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Using Porous Ceramic for Arsenic Contaminated
Groundwater Treatment

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Development of low cost arsenic adsorbent using porous ceramic for arsenic contaminated groundwater treatment

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Abstract

The efficient arsenic removal system in Cambodia is composed of an arsenic precipitation-filtration part which removes the arsenic up to 95% and arsenic adsorbent part which removes the rest of arsenic to be less 1 $\mu\text{g/L}$. The ceramic arsenic adsorbent (CAA) was developed successfully using the porous ceramic discarded from the factory of ceramic water purifier (CWP) as support and was loaded three times with ferric chloride. Using the arsenic groundwater with arsenic concentration of 800 $\mu\text{g/L}$, CAA absorbed the arsenic 200 $\mu\text{g/g}$ adsorbent (Std Dev = 8) at saturation. The adsorption capacity is comparable to various iron-based arsenic adsorbents. Interestingly, the production cost of CAA is very cheap. Unlike the anionic resin, the anionic resin embedded by hydrated ferric oxide and the cationic resin embedded by hydrated ferric oxide, the arsenic saturated CAA showed its adsorption stability when different water chemistry were used to mix it over several days and its regeneration ability using sodium hydroxide 2.5%. The ceramic embedded by ferric chloride before firing had shown a low arsenic adsorption capacity compared to CAA.

Keywords: Arsenic, Groundwater, Arsenic Adsorbent

1. INTRODUCTION

The arsenic pollution in the groundwater in Cambodia becomes serious in Kandal, Kampong Cham, Prey Veng, Kratie, Kampong Chhang and Kampong Thom provinces. More than 320 arsenicosis cases and few cancer patients have been recorded recently. The number will increase in the following years if serious measures will not be taken for stopping the problem since about one million of people are living in the areas where their groundwater is polluted by arsenic and about 230,000 Cambodians are drinking the

arsenic polluted water especially during the dry season when their rainwater run out (KAP 2006; KAP 2009). Though efforts from the government and UNICEF to raise the awareness on arsenic for the rural population, the percentage of the people who have been informed about arsenic increases slowly within 3 years from 12 to 30% from 2006 to 2009. The arsenic free water policy such as rainwater collection, surface and arsenic safe well water with the microbial treatment have been encouraged through the collective activities of government agencies and non-governmental organizations. However, the no-option

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locations for arsenic safe water source, the avoid using of arsenic groundwater can not be done due to the high investment cost for the poor populations. The arsenic removal system can then be used to provide the arsenic safe drinking water.

The efficient arsenic removal system is composed of two major steps such as the oxidation - coprecipitation - filtration of iron, arsenic and some phosphate to provide the clear water with arsenic concentration less than 50 $\mu\text{g} / \text{L}$ and the arsenic adsorption in a column using the media to remove the arsenic concentration to be less than 1 ppb regardless the initial concentration of arsenic in the groundwater (SenGupta *et al.* 2010). If the above previous steps are not included in the system, the arsenic removal efficiency is expected to be only up to 95% at the beginning and efficiency decrease rapidly over the long treatment time (Sarkar *et al.* 2010; Uy *et al.* 2009). Various technologies use different forms of oxide metals such as titanium oxide (Bang *et al.* 2005; Dutta *et al.* 2004), zirconium oxide (Suzuki *et al.* 2000) and iron oxide (Cumbal and Sengupta, 2005; Driehaus *et al.* 1998; Dong *et al.* 2009; Hug *et al.* 2008; Shafiquzzaman *et al.* 2011). However, the iron oxide based adsorbent is known to be used for its low cost. The use of ceramic water filter with the iron net to supplement the rusted iron was studied in the household scale (Shafiquzzaman *et al.* 2011) and the zero-valence iron particles was used to coat the porous ceramic granules for preparing the iron coated pottery granules (Dong *et al.* 2009).

In this study, the porous ceramic discarded from the ceramic water purifier factory was used to produce the arsenic adsorbent and the ferric chloride was used to embed the hydrated ferric hydroxide in the porous ceramic. The arsenic adsorption kinetic and the adsorption stability were also studied. The cost benefit of this new adsorbent can participate in valorizing broken porous ceramic from the ceramic water purifier factory for the preparation of low cost arsenic adsorbent which can participate in arsenic mitigation activity for the poor rural population.

