and contact time 3 hours. Regeneration throughout the unmodified zeolite, zeolite@AuNPs, and zeolite@AuNPs@MET with Na-EDTA has been successfully carried out by order of the success of regeneration is unmodified zeolite > zeolite@AuNPs@MET > zeolite@AuNPs. The experimental data isothermal adsorption of Mn$^{2+}$ ion and Fe$^{3+}$ ion by a zeolite@AuNPs@MET tend to follow the Langmuir equation because the resulting coefficient of determination ($R^2$) greater than Freundlich equation with the value of 0.990 for the manganese ion and 0.990 for ferrous ion.

Keywords: adsorbent, adsorption capacity, zeolite@AuNPs@MET, central composite design

Introduction

Various studies have been done to reduce or even eliminate harmful heavy metals from industrial effluent before discharge to waters. Adsorption is a method that is often used because it’s easy and simple, also effective to remove heavy metal ions. Among the various types of adsorbents such as activated carbon, silica gel and zeolite, zeolite is the best material to use because it has in sequence crystal form with cavities interconnected in all directions. To improve the character of natural zeolite that can use as catalysts, absorbents, or other applications, typically performed prior activation and modification. Adsorbent is required to have a large surface area, also have to be selective. One of the method to increase the selectivity of the zeolite is by modifying zeolite surface and cavity by means of
impregnation with organic and inorganic materials. Zeolites can also be modified by combining organic and inorganic materials simultaneously as having been reported in the research conducted by Rohatin (2011) which successfully modified zeolite with gold nanoparticles (in situ synthesized with NaBH₄ as reducing agent) and stabilized zeolite@AuNPs with organic substances 3 mercaptopropanoic acid ligands can increase the adsorption capacity to Zn²⁺ ion 46%.

Metal nanoparticles can be synthesized by reducing the metal ions into metal atoms by chemical and physical methods. However, this method highly depends on chemical reagents that are harmful to the environment and needs higher temperature and pressure [4]. Recently, the need for synthesizing nanoparticles using environmentally friendly techniques is developing [5]. Nurdiani et al. (2015) which successfully modified zeolite with gold nanoparticles (in situ synthesized with binahong leaf as reducing agent) and stabilized zeolite@AuNPs with organic substances mercaptoethanol acid ligands. The success of zeolite@AuNPs@MET modification needs to be tested for its adsorption power.

Furthermore, in this research, compared to the adsorption capacity of unmodified zeolite, zeolite@AuNPs, and zeolite@AuNPs@MET on the manganese and iron ion solution and applied to the razor blade factory and water wells. The final stage is the regeneration of all types of adsorbent by using Na-EDTA in order that all the adsorbent can be reused. In addition, the optimum experimental conditions of zeolite@AuNPs@MET adsorbent defined by Response Surface Method and isothermal adsorption. Therefore, this research applies the adsorption method using zeolite@AuNPs @MET as an inexpensive and efficient alternative method for the treatment of waste of several heavy metal ions in the solution system.

Material and Method

This research was conducted in eight stages. The first stage is the physical and chemical activation of natural zeolites at a temperature of 70°C. The second stage is the optimization of making binahong leaf bioreductor for optimization of Au nanoparticle synthesis. The third stage was immobilization of gold metal ions into activated zeolites, and after gold metal ions were immobilized into zeolites, gold metal ions were synthesized into gold nanoparticles using binahong (Anredera cordifolia) leaf extract bioreductor to form zeolite@AuNPs. The fourth stage is planting mercaptoethanol (MET) ligands on zeolite@AuNPs so that zeolite@AuNPs@MET adsorbent is formed. The stages one through four follow the procedures that have been carried out by Nurdiani et al. (2015). The fifth step was the effectiveness test of unmodified zeolite adsorption, zeolite@AuNPs, zeolite@AuNPs@MET against standard solutions of Mn⁺, and Fe⁺ ions with a concentration of 10 mg/L and repeated three times. Measurement of metal content before and after being absorbed is read by a UV-Visible spectrophotometer. The sixth stage was the test of unmodified zeolite application, zeolite@AuNPs, zeolite@AuNPs@MET in razor blade factory and well water. Measurement of metal content before and after being absorbed is also read using a UV-Visible spectrophotometer.

