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**Summary:** This study was conducted to investigate the arsenic removal efficiency of different adsorptive media from water. Different naturally occurring materials such as bauxite, plastic clay, plaster of Paris, lime, alum, and alumina etc. were used for the development of media to remove arsenic  $As^{+5}$  present in the artificially contaminated water. Different ratios of the selected materials were combined and ignited at 900°C to enhance its arsenic removing efficiency. It was found that the media bauxite, plastic clay, lime (1:1:1) has a maximum removal (99%) of  $As^{+5}$  species from aqueous media and can be used on-site to reduce the arsenic contamination of potable water. Furthermore, the materials used in this experiment were cheaply and abundantly available within the country. The method is very simple and economically viable, for removal of arsenic from potable water.

#### Introduction

Most of the diseases in the developing countries are related with the consumption of contaminated water [1, 2]. Contaminated water is one of the serious environmental issues that has further aggravated with the recent discovery of arsenic in drinking water. Arsenic is a ubiquitous element found in the atmosphere, soils and rocks, natural waters and organisms [3]. It is mobilized through a combination of natural processes such as weathering reactions, biological activity and volcanic emissions as well as through a range of anthropogenic activities. Most of the environmental arsenic problems are resulted from the mobilization under natural conditions [4]. However, man produces an additional impact on the environment through gold mining, combustion of fossil fuels and the use of arsenicals pesticides and herbicides [5], or of additives to livestock feed [6].

Numerous countries of the world including Argentina, Bangladesh, Chile, China, Hungary, India (West Bengal), Mexico, Thailand, USA, Vietnam and Pakistan have reported drinking water contamination with arsenic [7]. Recently, it has been found that the alluvial aquifer that underlies the Ganges-Brahamputra River basin contains arsenic in mineral form. During the past two decades about four million wells have been installed to utilize the groundwater from shallow aquifer layers, typically < 200 m deep [7]. Extraction of groundwater from these wells for both drinking and irrigation purposes has resulted the mobilization of arsenic [8].

The groundwater contamination with arsenic has occurred in a number of Asian countries that has

led to a major environmental concern. Currently, literature has mentioned that > 35 m people in West Bengal (India), Nepal and Bangladesh are potentially at risk from drinking water contaminated with arsenic [9]. Water contaminated with arsenic has emerged as a serious public health concern in Pakistan as well. In Punjab province, >20% of the population is exposed to arsenic contamination, the arsenic concentration being over 10 µgL<sup>-1</sup> in drinking water while nearly 3% of the population is exposed to over 50  $\mu$ gL<sup>-1</sup>. In Sindh, the situation is even worse; 36% of population is exposed to arsenic contaminated water with over  $10 \text{ µgL}^{-1}$  and 16% of population is exposed to 50  $\mu g L^{-1}$  [10]. Both shallow and deep water sources have also arsenic contamination. In District Mardan (KP), the presence of arsenic is reported to be over 50  $\mu$ gL<sup>-1</sup> [11].

Arsenic dissolved in water is acutely toxic and can lead to a number of health problems. It has been reported that long-term exposure to arsenic in drinking water in excess of 50  $\mu$ gL<sup>-1</sup> causes increase risks of cancer in the skin, lungs, bladder and kidneys. It also leads to other skin-related problems such as; hyperkeratosis and changes in skin pigmentation. Ingestion of arsenic through contaminated water leads to disturbance of the cardiovascular and nervous system functions and can eventually lead to death. These health effects, sometimes collectively referred to as arsenicosis, have been well documented previously [12].

The arsenic removal technologies include oxidation/reduction, precipitation, solid/ liquid

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biological processes. These separation and technologies are sometimes difficult and are not cost effective for application in poor countries. Coagulation processes are sometimes unable to remove arsenic effectively especially at very low levels (i.e at  $\mu g L^{-1}$  levels). Direct precipitation method has not played an important role in the arsenic removal. Arsenic as a result, various alternate technologies have been developed or adapted in order to remove arsenic to the minimum possible level. These advanced treatment options include ion exchange, and adsorption [13]. Adsorption and ion exchange techniques are relatively cheap and efficient for arsenic removal. Various solid materials, including iron and aluminum hydroxide flocs have a strong affinity for dissolved arsenic. Arsenic is strongly attracted to sorption sites on the surfaces of these solids, and is effectively removed from solution. Ion exchange can be considered as a special form of adsorption, though it is often considered separately. Ion exchange involves the reversible displacement of an ion adsorbed onto a solid surface by a dissolved ion. Each media has different associated performances and costs. Some are now available in small packet or tablet form for arsenic removal from drinking water. The efficiency of each media depends on the use of oxidizing agent(s) as aids to the sorption of arsenic [13].