2. MATERIALS AND METHODS

2.1 Preparation of ceramic arsenic adsorbent (CAA) and other adsorbents

For preparing the ceramic arsenic adsorbent (CAA), the porous ceramic was obtained from the factory producing the

ceramic water purifier (CWP) which is prepared by mixing the clay (62 %), fine rice husk (17 %) and water (21 %), pressed and fired at about 800 °C for about 3 h. The broken ceramic from this production was used to prepare the porous ceramic granules with desired size using a suitable sieve. The size from 0.6 - 1 mm is suitable for a good water flow and arsenic adsorption rate. Ferric chloride solution was prepared by mixing the ferric chloride 3 M and the final pH was adjusted to pH = 3 by sodium hydroxide or hydrochloric acid before using. CAA was produced by soaking the dry porous ceramic granules in ferric chloride solution above and was dried. Three cycles were used to maximize the iron content.

For the other adsorbents, we prepared as following: (i) the anionic resin (ANR-600) was purchased from the market, (ii) the anionic resin ANR-600 embedded by hydrated ferric oxide was prepared by adsorption of permanganate (MnO_4) on the anionic resin ANR-600 followed by adding iron sulfate (FeSO_4) and the reaction in the resin allow to precipitate the ferric hydroxide ($\text{Fe}(\text{OH})_3$) and the granules was dried, (iii) the cationic resin embedded by hydrated ferric oxide was prepared by mixing the cationic resin with the saturated ferric chloride solution and the obtained granules was dried, (iv) the commercialized resin used is arsenic-selective hybrid anion resin (Karkar *et al.* 2010), (v) the ceramic embedded by ferric chloride before firing is prepared by mixing the clay, ferric chloride, rice husk and water and was fired at 800 °C for about 3 h.

2.2 Arsenic adsorption and adsorption stability

The arsenic adsorption capacity was tested by mixing the ceramic arsenic adsorbent (CAA) or other kinds of adsorbent 1 g in the arsenic polluted groundwater with the arsenic concentration of 800 $\mu\text{g} / \text{L}$ collected from Kandal Province (the iron in the raw groundwater was removed by oxidation and centrifugation to avoid the effect of groundwater iron on the adsorption). The kinetic of arsenic adsorption by CAA till the saturation was studied by testing the arsenic adsorbed in CAA and verified with the remained arsenic concentration in the liquid. The same preparation without CAA was used to evaluate the effect of mixing on the soluble arsenic concentration. The stability of arsenic adsorption by CAA after saturation with arsenic was studied by testing the arsenic absorbed by CAA 1 g mixed with arsenic polluted groundwater and the arsenic on CAA and the arsenic concentration in the water were tested for several days.

2.3 Regeneration of CAA

The regeneration of CAA saturated by arsenic was tested by soaking the CAA in the solutions of sodium hydroxide and sodium chloride at different concentrations. The arsenic released from the CAA and the capacity of regenerated CAA in adsorption the arsenic again was studied. The regeneration produces the liquid waste rich of arsenic.

2.4. Characterization of CAA by SEM-EDAX

To further understand the property of CAA, the morphology and surface elements distribution of raw porous ceramic and iron impregnated porous ceramic was study by SEM and combined to EDAX. EDAX analysis revealed the key elements such as iron, silicon, oxygen and aluminum on the surface of CAA adsorbent.

2.5 Testing of arsenic

The arsenic concentration was tested using spectrophotometry method by generating the arsine gas using sodium borohydride and the released gas was colorized by using the silver diethyldithiocarbamate (Helrich, 1990). The silver diethyldithiocarbamate method was calibrated using an arsenic standard solution. The arsenic in the precipitate or solid form was dissolved by using nitric acid for digestion before testing.

3. RESULTS AND DISCUSSION

3.1 Ceramic arsenic adsorbent (CAA)

CAA produced from porous ceramic granules was produced by soaking the porous ceramic granules with the size of 0.6 - 1 mm. After soaking, the granules in ferric chloride solution, the granules were dried. After repeating three times, these ceramic granules are completely coated and appear in dark red color. This CAA can be used for preparing the arsenic adsorbent column for both household and community scales. The preparation of CAA needs no firing process after coating, a simple drying using sun light drying or other kinds are appropriate. The size of CAA of 0.6 - 1 mm can be used to maintain a high flow rate by the adsorbent column for a long run of water treatment (water flow data not shown). The adsorbent column is generally placed at the last stage of the arsenic removal system when the particles and precipitate from the groundwater have been already removed, if not, the raw water with particles and precipitate

can coat on the arsenic adsorbent surface and make it less effective.

