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ARSENIC AND HEAVY METALS REMOVAL BY IRON-IMPREGNATED CERAMIC GRANULES: A HOUSEHOLD-SCALE

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ABSTRACT

Clean water for drinking and cooking has been a serious issue in rural areas of Vietnam, which is mainly due to high-cost treatment of the available water sources in such areas. In order to reduce the treatment cost, iron impregnated ceramic granules (IICGs) was synthesized using a mixture of locally available montmorillonite and crushed rice husk (with the rice husk size < 0.2 mm, IICGs size 0.2 mm – 0.45 mm). This material was used as a simple and efficient adsorbent of pollutants in groundwater in this present work. The household-scale drinking water treatment unit (capacity of 0.13 L/h) consists of an air stripper, a slow sand filter and an adsorption column packed IICGs. This system was operated with the inlet flow comprising of total iron ion (1.1±0.1 mg/L), arsenic (300 ppb) copper ion (6.15 mg/L), cadmium ion (8.1mg/L), lead ion (0.41 mg/L), and zinc ion (0.515 mg/L). The derived IICG adsorbent was observed to significantly remove a wide array of dissolved metals including iron (99.3%), arsenic (99.92%), zinc (99.48%), copper (97.03%), lead (98.6%) and cadmium (99.6%). The effluent concentrations of most dissolved metals after the household-scale drinking water treatment unit were about ten times lower the Vietnamese standard for drinking water.

Keywords: *Household-scale drinking water treatment; Iron impregnated ceramic granules; Adsorption column; Low-cost; Arsenic.*

1. INTRODUCTION

Arsenic in the drinking water of more than 200 millions of people living in more than 105 countries of the world has been a focus of attention for public health scientists and engineers [1,2]. The crisis is slowly unfolding in Vietnam also, affecting several provinces such as Ha Nam, Ha Noi, Ha Tay, Hung Yen, An Giang, Long An, etc., with the average arsenic concentration of 159 µg/L in rural groundwater [3]. Groundwater serving as the primary source of potable water in these regions is favored by its availability, microbial safety and absence of proper infrastructure for treatment and distribution of surface water. It was estimated that the percentage of the 21% Vietnamese population currently consumes untreated and non-piped drinking water contaminated with high levels of inorganic arsenic [4]. It has been reported that drinking of arsenic-rich water (> 50 ppb) over a long period results in various health effects including skin problems, skin cancer, cancers of the bladder, kidney and lung, and diseases of the blood vessels of the legs and feet, and possibly also diabetes, high blood pressure and reproductive disorders [2, 5]. In many places along the Red river and Mekong delta of Vietnam, arsenic concentration in groundwater exceeds 100 µg/L [6]. The guideline value of the World Health Organization (WHO) for concentration of arsenic compounds in drinking water is less than 10 µg/L [7]. In order to save lives before such a changeover is possible, it is imperative to build arsenic removal systems on an emergency basis. Many arsenic removal technologies have been developed over the last two decades such as polymer beads coated with iron oxides [8], iron-oxide coated sand [9] or iron-impregnated sand [10], nanostructured adsorbents [11], Fe_3O_4 Nanoparticles [12], iron coated pottery granules [13], nano-sized iron-oxide-coated quartz [14]. Nevertheless, either investment or operation cost of these arsenic treatment units that can remove arsenic compounds to meet WHO standard for drinking water is still high as compared to the low-income of the villagers in rural areas of Vietnam. For further decrease cost of investment and operation of arsenic treatment, local montmorillonite was used as the base adsorbent and rice husk was employed to increase the specific surface area of the obtained adsorbent. The granular adsorbent column was operated with an air stripper and a slow sand filter as a pretreatment unit for groundwater treatment.