However, all the above mentioned media for removal of arsenic are expensive and the methods are cumbersome and tedious. It was, therefore, considered that an economically viable media for the removal of arsenic may be developed using indigenous materials. The materials used in the present study are abundantly available within the country and the process developed is economically viable and commercially feasible. The main objective of the study is to develop low cost media and technology by the combination of different naturally occurring materials capable to remove arsenic from potable water for on site treatment/removal of arsenic

## **Results and Discussion**

## Arsenic Removal Studies

Different ratios of the adsorbing media were used for the removal of arsenic; the details are given in Table-1. The temperature for calcination and the characteristics of the media are also illustrated in Table-1. The pH of the aqueous arsenic solution after passing through the media was also determined with a pH meter. As evident from Table-2, the pH of the eluted samples after being passed through the media containing Bauxite, Plastic Clay, Activated Alumina and Plaster of Paris have lower pH (1-6). Whereas the aqueous arsenic solution passed through the media containing lime and dolomite have higher pH (8-11.8). The lower pH of arsenic solution is probably due to the presence of plaster of paris and plastic clay having sulphate content in their luster which behaves like acid whereas the higher pH is due to presence of lime which forms  $Ca(OH)_2$  in aqueous media. Lime is known for increasing pH of solutions.

The efficiency of 06 materials is observed during lab work. These materials are bauxite, activated alumina, alum, plaster of paris, plastic clay, and lime. Standard addition of arsenic (500  $\mu$ gL<sup>-1</sup> solution was passed through these materials and results were determined by atomic absorption spectrophotometer. The results are shown in the Table-3.

Table-4 shows chemical composition of selected materials while in Table-5 loss of ignition and  $R_2O_3$  combined concentration of Aluminum Oxide (Al<sub>2</sub>O<sub>3</sub>) and Iron Oxide (Fe<sub>2</sub>O<sub>3</sub>) are mentioned.

Surface area analysis of the media before and after passing through standard-solution was undertaken. According to Langmuir Plot surface area of the media before passing was 521.83m<sup>2</sup>/g while after arsenic adsorption on the surface of the media the surface area was 79.27  $m^2/g$ . DR Plot was drawn showing average pore width 120.13 A<sup>0</sup>, adsorption energy was 2.16 KJ/mole, microscope volume was 0.01 cc/g and microscope surface area was 36.05 m<sup>2</sup>/g. DR Plot drawn after passing through standard addition of arsenic solution had surface area 13.77  $m^2/g$ , average pore width 102.07  $A^0$ , adsorption energy 2.55 KJ/mole, micro pore volume 0.00 cc/g, and micro pore surface area is 13.77  $m^2/g$  . Slope shown by Multi-Point BET Plot before passing through media was 184.741, intercept was 3.397e+01 and surface area was 15.92  $m^2/g$ . while after passing through media slope became 460.707, intercept 7.591e+01, and surface area was  $6.49 \text{ m}^2/\text{g}$ . Elemental analysis of the media was carried out before and after passing through standard-solution.

# Experimental

#### Preparation of Standard Arsenic Water

A stock solution of 500 µgL<sup>-1</sup>, 5mgL<sup>-1</sup>, 10 mgL<sup>-1</sup>, 15 mgL<sup>-1</sup>, 20 mgL<sup>-1</sup> and 25 mgL<sup>-1</sup> arsenic was prepared from a standard solution (1000 mgL<sup>-1</sup>) of arsenic. In order to run the samples through atomic absorption photometer standard solution for calibration curve (Arsenic: Blank, 5, 10, 15 µg-L<sup>-1</sup>) were prepared. The chemicals used were HCl 4mL and KI (20% w/v solution) 2mL

Tuble 1: Different media combination and then preparation used in this study.								
S. No	Media mix	Ratio	Temp(C <sup>0</sup> )	Characteristics of Media				
Media 1	Bauxite+ Plastic Clay+ C. Alumina	1:1:1	900	Porous, hard, soluble, light pink color				
Media 2.	Lime+ Plaster of Paris	1:1	900	Irregular, off-white, soluble in water, crack in structure				
Media 3.	Alum+ Plaster of Paris	1:1	900	Very light pink, less hard, soluble,				
Media 4.	Bauxite+ lime +Plaster of Paris+ plastic clay	1:1:2:2	900	Pink, hard, not much soluble, irregular				
Media 5.	Dolomite +PP	1:1	900	Grayish white, hard, soluble, slow heating, porous, irregular,				
Media 6	Plaster of Paris + Bauxite + Alum + Activated Alumina	1:1:1:1	900	Hard, slightly pink, not easily soluble, porous, slow heating				
Media 7	Plaster of Paris	-	900	Off white, very hard, water soluble but not much, irregular,				
Media 8	Lime	-	900	Not very hard, v. much soluble, irregular				
Media 9	Alum	-	900	White color, very fragile, soluble in water				
Media 10	Bauxite	-	900	Slightly pinkish, very hard, soluble				
Media 11	Plastic Clay		900	Very hard, insoluble, pink				
Media 12	Activated Alumina		900	White color, powder form, can't retain its shape				
Media 13	PC + PP + Lime + Alum	1:1:1:1	900	Hard, soluble, pink, porous				
Media 14	<b>B</b> + PC + Lime	1:1:1	900	Pink, hard, porous, not much soluble in water, slow heating				

Table-1: Different media combination and their preparation used in this study.