3.2 Property of CAA adsorbent

The morphology and surface elements distribution of raw ceramic granules and Fe-impregnated ceramic granules (CAA) were studied by SEM combined to an EDAX. The image obtained for the raw pottery granules showed that the material was constituted by many aggregated small particle (Fig. 1a), which led to a rough surface and the present of porous structure. However, it can be seen that on the surface of Fe-impregnated ceramic adsorbent (CAA) composed of tiny needle and spherical shape material which suspected to be iron oxide particle. The porous structure also was observed this adsorbent.

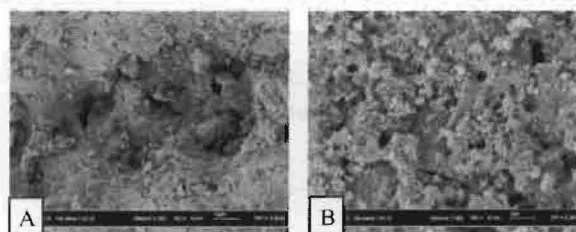


Fig. 1 SEM images of A: raw porous ceramic and B: iron-impregnated ceramic adsorbent (CAA).

The EDAX analysis (Table 1) revealed that the iron content on the surface of adsorbents increase from 3.56 - 8.87 % (raw porous granules) to 26.5 - 54.4 % (Fe-impregnated granules). Higher Fe content was associated to the higher arsenic adsorption at the condition that Fe is well-dispersed. A study (Muniz *et al* 2009) has shown the clear relationship between Fe content and arsenic adsorption. Fe (III) impregnation is very effective, increasing ionic adsorption in a wide range of pH.

Table 1: Main elements present on the surface of raw and Fe-impregnated porous ceramic granules (CAA).

Element	Weight (%)	
	Raw granules	Fe-impregnated granules
Iron	3.56 - 8.87	26.5 - 54.4
Silicon	21.6 - 27.9	2.00 - 6.34
Oxygen	47.8 - 53.5	29.6 - 38.6
Aluminum	8.13 - 11.0	0.69 - 2.29

It is reported that inner sphere complexes between iron and arsenic could formed for pH < pHzc. As (V) is specifically adsorbed onto an iron oxide surface via ligand exchange

mechanism and exists as an inner sphere surface complex (Manning and Goldberg 1997). The increase of iron content leads to a decrease of oxygen content. This is because the existence of oxygen functional group will increase the Fe adsorption due to the interaction of oxygenated functional group with iron. The iron is associated to oxygen and deposited on the entire surface of ceramic in the form of well dispersed nanoparticles. Small and highly dispersed iron oxide nanoparticles are those leading to the highest arsenic removal efficiency (Muniz et al 2009). Reduction of aluminum content is due to the substitution of iron hydroxides to form aluminum substitute iron hydroxide. Previous study shows that arsenic removal was enhanced during concurrent coprecipitation of As (V) with Fe and Al compared to either Fe/Al alone at circumneutral pH (Robins et al 2005). Besides that, the reduction of weight percent of silica shows that Fe-impregnated ceramic adsorbent can be used as promising adsorbents since silica, which has a pHzc of 2.2 and thus presents a negatively charged surface which is unfavourable for arsenate adsorption (Fierro et al 2009).

3.3 Kinetic of arsenic adsorption by CAA

CAA produced from porous ceramic granules is mixed in the arsenic groundwater having the arsenic concentration of 800 µg / L, phosphate of 4 mg / L, iron of 0.01 mg / L and pH = 7.05. The kinetic of the arsenic adsorption by CAA is presented in Fig. 2.

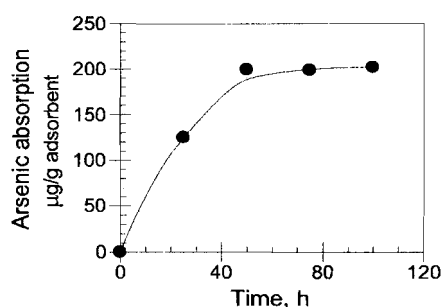


Fig. 2 Kinetic of arsenic adsorption by CAA.

The maximum arsenic absorbed by CAA is 200 µg / g CAA with the time of 50 h verified between the arsenic on CAA and the arsenic lost in the mixing water, while there is no significant lost of the arsenic concentration of the control solution without CAA. The arsenic adsorption capacity by CAA is almost tripled when the distilled water is used to mix with the arsenic (data not shown).