The seventh stage was to obtain optimum adsorption conditions from zeolite@AuNPs@MET which included variations in adsorbent weight, variations in adsorbate concentration, and variation of contact time in two heavy metal ions, namely Mn⁺⁺ ion and Fe⁺⁺ ion by using Response Surface Method and repeated 3 times. The last step is to regenerate metal ion-unmodified zeolites, zeolites@AuNPs-metal ion and zeolites@AuNPs@MET- metal ion by using Na-EDTA so that they can be reused as adsorbents.

**Immobilization and synthesis of au nanoparticles in zeolites** [11]

A total of 15 mL 0.4 mM Au solution was pipetted into a beaker containing 1 gram of activated zeolite, the solution was stirred with a magnetic stirrer for one hour at a speed of 150 rpm then added 15 mL of binahong leaf extract as a reducing agent and 5 mL NaOH 0.05 N is then put into the microwave with 50 power for 2 minutes. Stirring continues for 6 hours and is deposited for 24 hours. The solid phase was dried in an oven at 105°C.

**Modification of zeolite@auNPs with ligand mercaptoethanol (MET)** [11]

A total of 10 mL of 0.4 mM mercaptoetanol (MET) solution was pipetted into a beaker containing 0.1 gram of zeolite@AuNPs then stirred with a magnetic stirrer for 6 hours at a speed of 150 rpm and precipitated for 24 hours. After 24 hours the sediment is taken and dried at 105°C.

**Adsorption power and application test** [12]

The adsorption power test is the effectiveness test of unmodified zeolite adsorption, zeolite@AuNPs, zeolite@AuNPs@MET against standard manganese and iron solution with a concentration of 10 mg/L, and repeated 3 times. Application tests are carried out on razor blade factory and well water. Unmodified zeolite, zeolite@AuNPs, zeolite@AuNPs@MET were added as much as ±0.10 grams in 10 mL of standard manganese 10 mg/L solution, 10 mg/L iron, razor blade factory and well water then stirring with a magnetic stirrer for 30 minutes at a speed of 150 rpm, and precipitated for 24 hours. Then the mixture is centrifuged, the liquid phase is measured with a UV-Visible spectrophotometer to determine the concentration of the remaining heavy metal ions. Previously, analysis of manganese metal, iron, manganese content in razor blade factory, and iron content in well water with UV-Vis spectrophotometer were performed by reading the standard manganese metal and iron.

**Experiment determination of optimum adsorption capacity** [12]

Determination of optimum adsorption capacity was carried out using the Response Surface method in the Central Composite Design using 3 variations of factors, namely variations in the weight of zeolite@AuNPs@MET adsorbent (0.1 grams to 0.5 grams), variations in manganese and iron ion concentration (5 mg/L up to 20 mg/L) and variation of contact time (3 to 24 hours) each repetition three times. After processing using the Minitab software, the experimental design pattern is obtained as shown in Table 1.
Table 1: Central composite design (CCD) for determination capacity optimum adsorption of adsorbents for Mn\textsuperscript{7+} and Fe\textsuperscript{2+} Ions

<table>
<thead>
<tr>
<th>Absorbent Weight (gram)</th>
<th>Metal Ion Concentration (mg/L)</th>
<th>Contact Time (Hour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.18</td>
<td>8.00</td>
<td>7.30</td>
</tr>
<tr>
<td>0.30</td>
<td>12.50</td>
<td>3.00</td>
</tr>
<tr>
<td>0.30</td>
<td>20.00</td>
<td>13.50</td>
</tr>
<tr>
<td>0.42</td>
<td>17.00</td>
<td>22.00</td>
</tr>
<tr>
<td>0.30</td>
<td>12.50</td>
<td>13.50</td>
</tr>
<tr>
<td>0.42</td>
<td>8.00</td>
<td>7.30</td>
</tr>
<tr>
<td>0.18</td>
<td>17.00</td>
<td>7.30</td>
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<tr>
<td>0.30</td>
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</tr>
<tr>
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<td>13.50</td>
</tr>
<tr>
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<td>17.00</td>
<td>7.30</td>
</tr>
<tr>
<td>0.42</td>
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<td>22.00</td>
</tr>
<tr>
<td>0.42</td>
<td>17.00</td>
<td>22.00</td>
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<tr>
<td>0.50</td>
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<td>13.50</td>
</tr>
<tr>
<td>0.18</td>
<td>8.00</td>
<td>22.00</td>
</tr>
<tr>
<td>0.30</td>
<td>12.50</td>
<td>24.00</td>
</tr>
</tbody>
</table>