After 900C<sup>0</sup>, starting with slow heating

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Media	Vol of std. As <sup>+5</sup> solution (ml)	Wt. of media (g)	Peristaltic pump (RPM) L/hr	pH of original sol.	pH of treated sample	As+5 Removed (µgL <sup>-1</sup> )	% As <sup>+5</sup> removal
Media 1.							
Bauxite, Plastic clay and C.	250	140	25.2	9.3	3	183.85	48
Alumina							
Media 2.	250	120	16.9	11	1.60	294 5	05
Lime+ Plaster of Paris	250	150	10.0	11	1.00	304.5	95
Media 3.	260	125	16.9	65	1.96	401.0	01
Alum and Plaster of Paris	200	125	10.0	0.5	1.00	401.9	91
Media 4.							
Bauxite, Lime, Plaster of Paris	800	482	16.8	3.66	10.4	268.8	50.9
and plastic clay							
Media 5.	270	150	16.8	3.02	12 30	211.5	03
Dolomite and PP	270	150	10.0	5.02	12.50	211.3	20
Media 6.	540	311	8.4	3 55	4 90	רד רדר	75.6
PP, Bauxite, Alum and AA	540	511	0.4	0.00	4.20	2/2./2	75.0
Media 7.	500	255	16.8	3.98	8 83	164.2	72.8
Plaster of Paris	500	200	10.0	5.90	0.05	104.2	72.0
Media 8.	490	213	16.8	3.98	95	223 5	96.5
Lime	470	215	10.0	5.90	7.5	220.0	70.5
Media 9	190	2.8	16.8	4	6 30	4.6	37 3
Alum	170	2.0	10.0		0.00	4.0	07.0
Media 10	350	236	16.8	4	6 70	45	36.5
Bauxite	000	200	10.0		0.70	4.0	2013
Media 11.	300	229	16.8	4	5.91	0.3	2.4
Plastic clay	200		10.0	•	5.71	0.0	2.1
Media 12.	350	197	16.8	4	7.3	4.9	39.8
Activated Alumina	000		1010	•	110		0,10
Media 13.	500	238	16.8	5.90	9.5	204.4	40.88
PC, PP, Lime and Alum							
Media 14.	4701	233	16.8	3.82	11.52	744.9	100
B+ Lime + PC							
AA: Activated Alumina PP: Plaster of	of Paris P	U: Plastic Clay	B: Bauxite				

Table-3: Individual material efficiency for removal of arsenic.

Alum	Activated Alumina	Bauxite	Lime	Plastic Clay	Plaster of Paris
37.3 %	39.8 %	97.5 %	99 %	2.4 %	72.8

Standard solutions of 0, 5, 10, 15  $\mu$ g-L<sup>-1</sup> were prepared from 1000 mgL<sup>-1</sup> of arsenic standard solution (stock). Samples were also prepared in the same manner except addition of standard arsenic solution.

Bauxite, plaster of Paris, Alum, Activated Alumina, Dolomite, Limestone, Bentonite and Plastic clay were used for different media preparation for arsenic adsorption.

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S. No	Clay/ Material	Chemical Name
1.	Bauxite	Al2O3 (with less Si, Fe, Ti)
		Kaoline: Al2O3.2SiO2.2H2O Mica: XY2-3 Z4O10(OH,F)2:
2.	Plastic Clay	X = K, Na, Ba, Ca, CS (H <sub>3</sub> O), NH <sub>4</sub>
		Y= Al, Mg, Fe <sup>+2</sup> , Li, Cr, Mn, V, Zn
		Z= Si, Al, Fe <sup>+3</sup> , Be,Ti
		Quartz: SiO2
3.	Plaster of Paris	(Gypsum cement): CaSO4. 1/2 H2O
4.	Lime stone	Ca(Mg)CO3
5.	Alum	Al2(SO4)3.12(H2O)
6.	Activated Alumina	AI2O3
7.	Commercial Alumina	Al2O3

Table-5: Loss of ignition and  $R_2O_3$ .

