Introduction

Globally, several research studies have been reported that arsenic (As) is a carcinogen and its adverse effects are primarily due to consumption of as (100 μg/L) contaminated drinking water [1]. In Bangladesh and India, millions of people are suffering from cancer and keratosis because of chronic as poisoning from their drinking water [2]. Water contaminated with as has emerged as a serious public health concern in Pakistan. In Punjab province, >20% of the population is exposed to arsenic contamination, the as concentration being over 10 μgL-1 in drinking water while nearly 3% of the population is exposed to as over 50 μgL-1. In Sindh province, the situation is even worse; 36% of population is exposed to as contaminated water with over 10 μgL-1 and 16% of population is exposed to as 50 μgL-1. Both shallow and deep-water sources have also contaminated with As. In district Mardan, Khyber Pakhtunkhawa (KP), and the presence of as is reported to be over 50 μgL-1 [3].

The above-mentioned facts indicate that there is an urgent need for an inexpensive as treatment method. As occurs in ground and surface waters in both organic and inorganic forms, though the organic form is uncommon [4]. Arsenite (As III) is present mainly as H3AsO3 (Arsenic (III) trioxide) and predominates under reducing conditions. Arsenate (As V) is common under oxidizing conditions and mainly exists as HAsO42− (Dihydrogen Arsenate) and HAsO3− (Monohydrogen Arsenate) at pH ranging from 2 to 9 [4]. The detrimental health effects of as prompted the World Health Organization (WHO) and the United States Environmental Protection Agency (US-EPA) to reduce the drinking water as standard from 0.05 to 0.01 mg/L [5]. Effectively removing as from waters with concentrations >0.01 mg/L is costly, commonly requiring expensive man-made arsenic sorbents. Consequently, there is a real need in developing countries for low-cost materials and methods to remove as from drinking water. One of the promising methods appears to be the sorption of inorganic as compounds from solution using natural sorbents.

Adsorption is a mass transfer process where a substance is transferred from the liquid phase to the surface of a solid and becomes bound by chemical or physical forces. In water treatment in the developed countries, the adsorbent (solid) is typically granular activated carbon (GAC) or powdered PAC and it is used for taste and odor removal. In high-tech applications, adsorption is also used for the removal of Synthetic Organic Compounds (SOCs), Volatile Organic Compounds (VOCs), and...
Naturally Occurring Organic Matter (NOM). As is adsorbed onto the surface of granular materials, clays and processed cellulosic materials including: activated carbon; metal-treated activated carbon; oxides (e.g. hydrated ferric oxide, titanium oxide, silicon oxide); clay minerals (e.g. kaolinite, bentonite, Bijoypur clay); bauxite, hematite, feldspar; synthetic anion exchange resins; chitin and chitosan; bone char; iron oxide-coated or MnO₂-coated sand; cellulose materials (sawdust, newspaper pulp) [6].

Characteristically, each media has different associated performances and costs. Some are now available in small packet or tablet form for As removal from drinking water. The efficiency of each media depends on the use of oxidizing agent(s) as aids to the sorption of arsenic. The sorption capacities of various adsorbents were summarized. Some low-cost adsorbents are superior including treated slags, carbons developed from agricultural waste (char carbons and coconut husk carbons), bio sorbents (immobilized biomass, orange juice residue), goethite and some commercial adsorbents, which include resins, gels, silica, treated silica etc. The tested for arsenic removal come out to be superior. Immobilized biomass adsorbents offered outstanding performances. Desorption of as followed by regeneration of sorbents has been reported. Strong acids and bases seem to be the best desorbing agents to produce as concentrations [7].

The materials used for different media development are bauxite, plaster of paris, alum, activated alumina, commercial aluminia, limestone, and plastic clay. Bauxite is a rock composed mainly of aluminum oxide and aluminum hydroxide minerals. Alum (potassium aluminum sulfate) is a white mineral. A particularly stable oxide of aluminum, aluminum oxide (Al₂O₃) can be obtained from alum. Activated alumina is a media produced by the controlled calcinations of alumina trihydrate. It has been used for the removal of undesirable contaminants such as fluoride, hydrogen chloride, hydrogen sulfide, carbonyl sulfide, carbon dioxide, arsenic, alcohols and ethers. Activated alumina is primarily aluminum oxide (Al₂O₃). Plastic clay is an extremely rare minerals found in very few places around the world. It is also sometimes referred to as ball clay. Plastic clays are sedimentary in origin. Plastic clay usually contains three dominant minerals; kaolinite, mica, and quartz.

Limestone

Limestone is defined as a rock of sedimentary origin composed principally of calcium carbonate or the double carbonate of calcium and magnesium, or a combination of these two minerals. Chemical composition of all indigenous clay materials used is given in Table 1. The basic purpose of this study is to develop an economically viable media for removal of arsenic by using indigenous materials. The materials used in the present studies are abundantly available within the country and the process developed is economically viable and commercially feasible.

