

UTILIZATION OF LOCALLY AVAILABLE BENTONITES FOR WATER PURIFICATION BY ACTIVATION

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ABSTRACT

Acid activation of commercial bentonite was conducted and tested for adsorption of impurities in water and industrial products. The properties of adsorption/absorption of bentonite are also used to remove impurities for the processing of edible oils and fats, as well as for the purification of products like honey and alcohol. The design of various experiments in order to assess and simulate the effects of acid activation of commercial bentonite on the adsorption capacity of methylene blue dye is described in this paper. The key parameters of the acid activation, namely acid concentration, contact time, temperature and type of acid, were established. The results indicated effects of these variables on the effectiveness of adsorption. The Swelling Index value of activated bentonite was 20 ml per 2 gram in deionized water as compared to 8 ml per 2 gm in unactivated samples. The acid concentration exerts a predominant individual effect as compared to other parameters. Bentonite activated by 5N HCl has more adsorption capacity than 40% H₂SO₄. Excessive activation is discussed in terms of loss in both porosity and acid strength.

Keywords: Water purification, Bentonites, Absorption Index.

1. INTRODUCTION

Due to absorptive and catalytic properties of bentonite, it is used in wide variety of applications. Use of acid-activated clays are most common in adsorption studies of different materials. In the presence of metal cations in water, the interaction of montmorillonite with chitosane involves a complex coagulation-flocculation process that includes not only absorption, but also chelation and ion-exchange [1]. A series of features including the available surface area and acidity of the clay sheets, along with the exchangeable cations exert influence upon the bleaching capacity of a given clay [2-4]. Acid treatment is expected to improve the specific surface area and porosity, unless the clay framework collapses, more particularly under severe activation conditions. Nonetheless, the decay in bleaching effectiveness cannot be explained in terms of only clay structure collapsing, as reported by Kheok & Lim [5]. The acidic activation of bentonites must involve partial delamination, inducing an increase in the silica/alumina ratio. As a result, there is an increase in the number of weak acidic Si-OH groups,

and subsequently in the global acidity of the clay, though only up to certain levels. Nevertheless, this may occur at the expense of not only [Si-O-Al]H groups in the tetrahedral layers of the clay lamellae, if traces of beidellite are present, but also most of [Al-O-Metal²⁺]H groups, in the case of an extensive acid attack on the octahedral layer in montmorillonite. These removed groups are well known for displaying stronger acidities than terminal silanols [6] and are presumably involved in absorption site [7]. Consequently, both the acidity strength and negative charge of the clay surface will rather decrease, in contrast with results reported by Kheok & Lim [5]. Acid activated bentonite clays (which are usually known as bleaching clays) show a much higher bleaching capacity. During acid treatment of the clay, initially interlayer cations are replaced with H⁺ ions followed by partial destruction of aluminum octahedral and silicon tetrahedral sheets with subsequent dissolution of structural cations. It is believed that this process results in the delamination of the structure, which consequently increases clay specific surface area and pore volume that improves the adsorption capacity of color producing substances from the oil.

The mechanism of retention of the pigments, including carotene and carotenoids, at the surface of an activated clay is not clear. There are small quantities of chlorophyll found in nearly every type of edible oil that also contribute to the coloration. The chlorophyll molecule is believed to be adsorbed as a protonated species, pointing out the importance of the acidic properties of the bleaching clay. The surface acidity and the porous structure of bentonite can be changed to the desired extent by acid activation. These changes depend on: the smectite minerals, other clay minerals and non-clay minerals contained in the bentonite, as well as the chemical composition, the type of cations between the layers, the type of the acid, the mass percent of the acid in the bentonite-acid mixture, the process temperature, and the process period. The desired changes in the physicochemical properties of a bentonite occurring as a result of acid activation, depend considerably on the condition of acid activation such as the acid concentration and the duration and temperature of the activation process. Acid reactions of various bentonites have been intensively investigated to explain these changes. The present study was therefore carried out in order to evaluate the adsorption capacity of commercial bentonite after acid activation with HCl.