S. No		Bauxite	Plaster of Paris	Plastic clay	Limestone
1.	Loss on ignition	20-34%	66-68%	10-15%	35-45%
2.	R203	59-62%	<1%	20-25%	<1-5%

Preparation of Adsorbing Media

Different ratios of the above stated materials were ground and mixed thoroughly with the help of motor and doubled ionized water was added to the mixture to form thick slurry. The details of the mixing materials and their ratios are given in Table-1. Lumps of irregular shapes were prepared from the mixed materials, dried in oven at temperature 600 °C, ignited at 900 °C in a muffle furnace for two hours and cooled. The lumps were then filled in a glass column of length of 28 inch and with diameter of 5.5mm fitted with a stopper at the lower end. The standard solutions of known concentrations of arsenic were poured in the column filled with a media at a flow rate of 16.4 L/h. The solution was retained for different interval of times and then collected in a beaker through the stopper at the end of the column.



Fig: Schematically Representation of Glass Column Used in Experiment

# Analysis

Atomic Absorption Spectrometer (Hydride Generation mode) was used for the analysis of arsenic in water samples. All samples were analyzed on HFS-3 (Hydride Formation System) Hitachi model 8000. Atomic absorption spectrophotometer, Japan was used for all analysis. The Hydride technique makes use of fact that hydrogen liberated in the reaction of the weakly acidic sample solutions with sodium boro-hydride which combines with metal ions to form gaseous hydrides. These are carried to the hot quartz cell by the carrier gas and decomposed by collision processes in a series of steps, until free arsenic atoms are obtained. The percentage of arsenic which was removed was determined in different media.

#### Conclusion

Different naturally occurring materials like bauxite, plastic clay, plaster of Paris, lime, alum, alumina, bentonite etc were used for the development of media for the removal of arsenic. The materials were combined and calcined at 900<sup>o</sup>C to enhance its arsenic removing efficiency. It was found that the media bauxite + plastic clay +lime (1:1:1) has demonstrated a maximum arsenic removal efficiency from aqueous media. The materials applied for the preparation of different media are inexpensive and abundantly available locally. The method is simple and economically viable as no complicated operational units are involved in the process. The method could be applied for the removal of arsenic from potable and waste water.

#### References

- 1. R. Feachem, M. McGarry, D. Mara, *Water, Waste and Health in Hot Climates*, Wiley Interscience, New York, USA, p. 167 (1970).
- 2. H. M. Dix, *Environmental Pollution*, John Wiley and Sons, New York, USA. p. 172, (1981).
- M. M. Rahman, K. Paul, U. K. Chowdhury, B. K. Biswas, D. Lodh, G. K. Basu, S. Roy, R. Das, B. Ahmed. I. Kaies, A. K. Barua, S. K. Palit, Q. Quamruzzaman and D. Chakraborti, *Current Status of Arsenic Pollution and Health Impacts in West Bengal and Bangladesh*, An International Workshop on Arsenic Pollution of Drinking Water in South Asia and China, Tokyo (2001).
- 4. A. H. Welch and K. G. Stollenwerk, *Arsenic in Ground Water-Geochemistry and Occurrence. Kluwer, Dordrecht* (2002).

- 5. P. L. Smedley and D. G. Kinniburgh, *Applied Geochemistry* 17, 517 (2002).
- 6. A. J. Bednar, J. R. Garbarino, I. Ferrer, D. W. Rutherford, J. Wershaw and F. Ranville, *The Science of the Total Environment*, **302**, 237 (2003).
- S. Murcott, Appropriate Remediation Technologies for Arsenic- Contaminated Wells in Bangladesh, International conference on Arsenic in Bangladesh Ground Water Wagner College Staten Island, New York (1999).
- 8. P. Palf, E. Vircikova and L. Molnar *Waste Management*, **19**, 55 (1999).
- 9. M. F. Ahmed, *Water Supply Options in Arsenic Affected Rural Areas*, an International Arsenic

Conference, Dhaka Community Hospital, Dhaka, Bangladesh (1999).

- T. Ahmad, M. A Kahlown, A. Tahir and H. Rashid, Arsenic an emerging issue: Experiences from Pakistan, 30<sup>th</sup> WEDC International Conference, Vientiane, Lao PDR, (2004).
- 11. J. Matschullat, *The Science of the Total Environment* **249**, 297 (2000).
- D. Bonnin, Arsenic removal from water utilizing natural zeolites, Proceedings, AWWA Annual Conference. American Water Works Association, Denver, CO. (1997).
- G. Samanta, K. Uttam, Chowdhury, K. Badal, Mandal, D. Chakraborti, N. Chandra, Sekaran, H. Tokunaga and M. Ando, *Microchemical Journal*, 65, 113 (2000).