Development of a High Performance Arsenic Adsorbent and Use for the Adsorbent

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Abstract

In volcanic country Japan, in which exceed the environmental quality standard of arsenic in a drinking water. Moreover, removal of arsenic in hot spring drainage is also a big subject of future. Now, arsenic removal techniques are the hydroxide coagulation method use iron and aluminum etc. By this method, if a lot of drainage is treated, treating of the sludge generated in large quantities will become a problem. Moreover, operation management is troublesome and the problem that installation area is large. Then, it is cheap, and handling is easy, and it looks forward to the effective arsenic removing methods don't take installation area.

In this study, the adsorbent was put in the column, arsenic content imitation water was poured in it from the upper part, and flowed out from the rower part, treated water was water sampling, and arsenic concentration was analyzed. The optimal absorbent was chosen from the result, it investigated about the influence which raw water quality, treating conditions, etc. have on absorbent, and the validity as arsenic adsorption removing method was examined.

The arsenic absorption ability is 5mg/l, and it is always possible for stable processing, and long-term driving is possible. In addition, pH adjustment is uselessness or need, but there may be a little quantity of medicine use because a range of reasonable pH value is wide. We establish a manufacturing process of production in large quantities in future and develop higher-performance arsenic absorption materials

Key Words: *Arsenic removal technique, adsorbent*

Introduction

Arsenic is an industrially important chemical in semiconductor industry. On the other hand, it is a substance with a high risk in human health. Arsenic is designated as the poison by Poisonous and Deleterious Substances Control Law as well as designated as detriment by applicable laws and regulations such as the water quality and waste. In the chemical form of arsenic, the toxicity of inorganic arsenics such as As2O34 - and AsO43 – is extremely high compared with organic arsenic. The tap water standard to the arsenic provided by Act of Parliament is 0.01mg/l or less. The effluent standard of Water Pollution Control Law to the arsenic provided by Act of Parliament is 0.1mg/l or less. The soil and water pollution with arsenic are serious social issue in Asian nations. On an international basis, the water quality guideline value concerning arsenic is severe. The technologies to completely solve the problems as follow: ensuring safe water meeting the water quality criterion, development of the treatment technology and the adsorbent of the generation sludge to prevent cross-contamination, the medicine remaining in the drinking water that originates in the adsorbent, are urgent needs.

The arsenic pollution ground in Asia extends to a large area such as Japan, China, Taiwan, Philippines, Thailand, India, Bangladesh, Vietnam, Myanmar, Nepal, and Pakistan according to the material of NPO Asian Arsenic Network. Especially, in Bangladesh, hundreds of people are reported to drink highly density (0.05-number mg/l) contaminated groundwater. The polluters are mine operation, arsenic content coal combustion, geothermal power stations, abandoned chemical weapons, contaminated wells, and polluted groundwater. Also there are pollution by the natural phenomenon and pollution that originates in life and the productive activity. Particularly, the water resource pollution by the elution of a stratum and soil inside arsenic becomes serious as the soil and the underground water survey in each country of Asia proceed People are expecting the development of an effective, economical cleanup technology. What is the urgent need is to obtain the technologies to completely solve the problems as follow: ensuring safe water meeting the water quality criterion, development of the treatment technology and the adsorbent of the generation sludge to prevent cross-contamination, the medicine remaining in the drinking water that originates in the adsorbent. In the report, the treatment technology of the arsenic polluted water is described.

The method for removing arsenic for industrial use is cohesion and coprecipitation method, that uses the iron salt and the aluminum salt. However, this method cannot be used in the place without electricity and the technology such as Bangladesh. Moreover, there are a lot of places where underground water is used as tap water by the drop shipment when the well is used in Japan. We developed the efficient arsenic adsorbent used in such a place. We report on the result of examining the arsenic adsorption characteristic and the use.

Development of arsenic adsorbent

arsenic adsorbent

There is a report that ferrioxide covered sand was used as filter media to removal arsenic effectively. However, the process of baking the ferrioxide on sand surface is necessary to manufacture this sand, but the process is complex and is high in cost. Therefore, it doesn't expand on a large scale.
The base material of this adsorbent, that had been developed this time, is porous and is coated iron and the oxide of aluminum. There is no complex process like baking, and the process of manufacture is also easily. The characteristic of this adsorbent is shown in Table.1.