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It is known that clay minerals possess attractive properties as solid acids. Their acidities are due to active centers on the surface that exhibit Bronsted and Lewis acidities. Such an important property, which governs most of the clay's interactions in so many application areas, needs to be determined quantitatively in relation to structural changes during acid activation and thermal treatment. Bentonites are used as industrial raw materials in more than 25 application areas, including the production of selective adsorbents [8], bleaching earth [9], catalyst beds, carbonless copy paper and medication. The absorption capacity of the bentonite is increased many times by activation process. The process considerably increases the absorptive properties of montmorillonite without disturbing the layered crystal structure of these clays [10]. New pores are created by liberation of some ions, such as Al^{3+} , Fe^{2+} , Fe^{3+} , Mg^{2+} from the octahedral layer exposed at edges of smectite. Similarly, silicon (Si) released from tetrahedral layer precipitates in the form of amorphous silica with H^+ ions [11]. Activation process enhances the surface area and pores diameter [12,13,14] of the clays, thereby absorbing more amount of pigments. Increase in surface area is a function of acid strength and time of treatment of the clay [15] along with other parameters. It has been observed that bleaching capacity of clays is increased more than four times by acid activation process [16]. Tiny pores present in clays contain salts that are removed by the acid treatment thereby increasing the effective absorption area and the bleaching powder. It has been shown that activation with hydrochloric acid is more effective as compared to sulphuric acid treatment [17,18]. Therefore, hydrochloric acid (HCl) was used for activation of these clays.

The ingested or inhaled inorganic arsenic through medicinal, occupational and environmental exposures is well-documented as a human carcinogen of skin and lung. Using the prevalence of skin cancer among residents in an endemic area of chronic arsenicism and an unexposed control area [19], U.S. Environmental Protection Agency (EPA) made an estimation of potency index of developing skin cancer of 1.3×10^{-3} for an American male who is exposed to $1 \mu\text{g}/\text{kg}/\text{day}$ inorganic arsenic through drinking water, for a 76-year lifespan [20]. Based on the data from smelter workers in Anaconda (Montana) [21] and in Tacoma (Washington) [22], a potency index of developing lung cancer was estimated ranging from 4.6×10^{-3} to 2.4×10^{-2} for an American male who is exposed to $1 \mu\text{g}/\text{kg}/\text{day}$ inorganic arsenic through inhalation [23]. Significant associations between

ingested arsenic and malignant neoplasms of the liver, lung, bladder, and kidney among residents in the endemic area of chronic arsenicism were reported by Chen, et al., 1985, 1986, and 1988; Wu, et al., 1989 [31-33]. The elevated risk of internal organ cancers associated with inorganic arsenic exposure through drinking water is observed not only in the confined endemic area but also observed in 314 precincts and townships of Taiwan [24]. The first described health effect, reported by Agricola in *De Re Metallica* in 1556 [25], involved arsenical cobalt that ate away the skin of the hands of workmen. In 1888, Hutchison first described carcinoma of the skin in patients treated with arsenical mixtures for psoriasis and other skin conditions [26]. Subsequent investigations have confirmed that ingestion of inorganic arsenic can cause skin cancer and that inhalation of inorganic arsenic can cause lung cancer [27]. Both organic and inorganic arsenic are present in varying amounts in food. Fish, for example, contains relatively high concentrations of organic arsenic. However, inorganic forms of arsenic are much more toxic than its organic forms. Inorganic arsenic can be present as either arsenate [As(V)] or arsenite [As(III)]. Although As(III) is more toxic, human metabolism of As(V) involves reduction to As(III) before undergoing detoxification by methylation [27]. Arsenic is present in soil at levels ranging from 0.2 to $40 \mu\text{g}/\text{g}$ (rarely more than $10 \mu\text{g}/\text{g}$) and in urban air at levels around $0.02 \mu\text{g}/\text{m}^3$ [28], but for the general population the main exposure to inorganic arsenic is through ingestion. Although most major U.S. drinking water supplies contain levels lower than $5 \mu\text{g}/\text{L}$, it has been estimated that about 350,000 people might drink water containing more than $50 \mu\text{g}/\text{L}$ [29], the standard for arsenic set by the U.S. Environmental Protection Agency (EPA).