**Result and Discussion**

The three types of adsorbents, unmodified zeolites, zeolites@AuNPs, and zeolites@AuNPs@MET were applied to the liquid waste of a razor blade factory containing Mn\textsuperscript{7+} ions and well water containing Fe\textsuperscript{2+} ions. Before and after adsorption was measured using a UV Visible Spectrophotometer to determine the concentration of Mn\textsuperscript{7+} ions and Fe\textsuperscript{2+} ions attached to the adsorbent. The comparison graphs of the Mn\textsuperscript{7+} ion amounts in the adsorbed liquid razor blade factory (mg/g) in unmodified zeolite, zeolite@AuNPs, and zeolite@AuNPs@MET can be seen in Fig 1.

![Fig 1: Comparison of the number of Mn\textsuperscript{7+} ions in the effluent of the razor blade and the amount of Fe\textsuperscript{2+} ions in well water adsorbed (mg/g) in unmodified zeolite, zeolite@AuNPs, and zeolite@AuNPs@MET](image)

In the application test, the adsorption power of the three types of adsorbents in the effluent of the razor blade factory is similar to that of the previous experiments: the adsorption power of zeolite@AuNPs@MET is greater than that of zeolite@AuNPs and unmodified zeolites. Figure 1 shows that the adsorbent zeolite@AuNPs decreased adsorption power by 89.66% compared to unmodified zeolite. It is assumed that the zeolite pores have been filled by Au nanoparticles through the exchange of cations with Na\textsuperscript{+} contained in the zeolite cavity so that the Mn\textsuperscript{7+} ion absorbed in the pores of the zeolite is reduced. Adsorbent zeolite@AuNPs@MET has an adsorption rate increase of 30.27% due to modified mercaptoethanol ligands in zeolite@AuNPs that act to capture heavy metal ions. The next application test is on well water taken from Tanah Baru Bogor area to see application of adsorbent in adsorbing Fe\textsuperscript{2+} ion. Adsorbent zeolite@AuNPs@MET has a higher adsorption power than unmodified zeolite and zeolite@AuNPs with adsorption power sequence is zeolite@AuNPs@MET (0.428 mg/g) > unmodified zeolite (0.416 mg/g) > zeolite@AuNPs (0.264 mg/g) as in Figure 1.

**Adsorbent regeneration**

Regeneration was performed on all types of adsorbents that is unmodified zeolite, zeolite@AuNPs and zeolite@AuNPs@MET which have been tested on Mn\textsuperscript{7+}, Fe\textsuperscript{2+} ions, well water and effluent of razor blade using Na-EDTA. Na-EDTA has an active side that is able to both ionically and covalently coordinate with metal ions to form chelates capable of binding stronger metal ions than the bonds between metal ions and mercaptoethanol ligands. The steric factor becomes the main thing in the interaction between metal and Na-EDTA. Na-EDTA steric is stronger than mercaptoethanol ligand so metal ion is more easily attracted to Na-EDTA. Figure 2 shows that the percent of regeneration for all ion samples of both Mn\textsuperscript{7+}, Fe\textsuperscript{2+} ions, the effluent of the razor blade and the well water, is highest in the unmodified zeolite because Na-EDTA can easily attract metal ions absorbed into the zeolite compared to zeolite@AuNPs@MET because Na-EDTA must compete with mercaptoethanol ligand in capturing metal ions already attached to mercaptoethanol ligands. The percent order of Na-EDTA regeneration is unmodified zeolite > zeolite@AuNPs@MET > zeolite@AuNPs. This suggests that the strong cation-pulling properties of EDTA are due to EDTA being a hexadentat ligand (having 6 pairs of free electrons) while the mercaptoethanol ligand is only a monodentate ligand (having 2 pairs of free electrons).
In addition, EDTA-Mn complex has a high stability constant value of log Kst = 13.89 and stability constant value of EDTA-Fe complex for log Kst = 14.30. For the stability constant of OH complex with Fe(OH)₄ metal equal to log Kst = 4.6 [13]. The magnitude of the price of complex forming constants states the degree of stability of a complex compound. The greater the price of the constant formation of complex compounds, the complex compounds are more stable and otherwise the smaller the price of stability constant of complex compounds, then the complex compound is less (less) stable. Thus the metal ions are more likely to bind to EDTA than with the mercaptoethanol ligand.