Fig.1 Adsorbent of Arsenic (MP-C)

Table1. Characteristic of Absorbent

saturated hydraulic conductivity	6.6×10^{-2}cm/sec
high specific gravity	0.759
apparent specific gravity	1.508
absolute specific gravity	2.077
specific surface area	960m^2/g
porosity	0.50
grain diameter	0.46～2.2mm

	particle size (mm)	measured figure
Particle size (%)	2.2 以上	0.0
	1.71-2.2	0.1
	1.17-1.71	32.8
	0.78-1.17	47.4
	0.46-0.78	18.5
	0.46 or less	1.2

Fundamental Experiment

Confirmation of proper pH

Simulated water (AS (III) ・As(V)each 20mg-As/L) was adjusted by sulfuric acid and sodium hydroxide to PH2～12. The batch-wise adsorption examination was carried out. Fig.2 shows the result.

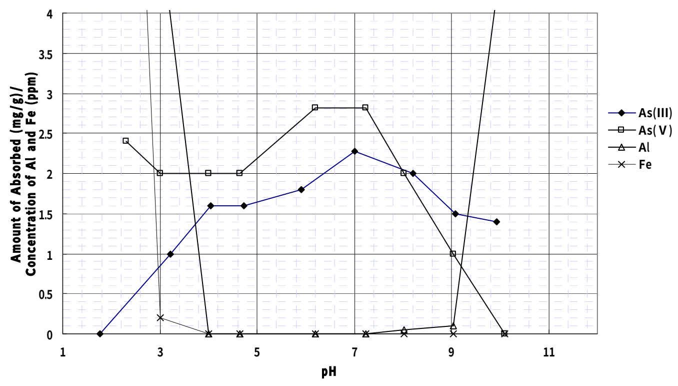


Fig.2 Amount of As Absorbed depend on Form of As and pH

Both As (III) and As (V) have the arsenic adsorption ability in the range of about pH4-9 according to Fig.2. However, the amount of adsorption of arsenic decreases when becoming a strong alkaline. As one can see the following reactive type, when the pH is acidity, the plus is electrified on the surface of the adsorbent. On the other hand, when pH is alkalinity the minus is electrified on it. Therefore, arsenic adsorbs depending upon the pH.

$$Fe\text{-}OH_2^+ \xleftarrow{+H^+} Fe\text{-}OH \xrightarrow{+OH^-} Fe\text{-}O^-$$

Moreover, the adsorption ability of As (III) cannot be seen when becoming a strong acid, and the elution of iron and the aluminum ion happens. Therefore, it can be said that a proper pH of the arsenic removal is the vicinity of the neutral.

As for the mechanism of arsenic eluting from the iron hydroxide colloid, by contacting with the high pH water, the charge state of iron colloid changes and arsenic desorbs. For this reason, after this adsorbent reaches saturation, arsenic can be desorbed by alkaline water, and recycling is possible.

Equilibrium adsorption test

To evaluate the arsenic adsorption ability of the adsorbent, batch-wise equilibrium adsorption test was run. Simulated water (AS (III) ・As(V)each 20mg-As/L) was adjusted to pH7 and the amount of adsorbent was changed and tested. The result is shown in Fig.3. The approximate formula is described in parallel in case of assuming that the actual measurement value is followed Equilibrium Adsorbed Isotherm of Freundlich.

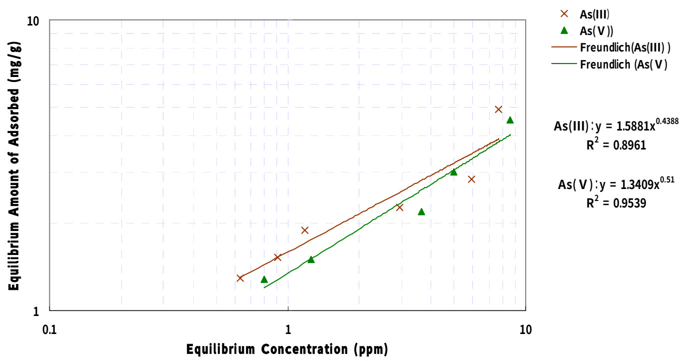


Fig.3 Equilibrium Adsorbed Isotherm

As(III): $q = 1.588 \times C^{0.439}$

As( ) : $q = 1.34 \times C^{0.51}$

q : equilibrium adsorption amount (mg/g)

C : equilibrium concentration (mg/l)

There is little difference for the removal of As ( ) and As ( ) ; so that a high adsorption ability in a wide density range can be expected.

