Arsenic is a carcinogenic element capable to get into water bodies and drinking water supplies from natural deposits and industrial practices. Its presence in drinking underground water is highly toxic to human health. The study is focused on the development of indigenous Iron-Coated Pottery Granules (ICPG) to remove As from groundwater of Hala City. The developed ICPG was agitated with local clay white flour and water. A low-cost adsorbent namely ICPG was synthesized for the expulsion of As from underground water. The ICGP was characterized with SEM and FTIR techniques. Furthermore, the impact of physical parameters including adsorbate concentration, dosage, mixing time, pH, and contact time on As removal efficiency was investigated in batch experiments. The maximum removal efficiency was achieved with an adsorbent dosage of 0.5 grams at pH =7 for a contact time of 90 minutes when agitated at a speed of 150 r/min. The arsenic removal efficiency was found highly dependent on contact time increase and optimum pH (maximum removal achieved at strong adsorption of As at pH 4–7), however, the rise of adsorbate concentration resulted in the decrement in the efficiency after certain range. Batch adsorption study of underground water sample collected from Hala, Sindh, Pakistan was performed with satisfactory results, i.e. 94 arsenic removal from water. All the water samples were analyzed through atomic absorption Spectrophotometer. The investigation has indicated that ICPG is an exceptionally favourable material for As removal from drinking underground water and can be applied to handle the arsenic issue in most of the regions of Sindh province.

Keywords—Drinking water, indigenous pottery granules, arsenic removal, batch adsorption study

1 Introduction

Arsenic is a lethal and cancer-causing element and WHO has considered it a priority issue among the poisonous substances [1]. Arsenic-rich rocks are the primary sources of As in ground water through which the water has permeated. Mining and industrial activities also contribute in receiving As in different regions [2]. Anthropogenic and industrial activities including mining, combustion of fossil fuels, agriculture and industrial waste discharges also contribute to arsenic contamination in potable water. A large number of individuals are enduring with skin diseases, cancers and other relevant infections because of the utilization of As contaminated groundwater around the world, mostly China, India and Bangladesh, etc [3]. WHO prescribed safe permissible limit of As in potable water is 10 ppb; whereas, that of EPA Pakistan is 50 ppb. Membrane separation, coagulation, Sorptive media filtration and adsorption are the most efficient technologies adopted to eliminate As from drinking water sources [4][5]. Among all the methods, adsorption is one of the economical and easily applicable techniques [6]. Filtration, precipitation and co-precipitation are three basic mechanisms employed for the removal of As from water through coagulation process [7][8]. At molecular level, Sorptive media filtration technique is used to mitigate dissolved As by addition of sorptive media [7]. Iron-coated pottery granules (ICPG) based method has been described for As expulsion
The main objectives of this study are: (a) to develop and synthesize iron-coated pottery granules through indigenous sand, (b) characterization of ICPG by SEM and FTIR techniques, (c) to acknowledge the effect of adsorbent dosage, pH, contact time and initial adsorbate concentration on As expulsion efficiency.

2 Material & Methods

2.1 Synthesis of Iron-Coated Pottery Granules

All analytical grade chemicals glassware were cleaned and soaked in 10% HCl, and properly washed with de-ionized water. Arsenite solution (100 ppm) was prepared by dissolving potassium arsenate monobasic (AsH$_2$KO$_4$) in distilled water, and one drop of nitric acid (HNO$_3$) was used for preservation of synthesized solution. The detailed development processes of ICGP is described in Figure 1, where important stages are involved in the synthesis of ICPG media: (1) firstly, pottery granules were produced by the adequate mixture of local clay (kaolinite, 97% pure), white flour (carbon source material) and water and heated in an oven first at 110$^\circ$C and then further to 500$^\circ$C for 3 hours, (2) synthesis of zero-valent iron was accomplished by mixing iron chloride hexahydrate solution with sodium borohydride solution resulting black solid particles, which were then washed with ethanol, dried and attached to pottery granules (3:7) with continuous stirring. Iron powder and granules were mixed for 20 minutes and put into an aluminum sheet, and (3) iron-coated pottery granules were heated again, first at 80$^\circ$C and then at 500$^\circ$C for 1 hour. Granules were observed to be strengthened by this re-firing process.

2.2 Characterization

The iron-coated pottery granule (ICPG) was characterized by different analytical instruments. Scanning electron microscope (JEOL, JSM-6380LV, USA) measured surface morphology of the adsorbent where surface characteristics of the material with an accelerated voltage of 5 kV and 1,000× magnification. To determine different functional groups of ICPG, FTIR spectrometer was utilized. The FTIR spectra were noted in the wavelength range of 4000-500 cm$^{-1}$. Atomic Absorption Spectroscopy (AAnalyst700, PerkinElmer, USA) was utilized for the determination of arsenic [As (V)] in the solution. China clay (DRK-7) was used as a basic constitute for the synthesis of the adsorbent. FTIR (PerkinElmer, USA) technique was also utilized to deduce internal bindings of As by the adsorbent.