The demand for effective and inexpensive adsorbents is to increase response to the deleterious health effects of arsenic exposure through drinking water. A novel adsorbent, aluminum-loaded Shirasu-zeolite P1 (Al-SZP1) was prepared and employed for the adsorption and removal of arsenic (V) (As(V)) ion from aqueous system. The process of adsorption follows first-order kinetics and the adsorption behavior is fitted with a Freundlich isotherm. The adsorption of As(V) is slightly dependent on the initial pH over a wide range [30]. Al-SZP1 was found with a high As(V) adsorption ability, equivalent to that of activated alumina, and seems to be especially suitable for removal of As(V) in low concentrations. The addition of arsenite, chloride, nitrate, sulphate, chromate, and acetate ions hardly affected the As(V) adsorption, whereas the coexisting phosphate greatly interfered with the adsorption. The

adsorption mechanism is considered as a ligand-exchange process between As(V) ions and the hydroxide groups present on the surface of Al-SZP1. The adsorbed As(V) ions were desorbed effectively by a 40 mM NaOH solution. Continuous operation was demonstrated in a column packed with Al-SZP1 [30].

Existing overviews of arsenic removal include technologies that have traditionally been used (oxidation, precipitation/coagulation/membrane separation) with far less attention paid to adsorption. No previous review is available where readers can get an overview of the sorption capacities of both available and developed sorbents used for arsenic remediation together with the traditional remediation methods. Some low-cost adsorbents are superior, including treated slags, carbons developed from agricultural waste (char carbons and coconut husk carbons), biosorbents (immobilized biomass, orange juice residue), goethite and some commercial adsorbents, which include resins, gels, silica; treated silica tested for arsenic removal came out to be most superior. Immobilized biomass adsorbents offered outstanding performances. The use of bentonite as adsorbent is also very cheap and effective for the removal of arsenic from drinking water.

The purpose of this study is to highlight the fact that the presence of arsenic in drinking water causes cancer in different body parts and it is very dangerous for health. In Bangladesh it is rapidly increasing the health dangers among the people who are continuously drinking arsenic containing water. Thus, it is suggested under the light of experiments that bentonite clay may be used as a good adsorbent of arsenic from drinking water, and by activation of bentonite its adsorption capacity is enhanced to get better results. Both natural and commercial bentonites can be used for adsorption because it is an inexpensive way to remove arsenic from drinking water.

The objectives of the study were:

- To improve the water quality containing arsenic by using adsorption techniques; and
- Maximum adsorption of arsenic from drinking water through activated and non-activated bentonite clay.

2. EXPERIMENTAL WORK

2.1 For Activation Study with HCl

Commercial bentonite clay was used for the study. Studies were performed on the air-dried and sieved (<149 μm) samples. 10 gm of the sample was mixed with HCl solution (100 ml) of concentration (5N), and the resulting suspension was heated at 80 ± 2 °C for 2 hours with continuous stirring. The slurry was cooled, filtered and washed thoroughly with distilled water to remove remaining chloride ions (tested by AgNO_3 solution). It was dried initially at room temperature and then heated at 70 °C for 3 hours. The lumps of dried clay were crushed and sieved again to less than 149 μm particle size.

2.2 For Activation Study with H_2SO_4

Ten gram sample of bentonite clay was taken in 250 ml conical flask. An amount of 80 ml of 40% H_2SO_4 was added and heated after fitting reflex condenser. The material was filtered and washed with distilled water until the filtrate shows neutralized pH, which is confirmed by pH paper. Then residue was dried in an oven at 100 °C and activated sample was crushed and sieved.

2.3 Adsorption Study of Methylene Blue

For the analysis of adsorption capacity of both above-mentioned activated samples (by 40% H_2SO_4 and 5N HCl), an experiment was performed with methylene blue dye. Stock solution of methylene blue was prepared by adding 0.1 gm of dye in 1000 mL distilled water. Then some dilutions were made ranging from 1 to 10%. After that 10 gm of sieved activated clay sample was taken in conical flask, and 30 mL of distilled water was added. The mixture was stirred and then drop by drop standard solution of dye was added till the point when solution retained its colour and discoloration (adsorption by bentonite) stopped.

2.4 Adsorption Study of Arsenic

Four samples of commercial bentonite were used for the experiment. Two of the these were acid activated and other two were non activated. Two of the samples of arsenic contained water of concentrations 1000 ppb and 2000 ppb. Ten to 15 grams of activated and non activated bentonite were treated with both samples of arsenic containing water, and these were allowed to sit for 4 to 5 days before filtering them. The used bentonite was separated and the concentration of

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arsenic in that treated water was checked.

3. RESULTS AND DISCUSSIONS

The results of the study are tabulated in Table 1-8, and Figure-1.

Studies have been undertaken on the bentonite clay samples (from Azad Jammu and Kashmir) procured from industry in connection with the commercial utilization. Different studies have been carried out. Activation of clay samples can be undertaken by acid as well as base. But clay samples were activated by 20% H_2SO_4 and the weight loss of clays was in the range of 5% to 33% in three clay samples.