Table2. Amount of As Absorbed depend on As Concentration

As Concentration (mg/l)		0.1	0.5	1.0	5.0	10.0	20.0
Amount of As Adsorbed	As( )	0.58	1.17	1.59	3.22	4.36	5.92
	As( )	0.41	0.94	1.34	3.04	4.34	6.17

Influence of coexistence negative ion

The coexistence material that adsorbs the adsorbent has the possibility of influencing the arsenic adsorption.

To become 100mg/l, other negative ions (PO43-、F-、B(OH)3-、SO42-、Cl-、HCO3-、NO3-) were added to As 20mg-As/L (Ⅴ) solution. The batch-wise adsorption test was carried out.

According to Fig.4, an adsorbent rank of the negative ion in the adsorbent used this time is As>PO43->NO3->CO32->SO42->Cl-.

It is unconfirmed how much affect PO43 give.

However, the adsorption ability decreases only by about 30% though five times the coexistence material are added compared with arsenic.

Therefore, the coexistence material of the low concentration will be almost unaffected.

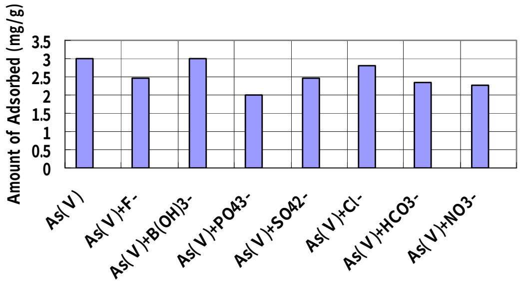


Fig.4 Influence of Coexistence Ion

Continuous passing water experiment

A special adsorbent was filled in the column, and the simulative water adjusted to As 5mg/L (Ⅴ) was passed to the column continuously in the direction of a downward style with a micro tube pump.

Experimental conditions

- Raw water density: 5.00mg/l
- Raw water pH:6.78
- Adsorbent volume: 159.20cm3
- Adsorbent weight: 93.0g
- SV:5h-1(796ml/h)

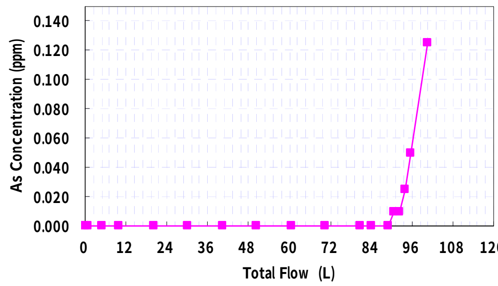


Fig.5 Breakthrough Curve

According to Fig.5, when the tap water standard is assumed to be a breakthrough point, the amount to the breakthrough of the arsenic theory adsorption is 5.13mg/g.

The densities of the treat water can be processed up to 0.001(detection limit) . It is possible to use it safely as a drinking water. If the arsenic density of processing water is 0.5mg/l, and the amount of processing is 1m3/h(SV:1), it takes the breakthrough adsorbent for about seven months. Therefore, this amount of adsorption can be called as a great outcome in the economical efficiency and automatic running perfomance as a disposable adsorbet.

Experiment that uses discharged water

Experiment 1

The density of arsenic was detected from the water obtained from the waterway in Takachiho-cho of Miyazaki Prefecture. Then, the column experiment was done by using MP-C.

Raw water properties

The raw water properties are shown in Table.3.

Table.3 Characteristic of raw water

	Concentration(simple analysis)	Concentration(Official analysis)
pH	6.9	7.1
As	0.02mg/l	0.036mg/l
PO_4^{3-}	0.2mg/l	0.03mg/l
Fe	0.05mg/l	0.08mg/l

Bench-scale column testing

In the column examination, the plastic column filter of 16mm in the diameter and 165mm in length is used.

Therefore, the amount of the adsorbent is 33ml.

Water that contained the arsenic of 36μg/l was poured in the column

by the flowing water with quantity of 5.6ml/min by using a micro tube pump.

