Preparation of Iron Oxide Nanoparticles Mixed with Calcinated Laterite for Arsenic Removal

Wint Myat Shwe1, Dr. Mya Mya Oo2, Dr. Su Su Hlaing3

Abstract— To overcome arsenic toxicity, which has become a major concern worldwide, it is needed to develop the technology with improved materials and systems with high efficiency. This paper was studied about a simple and efficient method that is synthesis of Fe3O4 (Iron Oxide) nanoparticles mixed with calcinated laterite to form effective adsorbent for removal of toxic arsenic from arsenic contaminated water. Ultrasound Fe3O4 powder synthesis firstly by a Novel Ageing process from a precursor FeO(OH), which was the hydrolysate of FeCl3 in the urea solution. Furthermore, the particle size of Fe3O4 nanoparticles is characterized by X-ray Diffraction (XRD), X-ray Fluorescence (XRF) and Scanning Electron Microscope (SEM) to study the particle sizes, compositions, morphology, structure and surface of the adsorption materials. These iron oxide nanoparticles got with the mean diameter about 20-26 nanometer in processing of different heating time (2, 2.5, and 3 hr) and different ageing time (3, 4, and 5 hr) respectively. Optimum particle size of 20nm can be found when 3 hr heating time and 5 hr ageing time processing. After preparing of these Fe3O4 powder, it was mixed with calcinated laterite grains to create more effective adsorption material. Next, adsorption experiments are conducted at room temperature for removing toxic arsenic. In this investigation, different adsorption parameters such as adsorbent dose of 0.03g, 0.05g, 0.07g and contact time period of 20min, 40min, 60min, 80min were determined. All of the arsenic contents both from raw and treated water were examined by using Atomic Absorption Spectrophotometer (AAS). The removal efficiency of this mixed adsorbent material was more than that of pure laterite (57%) or iron (61%) when the dosage amount of adsorbent was the same. The arsenic removal efficiencies of this mixed adsorbent were 75% for 0.3ppm initial arsenic concentration and 95% for initial arsenic concentration 0.03ppm with very low dosage of 0.05g in 80min adsorption time. Initial arsenic concentration 0.3ppm and 0.03ppm were decreased below the limit of WHO drinking water standard (0.01 ppm) after treated with this mixed adsorbent.

Keywords-- arsenic removal, novel ageing process, Fe3O4 (iron oxide nanoparticle), laterite, mixed adsorbent, adsorption, WHO drinking water standard

I. INTRODUCTION

Arsenic contamination of drinking water has been reported from many parts of the world. Access to clean drinking water is an enormous problem faced by many people all over the world and lack of access to clean water is public health hazard [1]. Of all the naturally occurring groundwater contaminants, arsenic is by far the most toxic. It is known that arsenic is a human carcinogen in water over a wide range of pH values, having harmful effects on both human health and environment, even at low concentration [2]. Because of arsenic threat to humans, the World Health Organization (WHO) and the US Environmental Protection Agency (USEPA) implemented a reduction of the Arsenic Maximum Contaminant (MCL) in drinking water from 50 to 10 μg/L in 2006. There is no effective treatment for arsenic toxicity. Only drinking of arsenic free water can prevent arsenic toxicity. To save millions of people from being affected with arsenic toxicity, appropriate and sustainable treatment of contaminated water is necessary.

In areas where the drinking water supply contains unsafe levels of arsenic, the immediate concern is finding a safe source of drinking water. There were two main options: finding a new safe source, and removing arsenic from the contaminated source [3]. Arsenic in drinking water can be effectively removed by using a variety of conventional treatment processes. This study looks at adsorption of arsenic on nano-sized magnetite; Fe3O4 particles mixed with calcinated laterite is beginning to show many advantages, especially in environmental science. Nowadays, Fe3O4 nanoparticles have been also widely used for magnetic materials, pigments, ferrofluids, and catalysts etc. [4].

Synthesis of nano size iron oxide (Fe3O4) can be made by various methods such as; co-precipitation, microemulsion, hydrothermal method, and some novel methods; sonochemical synthesis, arc discharge method, microwave hydrothermal, and one-step hydrothermal process. But in this study, Fe3O4 nanoparticles will synthesis via a Novel Ageing Process because of its simple procedure and pure Fe3O4 product [5]. These prepared nanoparticles will be then mixed with denaturized (calcinated) laterite to create new high performance adsorption materials because impregnation or coating with nanoparticles enhances the sorption capacity of adsorbents. Being iron oxide is the effective material for treating arsenic, laterite can be added the adsorption efficiency. Therefore, combination of these two effective materials can be obtained the best adsorbent material for arsenic removal [6].