Adsorption capacity of clay samples was studied before and after acid activation. Clay sample was taken in conical flask with potassium thiocyanide and distilled water, and was then titrated with ferric ammonium sulphate. On the addition of ferric ammonium sulphate, a reddish orange dye was produced, after which the adsorption of this dye by clay samples was observed. Activated samples adsorbed less as compared to inactivated samples. The volume adsorbed by activated samples was 9 ml and 7 ml, while on it was 26 ml and 28 ml for unactivated samples. Clay samples were then activated by 33% HCl and 40% H_2SO_4 . In order to compare the adsorption capacity of the two activated samples, the water solution of clay samples were titrated with methylene blue dye and allowed to sit for

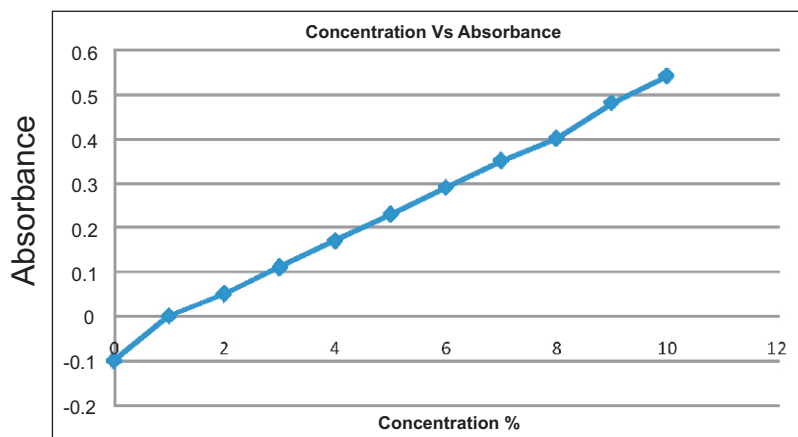


Figure-1: The Absorbance of Methylene Blue at Different Concentrations

Table-1: Loss of Weight during Activation of DYL-21-W at Different Times

Sr #	Time (min)	Initial wt (gm)	Final wt (gm)	Change in wt(gm)	Loss in wt (%age)
1	10	10	7.64	2.36	24
2	15	10	8.52	1.48	15
3	20	10	7.25	2.75	28
4	25	10	7.97	2.03	20
5	30	10	7.21	2.79	28

Table-2: Loss of Weight during Activation of DYL-21-G at Different Times

Sr #	Time (min)	Initial wt (gm)	Final wt (gm)	Change in wt (gm)	Loss in wt (%age)
1	10	10	7.46	2.54	25
2	15	10	9	1	10
3	20	10	8.87	1.13	11
4	25	10	7.77	2.23	22
5	30	10	7.05	2.95	30

Table-3: Loss of Weight during Activation of DYL-13 at Different Time

Sr #	Time (min)	Initial wt (gm)	Final wt (gm)	Change in wt (gm)	Loss in wt (%age)
1	10	10	9.53	0.47	5
2	15	10	8.15	1.85	19
3	20	10	6.68	3.32	33
4	25	10	6.27	3.73	37
5	30	10	7.28	2.72	27

Table-4: The Absorbance of Methylene Blue at Different Concentration $\lambda_{max}=620nm$

Concentration (%ge)	Absorbance
10%	0.536
9%	0.475
8%	0.414
7%	0.353
6%	0.292
5%	0.231
4%	0.178
3%	0.112
2%	0.051
1%	-0.007

Table-5: Absorbance of activated clay

Types of mixture	Commercial bentonite (33% HCl activated)	Commercial bentonite (40% H ₂ SO ₄ activated)
Blank	0.321	0.262
With sample	0.022	0.047

Note: 10 ml more of dye is added in following samples:

- i. Original commercial bentonite sample
- ii. 33% HCl activated commercial sample
- iii. 40% H₂SO₄ activated commercial sample

Table-6: The Absorbance of methylene blue by different clay samples

Sample name	Absorbance
Distilled water	0.00
Standard of dye	0.339
33% HCl activated	0.041
40% H ₂ SO ₄ activated	0.159
Original commercial bentonite	0.202

some days for adsorption. As a result, it was proved that adsorption capacities of 33% HCl activated clay samples was greater compared to samples activated with 40% H₂SO₄. Their absorption was 0.022 and 0.047, respectively. Using bentonite as adsorbent can reduce the content of arsenic in drinking water by 100 to 200 times.