**Optimum conditions of experiment**

After tested to better adsorption than unmodified zeolite, and zeolite@AuNPs, the zeolite@AuNPs@MET adsorbent continued experiment to see the optimum condition of its adsorption using Response Surface Method and the design used was Central Composite Design (CCD). This method combines several variables in an experiment so that interactions between variables can be known optimally with a small number of experiments that must be done. Variables used in this experiment were weight of adsorbent with range 0.1 - 0.5 gram, metal concentration with range 5 - 20 mg/L and contact time with range 3 - 24 hours. The results of the treatment using the CCD method obtained 15 experimental treatments tested on Mn⁷⁺ and Fe²⁺ ions as in Table 2.

![Fig 2: Percent regeneration of Mn⁷⁺ ion adsorbent on razor blade liquid, Fe²⁺ adsorbent on well water by Na-EDTA](image-url)

**Table 2: Percent of adsorption efficiency and adsorption capacity of zeolite@AuNPS@MET on the variety of adsorbent weight, metal ion concentration, and contact time for Mn⁷⁺ and Fe²⁺ ions**

<table>
<thead>
<tr>
<th>No</th>
<th>Adsorbent Weight (gram)</th>
<th>Metal Ion Concentration (mg/L)</th>
<th>Contact Time (hour)</th>
<th>% Adsorption Efficiency</th>
<th>Adsorption Capacity (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>8.00</td>
<td>7.30</td>
<td>49.12</td>
<td>53.62</td>
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<td>2</td>
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<td>3.00</td>
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<td>74.88</td>
</tr>
<tr>
<td>3</td>
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<td>20.00</td>
<td>13.50</td>
<td>71.20</td>
<td>73.10</td>
</tr>
<tr>
<td>4</td>
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<td>22.00</td>
<td>28.00</td>
<td>35.18</td>
</tr>
<tr>
<td>5</td>
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<td>13.50</td>
<td>58.40</td>
<td>69.76</td>
</tr>
<tr>
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<td>7.30</td>
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</tr>
<tr>
<td>7</td>
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<td>74.11</td>
</tr>
<tr>
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<td>13.50</td>
<td>1.00</td>
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</tr>
<tr>
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<td>17.12</td>
</tr>
<tr>
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<td>13.50</td>
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<td>55.52</td>
</tr>
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</tr>
<tr>
<td>1</td>
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<td>12.50</td>
<td>24.00</td>
<td>68.72</td>
<td>7.52</td>
</tr>
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</table>

In Table 2 it is known that the percent value of adsorption efficiency of zeolite@AuNPs@MET ranges from 11.00% - 82.72% for Mn⁷⁺ ions while for Fe²⁺ ions ranges from 7.52% - 74.88%. This shows that there has been a strong interaction between the 3 variables/ factors so that the resulting range is quite large. For Mn⁷⁺ ion at concentration 5 mg L⁻¹ contact time 13.50 hour with adsorbent weight 0.30 gram and Fe²⁺ ion at concentration 12.50 mg/L, contact time 24 hours with adsorbent weight 0.30 gram happened desorption process so that the adsorption efficiency for Mn⁷⁺ ion only reaches about 11.00% while Fe²⁺ ion only reaches about 7.52%.
Figure 3 shows that the effect of Fe$^{2+}$ ion concentration and the weight of the adsorbent gives the optimum adsorption capacity when the concentration of Fe$^{2+}$ ion is set between 18-20 mg/L and the adsorbent weight < 0.1 gram, the influence between contact time and the adsorbent weight gives the optimum adsorption capacity when the contact time is set between 3 - 17 hours and the adsorbent weight < 0.2 gram, the influence between contact time and Fe$^{2+}$ ion concentration gives the optimum adsorption capacity when the contact time is set between 3 – 10 hours and the Fe metal concentration between 17-20 mg/L.