2. METHODS

2.1. Preparation of iron impregnated ceramic granules

2.1.1. Materials

Local montmorillonite or clay (Binh Duong brick company) with the density of around 2.0 g/L was used due to its availability at extremely low price. Local rice husk (District 9, Ho Chi Minh City) with the bulk density before and after crushing of ca. 90 g/L and 465.8 g/L (rice husk size < 0.2 mm), respectively, was employed in this study. The ash content of this rice husk was determined at around 15%. Iron (III) nitrate ($Fe(NO_3)_3.6H_2O$, China), $Na_2HAsO_4.H_2O$ (Merck), $Cu(NO_3)_2$ (Merck), $Pb(NO_3)_2$ (Merck), $ZnSO_4$(China), $Cd(NO_3)_2$ (Merck) and, other chemicals were analytical grade and used as received. Crushed rock (0.2 – 0.45mm) used for slow sand filters was quite popular in Vietnam with low cost.

2.1.2. Synthesis and characterization of iron impregnated ceramic granules

The complete procedure for developing the iron-impregnated ceramic granule (IICGs) was described in Figure 1. Montmorillonite and crushed rice husk (< 0.2 mm) with the mass ratio of 5:1 were mixed manually to form a clay-rice husk mixture. After crushing, washing and drying, porous ceramic granules were mixed with iron (III) nitrate 0.2M to create IICGs. The obtained IICGs were used for lab-scale and household-scale column experiments.

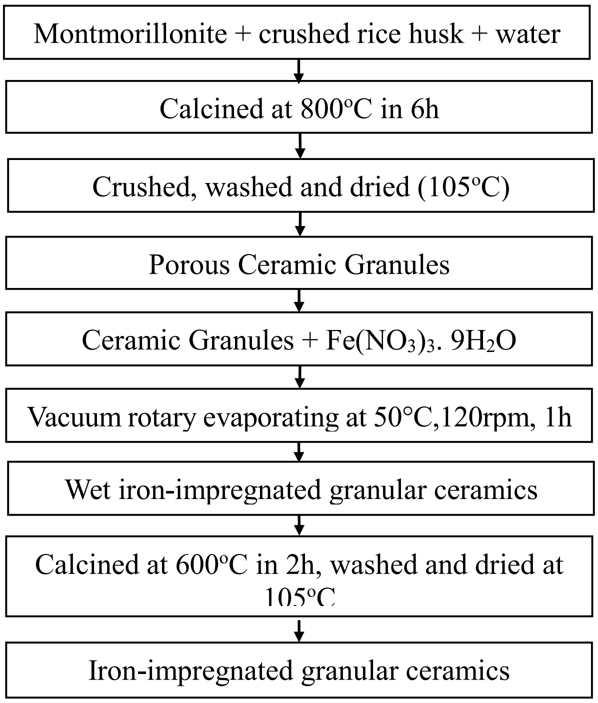

Figure 1. *Procedure of the synthesis of IICGs.*

2.2. Design and performance of household-scale drinking water treatment unit

Figure 2. *A household-scale drinking water treatment unit*

The household-scale essentially consists of an air stripper, a column filled with about 3.1 liter of sand (83.1 mm internal diameter), followed by a 57.4 mm internal diameter column filled with IICGs, operated by water flowing in a gravity-fed system (Figure 2).

Vietnamese groundwater with total iron ion and dissolved iron ion (1.1±0.1 and 0.82±0.02 mg/L, respectively), pH = 5-5.5 was added arsenic concentration (300 ppb) and metal ions which are typical in Vietnamese groundwater, such as copper, cadmium, lead, and zinc (6.15; 8.1; 0.41 and 0.515 mg/L, respectively).