4. CONCLUSION

This research paper was based on a study that focused on physical characterization and evaluation of activation parameters. Activation of bentonite clay was carried out with H₂SO₄ as well as with HCl, and subsequent adsorption capacity of natural and activated clay was determined by using

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Table-7: Adsorption Capacity of 33% HCl Commercial Activated Bentonite

More amount of dye (ml)	Time	Absorbance
25	After 3 days	0.012
15	After 4 days	0.016
30	After 1 day	0.045

Table-8: Adsorption of 20% H₂SO₄ Industrial Activated Bentonite with Methylene Blue Dye

More amount of dye (ml)	Time	Absorbance
20	After 1 day	0.009
30	After 2 days	0.017
50	After 3 days	0.012

spectrophotometer. The percentage weight loss was found from 4.6% to 9.6% and absorbance values 0.009 to 0.047, respectively, was found. The samples of Azad Jammu and Kashmir have reduced their adsorption capacity after treatment with dilute acid because of the presence of impurities. But in case of market sample, adsorption capacity was reduced by treatment with dilute acid because of purity or composition of sample. The adsorption capacity of commercial sample increased by treating with HCl. This was due to the composition of minerals. It is concluded that bentonite clay is an economical and effective source for the removal of arsenic from drinking water owing to its adsorption capacity. Cheap treatment methods can be developed for the removal of arsenic from water to prevent adverse health effects of arsenic, particularly by exploiting the potential of bentonite.

Bentonite can be used at large scale for water cleaning from heavy metals by using adsorption techniques. As bentonite is a cheap adsorbent, awareness should be created about its benefits, to create its widespread utilization for purification of drinking water even at domestic levels.

REFERENCES

1. Assaad, E., et al., 2007. Metals removal through synergic coagulation-flocculation using an optimized chitosan-montmorillonite system. *Applied Clay Science*, 37, pp. 258–274.
2. Güler, C., et al., 1992. Chlorophyll adsorption on acid activated clay. *Journal of American Oil Chemists Society*, 69, pp. 948–950.
3. Liew, KY., et al., 1982. Adsorption of beta-carotene: II. On cation exchanged bleaching clays. *Journal of American Oil Chemists Society*, 59, pp. 480–484.
4. Taylor, DR., et al., 1988. Acid activated clays. *Transactions of the Society of Mining Engineers*, AIME, 282, pp. 1901–1910.
5. Kheok, SC., et al., 1982. Mechanism of palm oil bleaching by montmorillonite clay activated at various acid concentrations. *Journal of American Oil Chemists Society*, 59, pp. 129–131.
6. Azzouz, A., et al., 1989. Assessment of the acid–base strength distribution of ion-exchanged montmorillonites through NH₃ and CO₂–TPD measurements. *Thermochimica Acta*, 449, pp. 27–34.
7. Taylor, D.R., Jenkins, D. B. & Ungermann, C. B., 1989. Bleaching with alterative layered minerals: a comparison with acid activated montmorillonite for bleaching soybean oil. *Journal of American Oil Chemists Society*, 66, pp. 334–341.
8. Barrer, R.M., 1978. Zeolites and Clay Minerals as Sorbents and Molecular Sieves. *Academic Press*, London, 5.
9. Siddiqui, M.K.H., 1968. Bleaching Earth, *Pergamon Press*, London.
10. James, O.O., et al., 2008. Bleaching performance of a Nigerian (Yola) Bentonite. *Latin American Applied Research*, 38, 45-90.
11. Tiwari, R.N., Chatterjee, R. N., & Naidu, S. R., 1996. Chemistry of acid activation of Kaolinite Clays and economization of the process. *Chemical Engineering World*, 31, 59-66.
12. Grim, R.E., 1962. *Applied Clay Mineralogy*. McGraw-Hill, New York, 422.
13. Srasra, E., Bergaya, F., Van Damme, H., & Ariguib, N.K., 1989. Surface properties of an activated bentonite. Decolorization of rape-seed oil. *Applied Clay Science*, 4, pp. 411-421
14. Kaviratna, H., and Pinnavaia, T. J., 1994. Acid hydrolysis of octahedral Mg 2+ sites in 2:1 layered silicates: An assessment of edge attack and gallery access, mechanisms. *Clays Clay Miner.* 42, 717-723.
15. Zaki, I., Abdel-Khalik, M., & Habashy, G. M., 1986. Acid leaching and consequent pore structure and bleaching capacity modifications of Egyptian