3.4 Comparison of the performance of CAA with other adsorbents

To compare the arsenic adsorption performance of CAA with other adsorbents, we used the groundwater sample above 1 L to mix with 1 g of each adsorbent, and then we mixed till the saturation. The maximum arsenic titer absorbed by each adsorbent at the saturation was tested on the adsorbents and verified with the lost of arsenic concentration in the groundwater used. The performance of these arsenic adsorbents with five times testing for each adsorbent is presented in Table 2.

Table 2. Performance of various iron based arsenic adsorbents.

Adsorbents	Adsorption capacity µg / g adsorbent	Regeneration ability	Adsorption stability
Commercialized anionic resin (ANR-600)	540	Yes	No
Cationic resin embedded by hydrated ferric oxide	200	Yes	No
Anionic resin ANR-600 embedded by hydrated ferric oxide	540	Yes	No
Commercialized arsenic-selective hybrid anion resin	560	Yes	Yes
Ceramic embedded with iron before firing	29	Not tested	Not tested
Porous ceramic embedded with iron hydroxide (CAA) after firing	200	Yes	Yes

The capacity of CAA in absorbing the arsenic is about 2.5 times less compared to commercialized anionic resin, anionic resin embedded by hydrated ferric oxide and arsenic-selective hybrid anion exchanger in the condition of using the above groundwater. Interestingly, the production price is less than USD 2 / Kg CAA. The arsenic adsorption capacity by CAA may be improved if higher porous ceramic is used. The cationic resin embedded by hydrated ferric oxide presents the same capacity of arsenic adsorption with CAA. CAA presents a comparable capacity with zero-valence iron coated pottery granules. However, the study used the solution prepared by mixing the arsenate and distilled water (Dong et al. 2009). The ceramic embedded with iron before firing is not a good arsenic adsorbent. This may be due to the low free hydrated ferric oxide in the structure after firing. Compared with other adsorbent, the regeneration of the adsorbent CAA can be done with the optimal sodium hydroxide solution of 2.5 %. However, as

the cost of CAA is cheap, it may not be necessary to regenerate the adsorbent when it is saturated with arsenic after use since the regeneration will produce the arsenic liquid waste which is more difficult to dispose properly than arsenic saturated CAA. For all adsorbents tested, only commercialized arsenic-selective hybrid anion exchanger and CAA present the arsenic adsorption stability. It is important to avoid using the unstable adsorbent in the arsenic removal system, as we could not know when the arsenic can be adsorbed or released from the adsorbent due to the water chemistry or other conditions.

3.5 Filtration performance of CAA

The filtration performance were studied in household scale (system produces the water from 40 – 100 L / day) using 4 layers filter (from top to bottom) composed of biosand, CAA, small gravel and big gravel the thickness of all layers are respectively 40, 20, 20 and 20 cm. (Fig. 3). The arsenic raw water is poured from the top and the treated water is received from the pipe outside of the system.

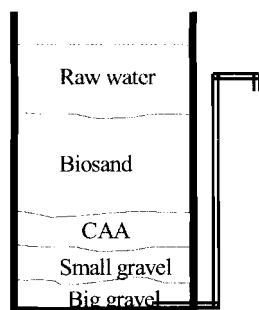


Fig. 3 Household arsenic treatment system.

The biosand layer plays an important role to remove microorganisms and chemicals such as iron, phosphate and manganese and arsenic depending on the groundwater composition. CAA layer removes the remained arsenic after the sand layer. When we used the groundwater with arsenic concentration about 800 – 1000 $\mu\text{g} / \text{L}$ ($\text{Fe} = 4.2 \text{ mg} / \text{L}$, $\text{PO}_4 = 5.8 \text{ mg} / \text{L}$ and $\text{pH} = 6.99$), the system produce the water with undetected concentration of arsenic for the study period of 6 months. Kinetics of arsenic treatment of this system for long period is under study.

4. CONCLUSIONS

The ceramic arsenic adsorbent (CAA) was produced successfully at low cost using the porous ceramic discarded from the ceramic water purifier factory. CAA is a stable

arsenic adsorbent which can be used in the arsenic removal system at the end stage of filtration after the pretreatment by sand filtration. CAA can play an important role to decrease the arsenic concentration to be less than 1 $\mu\text{g} / \text{L}$. This adsorbent can be used for both household arsenic treatment (Uy *et al.* 2009) and community based arsenic removal system scales (Uy, 2011) for the future mitigation program of Cambodia.

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