The influent water from air stripper located above the slow sand column sprays down the splash plate before flowing in the sand column. In this step, the dissolved air helps oxidize the ferrous iron in the raw water to form fine precipitates of hydrated ferric oxide (HFO) according to the following reaction:

$$4\ Fe^{2+}(aq) + O_2(g) + 10H_2O \rightarrow 4Fe(OH)_3(s) + 8H^+$$

Freshly precipitated hydrated Fe(III) oxide (HFO) particle surfaces are considered to be a diprotic acid capable of forming the surface functional groups of $Fe(OH)_2^+$ and FeOH at circum-neutral pH [15]. Iron is not a regulated element for safe drinking water, but is aesthetically displeasing and the presence of dissolved iron in raw water helps to remove arsenic through the oxidation and subsequent precipitation of HFO particles while adsorption of arsenic as a polishing step takes place at IICGs column. HFO particles with these surface groups can selectively bind both arsenites or As(III) and arsenates or As(V) through formation of bi-dentate and/or mono-dentate inner-sphere complexes where Fe(III), a transition metal, serves as electron-pair acceptor or Lewis acid [16]. HFO precipitates inside the sand filter adsorb a significant portion of influent arsenic. The bed of IICGs column removes the remaining arsenic and other dissolved metal ions in the inlet water. The flow rate, however, diminishes over time due to the precipitation of the HFO particles within the bed. Backwashing of the column every week to drive out the HFO particles is necessary to maintain a good flow rate through the column.

3. RESULTS AND DISCUSSION

3.1. Characterization of IICG

The porosity of the original clay was also observed to be less than that of the clay prepared with rice husk. The BET specific surface area of the original clay (ca. 16 m^2/g) was accordingly lower than that of the rice husk – based clay (ca. 26 m^2/g). As the rice husk – based clay was impregnated with iron oxides, BET specific surface area of the resulting IICGs was slightly decreased to around 23 m^2/g.

Figure 3. *Iron-impregnated granular ceramics*

3.2. Pollutant removal efficiency of household-scale drinking water treatment units

In this study, the efficiencies of dissolved metal ions removal were evaluated by comparing between the efficiencies of each column (slow sand filter and IICGs filter) and the whole household-scale drinking water treatment unit.

3.2.1. Pollutant removal efficiency of slow sand column

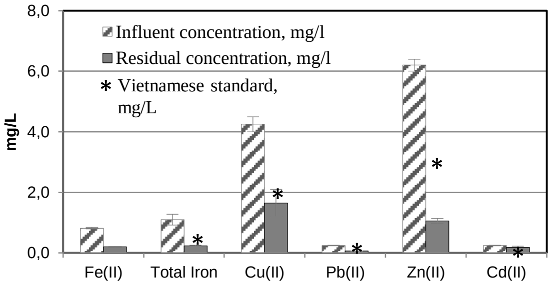

Figure 4. *Removal efficiency of slow sand column for some dissolved metal ions (Influent concentration (mg/L): $Fe^{2+} = 0.82\pm0.02$; Total Fe = 1.1 ± 0.1; $Cu^{2+} = 4.25\pm0.25$; $Pb^{2+} = 0.25\pm0.01$; $Zn^{2+}=6.2\pm0.2$; $Cd^{2+}=0.25\pm0.01$).*

The slow sand column was carried out with influent groundwater (at near-neutral pH, total iron ion was 1.1±0.1 mg/l and dissolved iron ion was 0.82±0.02 mg/L in groundwater) and under identical hydrodynamic conditions. Figure 4 shows that the removal efficiency of Fe(II) and total dissolved iron was investigated on the amount of HFO removed onto the slow sand column. Precipitated iron (HFO) which was oxidized from the ferrous iron in the raw water, was kept inside the sand filter. The outlet concentration of total dissolved iron was about 0.24 mg/L that was much lower than the Vietnamese standard for drinking water (0.5 mg/L).

Figure 4 was also found to remove other dissolved metals slightly. It was observed that the removal efficiencies of the slow sand column for most of the dissolved metals were over 60% (except for cadmium, 26%). The removal efficiency of this column for dissolved zinc was too high (>82%). With those influent concentrations, the effluent concentrations of dissolved zinc and copper get WHO standard for drinking water (3 mg/l and 2 mg/L, respectively). However, dissolved lead and cadmium should be removed by the next column in the household pilot.