- clays. *Colloids Surf.* 17, 1986, 241-249.
16. Rhodes, C.N., et al., 1992. Structural characterization and optimization of acid-treated montmorillonite and highporosity silica supports for ZnCl₂ alkylation catalysts. *Journal of the Chemical Society, Faraday Transactions*, 88 (15), pp. 2269-2274.
 17. Kardy, N.S., et al., 2007. Sedimentological and Technical studies on the Montmorillonitic clays of Abu Tartur Plateau, Western Desert, Egypt. *Physicochemical Problems of Mineral Processing*, 41, pp.89-99.
 18. Siddiqui, M.K.H., 1968. Bleaching earths. Pergamon Press, Oxford, pp. 32-55.
 19. Salawudeen, T.O., et al., 2007. Performance evaluation of acid treated clays for palm oil bleaching. *Journal of Engineering and Applied Sciences*, 2(11), pp. 1677-1680.
 20. Tseng, W.P., et al., 1968. Prevalence of skin cancer in an endemic area of chronic arsenicism in Taiwan. *Journal of the National Cancer Institute*, 40, p. 453.
 21. Brown, K.G., et al., 1989. A dose-response analysis of skin cancer from inorganic arsenic in drinking water. *Risk Analysis*, 9, pp. 519.
 22. Brown, C.C., and Chu, K. C., 1983. Implications of the multistage theory of carcinogenesis applied to occupational arsenic exposure. *Journal of the National Cancer Institute*, 70, 455.
 23. Lee-Feldstein, A., 1983. Arsenic and respiratory cancer in man: follow-up of an occupational study. In *Arsenic: Industrial, Biomedical and Environmental Perspectives*, Lederer, W. & Fensterheim, R. (eds). Van Nostrand Reinhold: New York.
 24. Higgins, I., et al., 1982. Mortality of Anaconda smelter workers in relation to arsenic and other exposures. *Department of Epidemiology, University of Michigan: Ann Arbor, MI, USA*. Enterline, P.E., and Marsh, G. M., 1980. Mortality studies of smelter workers. *American Journal of Industrial Medicine*, 1, p. 251.
 25. Enterline, P.E., and Marsh, G. M., 1980. Mortality studies of smelter workers. *American Journal of Industrial Medicine*, 1, p. 251.
 26. Chen, C.W., and Chen, C. J., 1991. Integrated quantitative cancer risk assessment of inorganic arsenic. In *Proceedings of the Symposium on Health Risk Assessment on Environmental, Occupational and Lifestyle Hazards*, Wen, C.P. (ed.). 66. *Institute of Biomedical Sciences, Academia Sinica: Taipei*.
 27. Chen, C.J., and Wang, C.J., 1990. Ecological correlation between arsenic level in well water and age-adjusted mortality from malignant neoplasms. *Cancer Research*, 50, pp. 5470
 28. Hunter, D., 1957. *The Diseases of Occupations*. English Universities Press, London.
 29. Yan-Hua, X., Tsunenori, N., Akira, O., 2002. Adsorption and removal of arsenic(v) from drinking water by aluminum-loaded shirasu-zeolite, *department of bioengineering, faculty of engineering, Kagoshima university*, 1-21-40, Korimoto, Kagoshima 890-0065, Japan, 92, 275-28
 30. Mohan, D., and Pittman, C. U., 2007. Arsenic removal from water/wastewater using adsorbents—A Critical Review, *Journal of hazardous materials*, 142, pp. 1-53.
 31. Chen, C. J., Chuang, Y. C., Lin, T. M., and Wu, H. Y., 1985. Malignant neoplasms among residents of a blackfoot disease-endemic area in Taiwan: high-arsenic artesian well water and cancers. *Cancer Res.*, 45, pp. 5895-5899.
 32. Chen, C. J., Chuang, Y. C., You, S. L., Lin, T. M., and Wu, H. Y., 1986. A retrospective study on malignant neoplasms of bladder, lung and liver in blackfoot disease endemic area in Taiwan. *Br. J. Cancer*, 53, pp.399-405.
 33. Chen, C. J., Kuo, T. L., and Wu, M. M., 1988. Arsenic and cancers. *Lancet*, I. pp. 414-415.