II. EXPERIMENTAL METHOD

In general there were two main parts in this research; where the first part was preparation of mixed adsorbent material and the second part was the arsenic removal by adsorption technique. And there were also three steps in this first part (preparation of mixed adsorbent material) roughly.
Iron oxide ($\text{Fe}_3\text{O}_4$) nanoparticles were synthesized by novel ageing process firstly. Then calcination of laterite was carried on to mix with these iron oxide particles. Finally, creating of mixed adsorbent for arsenic removal was done by mixing these two adsorbent materials.

A. Synthesis of Iron Oxide Nanoparticles

The chemical reagents used in this preparation of iron oxide particles were Urea ($\text{(NH}_2\text{)}_2\text{CO}$), Ferric chloride: $\text{FeCl}_3.6\text{H}_2\text{O}$, Sodium hydroxide: NaOH, Ferrous Sulphate: $\text{FeSO}_4.7\text{H}_2\text{O}$, and acetone.

A typical approach for this research work was given as follows. 5.41g $\text{FeCl}_3.6\text{H}_2\text{O}$ and 3.6g $\text{(NH}_2\text{)}_2\text{CO}$ were dissolved in 200ml distilled water in a container. After that, this solution was placed in a water bath at a constant temperature 90±3°C. Various heating time parameters tested in this process were 2, 2.5, 3 hr respectively. The solution turned into a kind of khaki slurry gradually and then it was cooled to room temperature. 1.99g $\text{FeCl}_2.4\text{H}_2\text{O}$ was dissolved in the above mixture with mechanical stirring at a speed of 546 rpm for 10 min. Then, NaOH solution (2mol/L) was dropped into the reaction mixture until the pH>10. Greenish precipitate can be observed at that time. The molar ratio of Fe(III) to Fe(II) in the observed system was nearly 2. When the pH reached greater than 10, the mixture was transferred into an ageing container with a cubage of 500 ml. Additional distilled water was added to make the ageing container full and then it was sealed by a capsule to prevent the air from entering. Finally, the container was aged at a room temperature with different ageing times such as 3hr, 4hr, and 5 hr. The black magnetic precipitate was separated by filtration, followed by washing with distilled water of 500 mL and acetone of 100 mL in order. Then, the obtained powders were oven-dried at 50°C for 7 hr. This chemical preparation route was shown in Fig. 1.

![Chemical preparation route of Fe$_3$O$_4$ nanoparticles](image)

B. Laterite Calcination

After synthesized these nanoparticles, laterite calcination step was carried on. The collected iron rich raw laterite (collected from Mon State) was then calcinated at 400°C for 4 hours. After calcination, the laterite was crashed and sieved to obtain powder laterite with a particle size less than 75μm. These laterite powders were washed with deionized water at least three times. If not washing like this it can not remove the laterite dust, as well as other undesired particle. It was dried at 110°C for 12 hr; then it was stored in a desiccator for use in the next step of mixing experiments.

C. Preparation of Mixed Adsorbent

In the final step, prepared nanodimensional particles were mixed with denatured laterite in a grinder about ten minutes to create new high performance adsorption materials. The mixing ratio of these two materials was 1:1 ratio (1g Laterite:1g Fe3O4). Finally, the prepared mixed adsorbent materials were stored in an airtight plastic bag and it was ready for removing arsenic. Due to its abilities, iron oxide nanoparticle was so famous for arsenic adsorption. On the other hand, iron rich laterite was very advantageous for removing arsenic because it is locally available adsorbent material. Therefore mixing of these two particles got double benefits; effective adsorbent formation and process cost reduction.

D. Arsenic Removal by Adsorption

The second part of this research was treating toxic arsenic from arsenic contaminated water by adsorption technique with the help of mixed adsorbent material. The adsorption technique is the best method among variety of conventional treatment processes for arsenic removal due to its obvious advantages. Moreover using of this mixed adsorbent was better than using some of the common adsorbents.