The time course of the arsenic density was measured at the column exit.

And the arsenic adsorption ability of MP-C was confirmed.

Table.4 Condition of Experiment

Internal diameter of culum	16mm
Length of filling up	165mm
Volume	33ml（17.1g）
Amount of flowing	336ml/h
	5.6ml/min
SV	$10.1h^{-}$

Result

Table.5 and Fig.7 show the result of continuous pass water experiment.

Table.5 Result of Experiment

Total flow (L)	As Concentration (mg/l)		pH
	simple analysis	Official analysis	
1	under0.005	under0.005	5.8
8	under0.005	under0.005	5.8
10	under0.005	under0.005	6.0
16	under0.005	under0.005	6.4
20	under0.005	under0.005	6.5
24	under0.005	under0.005	6.6
30	under0.005	under0.005	6.8
36	under0.005	under0.005	6.9
40	under0.005	under0.005	6.9
44	under0.005	under0.005	6.9

Fig.6 Setting of Experiment

Arsenic was treatable below environmental standards from the outcome of the experiment.
The symptom of the saturation of MP-C was not seen.
Moreover, because the raw water density was 0.036mg/l and a low concentration, it has been understood that it can also process the arsenic polluted water of the fairly low concentration.
＊ The amount of the arsenic wear in this experiment was 0.093mg/g. Moreover, with a past performance, 2,375L can be processed.

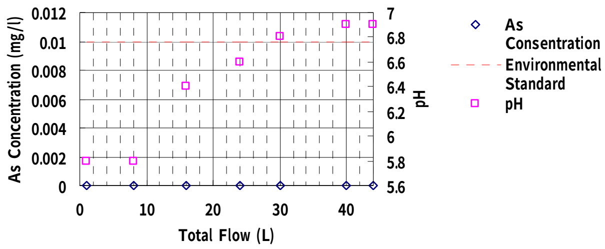


Fig.7 Result of Experiment

Experiment 2

As for the arsenic contained in the wastewater in tha pit of Torokyu,
the arsenic removal performance of the adsorbent was confirmed with the continuous pass water experiment using MP-C (our newly developed arsenic adsorbent)

Raw water properties

The raw water properties are shown in Table.6.

Table.6 Characteristic of raw water

	Concentration(Official analysis)
pH	7.8
As	0.11mg/l

Bench scale column examination

In the column examination, a plastic column filter that is 16mm in the diameter and 155mm in length was used.
Therefore, the amount of the adsorbent is 31ml.
Water that contained the arsenic of 0.11mg/l was poured in the column by the passing water with the quantity of 5.0ml/min by using a micro tube pump. The time course of the arsenic density was measured at the column exit. And, we confirmed the arsenic adsorption ability of MP-C.

Table.7 Condition of Experiment

Internal diameter of culum	16mm
Length of filling up	155mm
Volume	31ml（15.5g）
Amount of flowing	300ml/h
	5.0ml/min
ＳＶ	9.7h^{-}

Result

The result of the continuous pass water experiment is shown in Table.8.

Table.8 Result of Experiment

Total flow (L)	As Concentration (mg/l) Official analysis	pH
1	under0.005	6.8
6	under0.005	7.3
10	under0.005	7.3
15	under0.005	7.3
20	under0.005	7.3

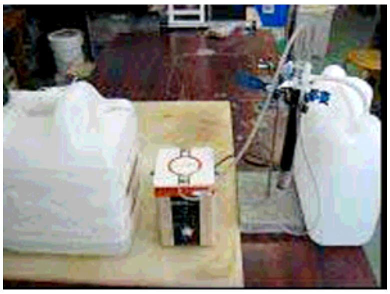
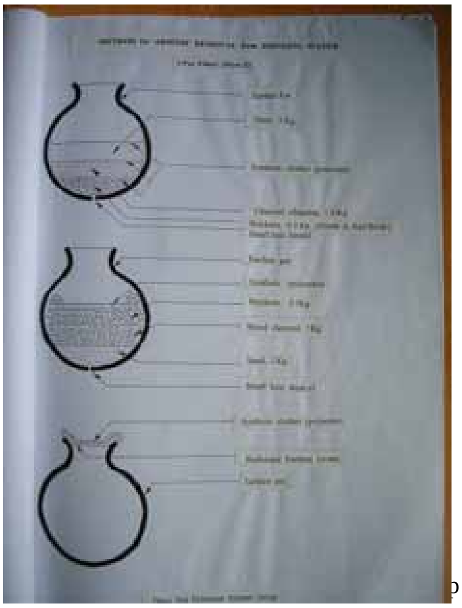