3.2.2. Removal efficiency of only household-scale IICGs column for other dissolved metals

Although IICGs were deliberately synthesized to absorb arsenic compounds in groundwater, it was also found to significantly remove other dissolved metals as shown in Figure 5.

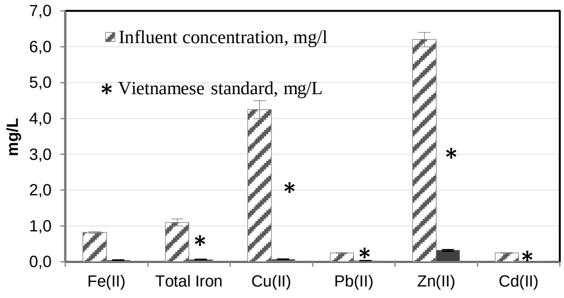

Figure 5. *Removal efficiency of only household-scale IICGs column for some dissolved metals (Influent concentration (mg/L): $Fe^{2+} = 0.82 \pm 0.02$; Total Fe = 1.1±0.1; $Cu^{2+} = 4.25 \pm 0.25$; $Pb^{2+} = 0.25 \pm 0.01$; $Zn^{2+} = 6.2 \pm 0.2$; $Cd^{2+} = 0.25 \pm 0.01$.*

It was observed that the removal efficiencies of the only household-scale IICGs column for most of the dissolved metals were over 90% (except for lead, 88.3%). The removal efficiency of this column for dissolved cadmium was too high (98.8%). Compared to dissolved cadmium removal efficiencies of the slow sand column, those of the IICG column were consistently present higher (98.8% compared to 26%). Therefore, IICGs can assist the slow sand column to remove an amount of dissolved cadmium in influent water. The household-scale IICGs column was also found to significantly remove dissolved copper and zinc significantly. The effluent concentrations of dissolved copper and zinc were low (0.07 and 0.32 mg/L, respectively) as compared to the influent counterparts (4.25 and 6.2 mg/L, respectively). These results inferred that IICGs would be a potential low-cost material to treat groundwater for drinking water.

3.2.3. Removal efficiency of household-scale drinking water treatment unit for dissolved metals

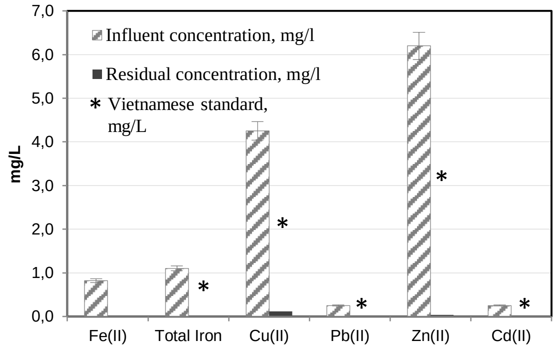

Figure 6. *Removal efficiency of the household-scale drinking water treatment unit for some dissolved metals (Influent concentration (mg/L): $Fe^{2+} = 0.82 \pm 0.02$; Total Fe = 1.1±0.1; $Cu^{2+} = 4.25 \pm 0.25$; $Pb^{2+} = 0.25 \pm 0.01$; $Zn^{2+} = 6.2 \pm 0.2$; $Cd^{2+} = 0.25 \pm 0.01$).*

In the household-scale drinking water treatment unit, owing to the partial removal efficiency of the slow sand filter as a pretreatment unit, removal efficiency of the household-scale IICGs column for dissolved metals remarkably increased (Figure 6). It was also found in Figure 6 that the effluent concentrations of most dissolved metals after the household-scale drinking water treatment unit lowered the detection threshold of the spectrophotometer used for analysis in this present work. The concentration of all effluent dissolved metals did not exceed the Vietnamese standard for drinking water.