Taking about 50ml of arsenic contaminated water into a beaker and added the different adsorbent dosage for various batch on the magnetic stirrer. The used adsorption process parameters in this research were 0.03g, 0.05g, 0.07g adsorbent dosage and 20min, 40min, 60min, and 80min adsorption time for the initial arsenic concentration about 0.3ppm. Next testing with 0.05g dosage for initial arsenic concentration 0.03ppm was also examined in these adsorption times. Moreover comparison of adsorption capacities for pure laterite adsorbent and pure Fe3O4 nanoparticles adsorbent with this mixed adsorbent material was carried on.

III. RESULTS AND DISCUSSIONS

A. XRD and SEM Results of Fe3O4, Laterite, Mixed Adsorbent

The ultrafine Fe$_3$O$_4$ powders obtained from novel ageing process were characterized by X-ray Diffraction (XRD) analysis to examine their particle size in nanometer scale. The average particle sizes of prepared Fe$_3$O$_4$ particles were calculated by “Scherrer’s Equation” using the XRD line broadening method.

$$D = \frac{K\lambda}{B\cos\theta}$$

where, D was crystal size, K was a shape factor (about 0.89
for magnetite), $\lambda$ was the wavelength of X-ray (1.54056Å), $B$ was the full width at half maximum (FWHM) of the peak in radians, and $\theta$ was the diffraction angle (or) the Bragg angle of the peak, respectively [7]. All these require values can be obtained from their corresponding XRD peak search report.

The X-ray diffraction spectrum of Fe$_3$O$_4$ particle prepared by process 1 is shown in Fig. 2(a). From the analysis of the peak width for process 1 using Scherrer's equation it was determined that Fe$_3$O$_4$ particle had an average grain size of 20nm. This process can produce smaller particle size than other methods.

The chemical compositions of synthesized Fe$_3$O$_4$ particle can be known in detail by seeing the XRF result. Fe, the best element for removing toxic arsenic, was the main composition in this prepared particle about 99 % and other minor compositions are Mn, Zn, and Cu. And Scanning Electron Microscopy (SEM) shows in the measurement range within 1µm and can be seen the morphology of this prepared Fe$_3$O$_4$ particle [Fig. 3(a)]. The prepared particle shapes were mainly in circular shapes.

For creating mixed adsorbent, pure laterite should be analyzed firstly by XRD analysis which is shown in Fig. 2(b) and the particle size of laterite was found about 25 nm.

The chemical composition of laterite can be determined by XRF analysis result and it was clear that iron was the main composition and other metal such as Ti and Zr were also contained in this laterite. Moreover the morphology of this laterite was also examined by SEM analysis [Fig. 3(b)]. According to this result it can be seen that the pore size and particle size of laterite was larger than the prepared Fe$_3$O$_4$ particle.

Next for the particle size calculation of this mixed adsorbent, the required data of XRD analysis result is shown in Fig. 2(c). In this spectrum the highest peak of this material was peak number 104 and all the necessary data for Scherrer’s Equation were taken from their peak results. After calculation, the size of particle was 27 nm. Unlike pure Fe$_3$O$_4$ particle, size of mixed adsorbent was slightly larger than laterite.

After combination, all the chemical compositions (these are Fe, Ti, Mn, Cu and Zn) of pure Fe$_3$O$_4$ and pure laterite were found altogether in this mixed adsorbent by examining their XRF result. Moreover pore size of its also higher and which can be seen clearly in SEM photo [Fig. 3(c)].

**B. Effect of Heating and Ageing Time on Fe$_3$O$_4$ Preparation**

The resultant sizes of iron oxide particle obtained from different processes are expressed in the following Table I.

<table>
<thead>
<tr>
<th>Process</th>
<th>Heating time (hr)</th>
<th>Ageing time (hr)</th>
<th>“B” (rad)</th>
<th>“θ”</th>
<th>Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>5</td>
<td>0.0719</td>
<td>17.933</td>
<td>20.0433</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2.5</td>
<td>5</td>
<td>0.0616</td>
<td>18.0385</td>
<td>23.4087</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>5</td>
<td>0.0538</td>
<td>18.0205</td>
<td>26.7997</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>4</td>
<td>0.0676</td>
<td>18.1185</td>
<td>21.3407</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>3</td>
<td>0.0630</td>
<td>18.0312</td>
<td>22.8875</td>
</tr>
</tbody>
</table>

According to Table I, it can be said that although varying on heating time can significantly affects the particle size, varying on ageing time can slightly affect particle size. Among these processes, the best conditions for the preparation of Fe$_3$O$_4$ nanoparticles were 3 hours heating time and 5 hours ageing time to get smaller particle size. So Novel Ageing process can produce smaller particle size than other processes.