Table 1: Chemical Composition of Clay’s materials.

| S. No | Clay/ Material | Chemical Name |
|-------|----------------|---------------|
| 1     | Bauxite        | Al₂O₃ (with less Si, Fe, Ti) |
| 2     | Plastic Clay   | Kaoline: Al₂O₃, SiO₂, H₂O |
| 3     | Plaster of Paris | Ca(Mg)CO₃ |
| 4     | Lime stone     | Ca₃(SO₄)₂, 1/2 H₂O |
| 5     | Alum           | Al₂(SO₄)₃, 1/2 H₂O |
| 6     | Activated Alumina | Al₂O₃ |
| 7     | Commercial Alumina | Al₂O₃ |

Table 2: Individual Material Efficiency for removal of arsenic.

| Alum | Activated Alumina | Bauxite | Lime | Plastic Clay | Plaster of Paris |
|------|-------------------|---------|------|--------------|------------------|
| 37.30% | 39.80% | 97.50% | 99%  | 2.40%        | 72.8             |

Results and Discussion

Different media were prepared for removal of As from an aqueous system. The mixture is preferably calcined and is realler converted into granular form. Removal of as from the aqueous system is readily accomplished by contacting the aqueous system with the media until the arsenic is substantially removed from the aqueous solution. Pseudo arsenic solution of 500 μgL⁻¹ was prepared for this study. A total of six adsorbing materials (alum, activated alumina, bauxite, plastic clay and plaster of paris) were initially evaluated individually (Table 2). The different temperature levels for calculations and the characteristics of the media were used (Table 3). The pH of the aqueous as solution after passing through the media was also determined to know about the pH changes due to the materials used for as removal. The present study findings indicate that samples passed through the media containing bauxite, plastic clay, activated alumina and plaster of paris have lower pH in the range of 1-6. Whereas the aqueous as solution passed through the media containing lime have higher pH in the alkaline range of 8-11.8.
Note: After 900°C, starting with slow heating.

The lower pH of the solution is probably due to the presence of plaster of paris and plastic clay having sulphate contents in their luster (ref) which behave like acid whereas the cause of higher pH in the alkaline range may be due to presence of lime having basic characteristics. When bauxite alone was used 97.5% removal is achieved (Figure 1). Nil removal is achieved, when bauxite was mixed with plaster of Paris in 1:1 ratio and lumps were made after heating to 900°C in 2 hours (Figure 2). Physically the media was pinkish in color, very hard and less soluble in water. Arsenic solution with concentration of 500 μgL⁻¹ was passed through the column containing the media and was thoroughly mixed. Elute was taken after an hour and it was analyzed through Hydride Formation System of AAS for arsenic content and the results show 0% arsenic removal. It was indicated that bauxite and plaster of paris was not effectively contributing in the removal of arsenic. Plastic clay was added with plaster of paris and bauxite in the ratio of 1:1:1. This media had 52.4% removal efficiency. In the next trial commercial alumina and plastic clay was mixed with bauxite in the ratio of 1:1:1.

This media had 48% removal efficiency. But when bauxite was mixed with lime and plastic clay in the ratio of 2:1:1 (Figure 3), it removed 89% arsenic from 500 μgL⁻¹ standard solutions. The efficiency increased up to 100% when the same materials were mixed in the ratio of 1:1:1 (Figure 4). 72% of arsenic removal was obtained by a media containing bauxite, lime and plaster of paris in the ratio of 1:1:1 (Figure 5). Removal efficiency was decreased to...
75.6% when bauxite, plaster of paris, alum and activated alumina were used in media (Figure 6). The media containing bauxite, plaster of paris, alum and commercial alumina were less effective and only 54% arsenic was removed with it. The efficiency of bauxite, alum, plaster of paris and plastic clay (1:1:1:1) was about 77%. Plaster of paris removes 72.8% (Figure 7). Plaster of paris when added with AA reduced as up to 70% from standard solution (Figure 8). Alum removed 37% arsenic from standard solution but when mixed with plaster of paris (1:1 ratio) its removal efficiency increases up to 91%. Plastic clay did not show any affiliation for adsorption of arsenic (Figure 9).

Figure 4: B+PC + Lime (1:1:1).

Figure 5: B+ Lime + PP (1:1:1).

Figure 6: B + Alum+ Commercial Alumina+ PP.

Figure 7: Plaster of paris.

Figure 8: Activated Alumina + Plaster of Paris (1:1).

Figure 9: Plastic clay.

Figure 10: B+PP+ PC+Lime (1:1:1:1).