Owing to high influent arsenic concentration (300 ppb) in the experiments, the effect of each column and both columns on arsenic removal efficiency was also investigated in this study with the results presented in Figure 7. Although the arsenic removal efficiency was found comparable, the effluent arsenic concentration of the IICGs column was three times lower than that of the slow sand column (2.2 µg/L and 7.1 µg/L, respectively). The average removal efficiency of the slow sand column and the household-scale IICGs column for the influent As(V) of 300 µg/L were 99% and 99.3%, respectively. It was also found in this study that arsenic removal efficiency of the slow sand column was strongly dependent on the amount of HFO which precipitated on the surface of sand particles. With IICGs, arsenites or As(III) and arsenates or As(V) can be also selectively bound with both inner-sphere Fe(0) and outside Fe(0). In addition, the flow of the drinking water through internal pores may not reduce the arsenic concentration but it would help remove small microscopic particles from the water [11] (precipitation of HFO particles). HFO particles with these surface groups can selectively bind both arsenites or As(III) and arsenates or As(V) through formation of bi-dentate and/or mono-dentate inner-sphere complexes where Fe(III), a transition metal, serves as electron-pair acceptor or Lewis acid [10]. HFO precipitating inside the pores adsorbs a portion of arsenic. This could explain why the arsenic removal efficiency of IICGs column was generally higher than that of the slow sand column.

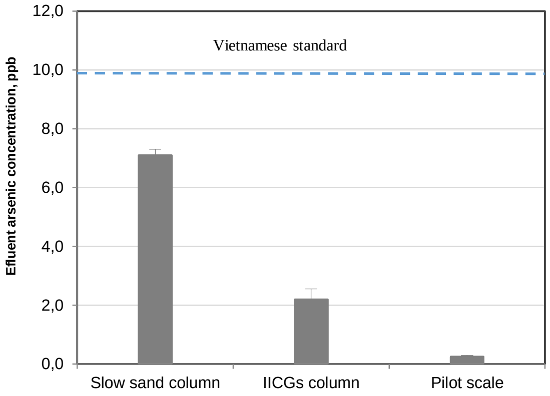

Figure 7. *Removal efficiency of slow sand filter, household-scale IICGs and drinking water treatment unit for Arsenic (Influent arsenic concentration C_o= 300 ppb)*

For the experiment of household-scale drinking water treatment unit, with the arsenic concentration of 300 mg/L, the effluent concentration of arsenic solution significantly reduced to 0.25 mg/L that corresponds to the detection threshold of the spectrophotometer used for arsenic analysis in this present work. The presence of dissolved iron in raw water helps to remove arsenic through the oxidation and subsequent precipitation of HFO particles which happens at the slow sand column. Therefore, the slow sand column can help remove an amount of arsenic when the influent arsenic concentration is high. At the same time, it brings advantage for regeneration because the arsenic-laden HFO particles of the slow sand column are easy to waste after back washing.

4. CONCLUSION

Iron impregnated ceramic granules (IICGs) synthesized using local clay and rice husk was employed as the low-cost adsorbents of dissolved metals in a household-scale drinking water treatment unit in this present work. With the arsenic concentration of 300 µg/L in the inlet water, the lab-scale IICG column was observed to remove Arsenic to a level of less than 10 µg/L with the bed volume of ca. 1,500. Meanwhile, for the household-scale IICG column, it was found to remove from 88% to 99% of dissolved metals including Fe, As, Cu, Cd, Zn and Pb. A combination of the slow sand filter and this IICG column in the household-scale drinking water treatment unit was observed to increase the removal efficiency of the above-dissolved metal. Due to the IICGs unit, the removal efficiency of household-scale is also capable of achieving a high removal efficiency of dissolved metal ions presented in the raw water. The effluent concentrations of most dissolved metals after the household-scale drinking water treatment unit was about ten times lower than those after the household-scale IICGs column alone and much lower than the Vietnamese standard for drinking water. The pilot-scale treatment unit does not require any electricity, the addition of chemicals or pH adjustment for operation. This indicated that IICGs is one of the suitable adsorbents which can be used for the household treatment of arsenic in groundwater in rural areas.

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