![Fig. 2 XRD Spectrum of (a) Fe$_3$O$_4$ Particles (b) Laterite (c) Mixed Adsorbent](image)

![Fig. 3 SEM of (a) Fe$_3$O$_4$ (b) Laterite (c) Mixed Adsorbent](image)
C. Studies of Arsenic Removal

Furthermore studies on the effect of adsorbent dose and adsorption time were conducted for initial arsenic concentration of 0.3 ppm. The Fig. 4 illustrates that the aqueous arsenic concentration decrease with the increasing adsorbent dose as well as with adsorption time. This is due to more availability of the surface-adsorbent sites and more contact time. By comparing these two adsorbent, it can be said that the removal efficiency of pure Fe$_3$O$_4$ nanoparticle adsorbent was higher than that of pure laterite adsorbent in the same conditions.

Then Fig. 5 expresses the comparison of three type of adsorbent (Laterite, Fe$_3$O$_4$, and Mixed Adsorbent) and their removal efficiency in the same conditions of 0.05 g adsorbent dosage and 20, 40, 60, and 80 min adsorption time. In which the removal efficiency of mixed adsorbent is the best in the same parameters. Although other adsorbent dose parameter such as 0.03 g and 0.05 g adsorbent dosage were not identified, mixed adsorbent may also be removed more than the other two adsorbents in these dosages. The best removal efficiency of this mixed adsorbent from initial arsenic concentration about 0.3 ppm was over 75 % within the short adsorption time of 80 min using the adsorbent amount of 0.05 g. Finally, it can be noted that although in the same parameter, the removal percent of the mixed adsorbent was the best in these three adsorbents.

![Fig. 4 Arsenic Removal by different adsorbent dose via different adsorption time using (a) Laterite adsorbent (b) Fe$_3$O$_4$ nanoparticle adsorbent](image)

![Fig. 5 Arsenic removal of different adsorbents](image)

![Fig. 6 Arsenic removal of different concentrations](image)
However when we used the initial concentration 0.03ppm, its removal efficiency was increased to 95% at the same adsorption parameters. Therefore the effect of initial arsenic concentration was significantly affected on arsenic adsorption and Fig. 6 shows the comparison of these two concentrations with their removal efficiencies.

IV. CONCLUSION

Iron oxide (Fe$_3$O$_4$) nanoparticles are prepared by novel ageing process with various parameters for examining which process can produce the smaller particle size. After checking the particle sizes with the XRD results, the best parameter is coming out with the size of 20 nm. That is process number one (process 1) and its conditions are 3 hr Heating time and 5 hr Ageing time. When we changed the heating time, the sizes of which products are 20, 23, 26 nm and the sizes of product from changing the ageing time are 20, 21, 22 respectively. That is why we can say that changing the heating time is more important to the process than changing the ageing time.

The arsenic removal efficiency of pure laterite is over 57% when we used the small amount of 0.05 g within 80 min. In the same condition, like laterite, Iron oxide (Fe$_3$O$_4$) nanoparticles can removed about 61% toxic arsenic from aqueous solution. However the removal efficiency of the mixed adsorbent is 75% (at 0.3ppm initial concentration) or 95% (at 0.03ppm initial concentration). Therefore, its removal efficiency is obviously higher than that of the two adsorbents in these conditions (0.05 g dosage and 80 min adsorption time). Because both laterite and iron were very effective materials for arsenic removal; the combination of these two materials is the best for arsenic removal. Therefore, it is obvious that the removal efficiency of this mixed adsorbent is greater than that of the other two adsorbents (pure state). Finally this mixed adsorbent can successfully remove naturally existing arsenic (about 0.03ppm) from groundwater.

ACKNOWLEDGMENT

The author wishes to acknowledge to Dr. Mya Mya Oo, Rector of Yangon Technological University and Head of Department of Chemical Engineering in allowing for my research works. The author also thank to Dr. Su Su Hlaing and all the teachers from Chemical Engineering Department.

REFERENCES