It had only 2% removal efficiency when used alone. The combination of lime, bauxite, and plaster of paris and plastic clay 1:1:1:1 decreased arsenic by 88.7% (Figure 10). The efficiency decreased to 50.9% with the media containing plastic clay, plaster of paris, lime and bauxite (2:2:1:1). 75% removal was achieved with plastic clay and plaster of paris. Lime is quite effective for arsenic removal. It has 99% efficiency for arsenic removal. Lime with PP in 1:1 ratio can remove arsenic up to 95%. The efficiency of the media lime, bauxite and plastic clay (1:1:1) remained maximum (100%). The results showed that the minimum as removal was observed in media without lime. The mixture of bauxite, alumina, plastic clay and plaster of paris has low efficiencies for the removal of arsenic from the aqueous solution. The arsenic removal efficiency varied among different media in the materials and raised from 0-50%, whereas, the media having lime have maximum efficiency in the removal of arsenic. The arsenic removal in these media varied from 50-100% using materials in different ratios (Table 4).
### Table 4: Removal of arsenic (%) using different adsorbing media.

| Media | Vol of pseudo solution (ml) | Wt. of media (g) | Rotation/min (l/hr) | pH of pseudo sol. | pH of elude | Standard solution (μgL⁻¹) | As remaining (μgL⁻¹) | Removal (μgL⁻¹) | Removal (%) |
|-------|-----------------------------|------------------|---------------------|-------------------|-------------|---------------------------|--------------------|----------------|----------------|
| Media 1. Bauxite | 350 | 236 | 16.8 | 4 | 6.7 | 12.3 | 7.8 | 6.5 | 97.5 |
| Media 2. Bauxite and Plaster of Paris | 260 | 135 | 16.8 | 5.8 | 1.8 | 404.5 | 526.2 | 0 | 0 |
| Media 3. Bauxite, Plastic Clay and Plaster of Paris | 250 | 160.62 | 16.8 | 3.8 | 5.25 | 632.6 | 301.07 | 331.53 | 52.4 |
| Media 4. Bauxite, Plastic clay and C. Alumina | 250 | 140 | 25.2 | 9.3 | 3 | 382 | 198.15 | 183.85 | 48 |
| Media 5. Bauxite, Lime, and Plastic clay (2:1:1) | 250 | 120 | 16.8 | 11.6 | 11.7 | 404.5 | 42.2 | 362.3 | 89 |
| Media 6. Bauxite, Lime and PC (1:1:1) | 470 | 233 | 16.8 | 3.82 | 11.52 | 751 | 6.1 | 744.9 | 100 |
| Media 7. Lime, Bauxite and PP | 250 | 250 | 16.8 | 3.67 | 10.25 | 335.74 | 93.39 | 242.35 | 72 |
| Media 8. PP, Bauxite, Alum and AA | 540 | 311 | 8.4 | 3.55 | 4.9 | 360.57 | 87.85 | 272.72 | 75.6 |
| Media 9. Bauxite, Alum, Commercial Alumina and Plastic of Paris | 250 | 136 | 25.2 | 6.5 | 5 | 764 | 225.07 | 538.93 | 54 |
| Media 10. Alum, Plastic of Paris, Bauxite and Plastic Clay | 250 | 135 | 16.8 | 5.5 | 6.2 | 441.3 | 101.2 | 340.1 | 77 |
| Media 11. Plaster of Paris | 500 | 255 | 16.8 | 3.98 | 8.83 | 225.4 | 61.2 | 164.2 | 72.8 |
| Media 12. Activated Alumina and PP | 360 | 346 | 16.8 | 4.31 | 8.46 | 500 | 149.4 | 350.6 | 70 |
| Media 13. Alum | 190 | 2.8 | 16.8 | 4 | 6.3 | 12.3 | 7.7 | 4.6 | 37.3 |
| Media 14. Alum and Plaster of Paris | 260 | 125 | 16.8 | 6.5 | 1.86 | 404.5 | 39.4 | 401.9 | 91 |
| Media 15. Plastic clay | 300 | 229 | 16.8 | 4 | 5.91 | 12.3 | 12 | 0.3 | 2.4 |
Experimental

Preparation of Adsorbing Media

The different indigenous materials were used for the preparation of adsorbing media (alum, activated alumina, bauxite, plaster of paris, plastic clay and limestone). Different ratios of these materials were ground and mixed thoroughly in a motor and enough water was added to the mixture to form thick slurry. Lumps of irregular shapes were prepared from the mixed materials, dried, ignited at 900°C in a muffle furnace for 2-h and then cooled in a desicator. The lumps were then fed in a glass lined vertical column fitted with a stopper at the lower end. The pseudo solution of as with a known concentration was 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.

Instrumentation

Atomic absorption spectrometer (Z-8000-Hitachi Japan) in the Hydride Formation System (HFS) mode was used for the analysis of as in water samples. All samples were analyzed on HFS-3 (Hydride Formation System), an accessory (AAS, Vario 6 Analytik Jena AG) to avoid carbonates formation. 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 as atoms were obtained. From the selected materials, 14 different media were prepared with different combination and ratios and it was noted that the media prepared from limestone, bauxite and plaster of paris gave excellent results in terms of adsorbing and a better removal of as from solutions containing As.

Conclusion

Based on the results obtained, it is concluded that as could be removed from an aqueous solution using indigenous materials. The materials involved in these studies are inexpensive and abundantly available within the country. The method is simple and economically viable and could be employed for the removal/reduction of as in potable water. These bench scale studies could also be scaled up to pilot plant scale to find out the techno-economic feasibility of this method. It is low cost/technology and may also be employed in the backward areas of the country for the reduction of as from drinking water.

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Note: AA: Activated Alumina; PP: Plaster of Paris; PC: Plastic Clay.