Fig.8 Setting of Experiment

Field survey

Myanmar



There was a request through Dr. KUnio Watanabe of The Geosphere Research Institute of Saitama University（GRIS), who is the director of Japan Myanmar Interchange Association (AJMMC). The survey of the arsenic pollution underground water in the pollution area was carried out. We had meetings and workshops with Ministry of Public Health of Myanmar, the Rangoon Institute of Technology, the Myanmar maritime affairs universities, the industry associations of Myanmar.

Information including the purification processing experiment was exchanged.

We visited Myanmar from September, 24th to September, 27th, 2005.

The performance of the field survey and the arsenic adsorbent was checked.

When we visited the laboratory of Ministry of Public Health in Rangoon, we also observed jar type filtration system (3pot filter).

The filter media were natural sand including iron, river sand, gravel, brick rubbishs, minute sand, the activated carbons, and the crushing activated carbons.

As a result, both system could treat the one of 100ppb arsenic desity below the detection limit.

The excellent performance and high technology of MP-C were proven.

Moreover, We demonstrated the arsenic removal by MP-C for the Ministry of Transport by using the water gathered in the well in the Irrawaddy river delta region.

We chould show the changes that the water that had browned with the iron content becomes transparent.

Moreover, after brownish water was passed MP-C water, the arsenic density was removed till about 5ppb (1/100).

It was a high appraisal.

Fig.10 Three Pot Filtration System

Future tasks are to grope for better use by using MP-C with the jar filtration system.

Moreover, there are some to action assignment remained such as possibility of manufacturing MP-C in the locale, the investigation of the raw procurement, and more experimental proof test on site.

Bangladesh

We visited Bangladesh from July, 3rd to July, 6th, 2006 with assistant professor Mr. Sezaki, the Department of Civil and Environmental of at Miyazaki University.
We surveyed the DTW construction site and the purification processing site.
The purification and the measures in Bangladesh were the construction of the deep well, Gravel Sand Filter, Rain Water, and UNICEF's arsenic removal devices.

Neither purification nor countermeasures were able to obtain a safe drinking water.
Arsenic that exceeded the environmental standards value was detected even as for the water pumped up from the deep well.
The filtration method called Gravel Sand Filter
in which water was poured from the gravel to the layer of sand. The treatability was depended upon quality of raw water.
The Gravel Sand Filter could treat low density arsenic polluted water, but it could not do high density with low iron concentration
The arsenic removal device of UNICEF is an absorptive treatment with sand filtration and active alumina.
This device is very expensive, the manufacturer check is every two years and safety is low.
We felt that recovering the administration, before the arsenic processing took place, was necessary, and the system making by the resident was also necessary.
When such a system is established, the management of the arsenic removal device by the resident becomes possible.


Fig.10 Gravel Sand Filter


Fig.11 Gravel Sand Filter (L: Raw Water R: Treated Water)

Summary

The adsorbent that is able to purify the arsenic polluted water 0.001(detection limit)or less was developed. To confirm the adaptability for the filtration processing method, the laboratory experiment was held.
As a result, regarding the coagulation treatment and processing with active alumina, adding oxidant is necessary to make three values arsenic to five values and pH adjustment is also necessary to set pH to the appropriate range for processing. However, these processing was not necessary in the arsenic adsorbent that our company had developed. It has been understood that the influence of the coexistence material is hardly received and selectivity to arsenic is very high. As for the use propriety pH is about neutral, and the amount of this arsenic adsorbent for each unit adsorption is about 5mg/g. Moreover, the adsorption ability similar to five values was shown in three values arsenic. he manufacturing method that can develop a more efficient adsorbent and mass-produce it at a low price is examined as future tasks.

The address of thanks:
We sincerely would like to express our gratitude for undertaking this research, and cooperating people concerned and related to assistant professor Mr. Sezaki, the Miyazaki University, Dr. Watanabe of Saitama University.