Figure 3b shows that the effect of Mn$^{7+}$ ion concentration and the weight of the adsorbent gives the optimum adsorption capacity when the Mn$^{7+}$ ion concentration is set between 18-20 mg / L and the adsorbent weight < 0.1 gram, the influence between contact time and the adsorbent weight gives the optimum adsorption capacity when the contact time is set between 3 - 24 hours and the adsorbent weight < 0.1 gram, the influence between contact time and Mn$^{7+}$ ion concentration gives optimum adsorption capacity when contact time is set between 3-24 hours and concentration between 18-20 mg/L. Zeolite@AuNPs@MET has a range of adsorption capacity for Mn$^{7+}$ ions from 0.11-0.92 mg/g and for Fe$^{2+}$ ions from 0.03 to 0.92 mg/g, but this capacity has not shown optimum adsorption conditions. The optimum adsorption capacity value was obtained by processing at the Central Composite Design (CCD) program and the optimum conditions obtained for both Mn$^{7+}$ and Fe$^{2+}$ ions were 0.10 gram of adsorbent, 5 mg/L metal concentration and 3 hours contact time.

**Isothermal adsorption**

The determination of adsorption capacity of Mn$^{7+}$ and Fe$^{2+}$ ions for adsorbents zeolites@AuNPs@MET was done at room temperature using the optimum conditions already obtained. In this experiment, variation of concentration from 1 mg/L to 15 mg/L while weight of adsorbent and contact time was made, ie 0.10 gram adsorbent weight and 3 hours contact time. The experimental data of adsorption adsorption of Mn$^{7+}$ ion and Fe$^{2+}$ ion by zeolites@AuNPs@MET adsorbent were analyzed using 2 models of isothermal equations ie Langmuir and Freundlich models. This equation is used to find the optimum adsorption capacity of zeolite@AuNPs@MET adsorbents for Mn$^{7+}$ and Fe$^{2+}$ ions. The results obtained tend to follow the Langmuir equation because the resulting coefficient of determination (R2) is greater than the Freundlich equation with a value of 0.990 for Mn$^{7+}$ and 0.990 ions for Fe$^{2+}$ ions (Fig. 27). This indicates that the adsorbent of zeolite@AuNPs@MET is monolayer and homogeneous so that the adsorbent interaction with adsorbate only forms 1 layer and the adsorption capacity is determined by the ratio of availability of the active side of the adsorbent to the number of metal ions.

**Conclusion**

Zeolite@AuNPs@MET adsorbent shows better adsorption power than unmodified zeolite adsorbent and zeolite modified with Au nanoparticles (zeolite@AuNPs). The adsorption power of Mn$^{7+}$ ion is zeolite@AuNPs@MET (0.664 mg / g) > unmodified zeolite (0.274 mg/g) > zeolite@AuNPs (0.229 mg/g) while adsorption for Fe$^{2+}$ ion is zeolite@AuNPs...
The optimum adsorption condition of zeolite@AuNPs@MET with adsorption capacity for Mn$^{7+}$ ion is 0.39 mg/g and Fe$^{2+}$ ion 0.41 mg/g is achieved at the condition of adsorbent weight of 0.10 grams, metal concentration of 5 mg/L and contact time 3 hour. The percent value of zeolite@AuNPs@MET adsorption efficiency ranged between 11.00% - 82.72% for Mn$^{7+}$ ions while for Fe$^{2+}$ ions ranged between 7.52% - 74.88%. Regeneration of all unmodified zeolite adsorbents, zeolite@AuNPs, and zeolite@ AuNPs@MET with Na-EDTA has been successfully carried out in the order of success of regeneration is unmodified zeolite > zeolite@AuNPs@MET > zeolite @AuNPs.

Acknowledgements
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