2.3 Batch Adsorption Experiments

The adsorption features of arsenic onto ICPG were considered under equilibrium and dynamic conditions. All the batch experiments were conducted in a 100 ml flask to examine the As removal efficiency of ICPG media while considering the wide ranges of each physical parameter’s adsorbent dosage (0.25 to 1.5 grams/50ml), pH (2-10), contact time (0.5 to 02 hours), and mixing speed of 150 r/min at a regulated room temperature of 24°C ± 2°C [11]. Each sample was further processed to gravity filtration process by using normal lab filters and then the residual concentration of As for all samples were analyzed using atomic absorption spectrometer.

3 Results

This section presents the results of this study.

3.1 Scanning Electron Microscope (SEM)

The SEM test of ICPG, i.e., unused iron coated pottery granules (before adsorption) was carried at a magnification of 250× and 100× (Figure 2a) in order to relate with exhausted ICPG adsorption (by AS) at a magnification of 250× and 100× (Figure 2b). Figure 2a and Figure 2b relate the surface structures of unused ICPG (before the arsenic test) with exhausted ICPG (after arsenic test) at a magnification of 250× and 100× respectively. Figure 2a represents that a rough surface has been build up for As adsorption by the iron and clay substrate on ICPG surfaces. The smooth surface structure appears to some extent due to extensive flow by contact during arsenic adsorption (Figure 2b). Arsenic adsorption takes place at the surface media, apparently including inner surface areas of the media pores.
3.2 Fourier-Transform Infrared Spectroscopy (FTIR)

In order to analyze different functional groups of As (before and after) adsorption, the FTIR bands of ICPG was measured (Figure 3a and Figure 3b). The existence of band at 3414.58 cm$^{-1}$ is because of bonded OH groups, which specifies the occurrence of water crystallization. The band at 2882.01 cm$^{-1}$ is the result of amide group, but after adsorption, it is shifted to 2994.19 cm$^{-1}$ by means of little broadening. The band at 1612.42 cm$^{-1}$ is because of the presence of $C=O$ stretching groups available information [12].

3.3 Batch adsorption studies

3.3.1 Effect of Adsorbent Dose

Adsorbent dosage has a significant effect on arsenic removal. Weights of adsorbent were varied from (0.1 to 1.0 g/50ml). Each flask of different dose in 50 ml solution with 50 ppb initial concentration adjusted to required pH7 was shaken in agitator (MIDGET STIRRER, MZ-800H) with 150 rpm at 25°C ± 1°C for required incubation time (90 min). The results
revealed that maximum adsorption of As by ICPG was 95% with 0.5g/50ml of the adsorbent as shown in Figure 4. It could be seen in Figure 4 that As expulsion efficiency significantly increased with the addition of adsorbent dosage. The change in dose from 0.1 to 0.5 g/50ml brought about an increment from 52.4 to 95% in adsorption of As. This might be because of the more availability of the interchangeable sites at elevated concentrations of the adsorbent [13][14]. No substantial growth in As expulsion efficiency was seen on further addition of adsorbent dosages from 0.5g onwards.

3.3.2 Effect of Contact Time

The impact of contact time on arsenic expulsion efficiency was calculated in the range of 30 min to 120 min at pH=7 and adsorbent dose of 0.5 grams. A weighed amount of ICPG was utilized in 50 ppb arsenic and agitated in a shaker at 150 r/min at varied time intervals of 30, 60, 90 and 120 mints. It was found that As adsorption attained a maximum value (i.e. 94.5%) after 90 min, after which no considerable variation was detected. The fast adsorption rate at early stage is due to greater presence of active binding sites on the adsorbent surface 15. Therefore, a 90 minutes contact time for ICPG was satisfactory to attain equilibrium.

3.3.3 Effect of pH

To observe the impact of pH on arsenic removal efficiency, the adsorption behaviour of the ICPG was assessed in various arrangements of analyses at varying pH of 2, 4, 6, 7, 8 and 10. It was observed that As adsorption is good in limits between 4.0-7.0 and maximum at pH=7.0 (92.7%), and it was considered an ideal pH state for more experimentation [16]. The arsenic removal efficiency was seen to be decreasing sharply at higher pH range, i.e. at pH=8.0 and pH=10.0. The reduction in Arsenic removal with increasing pH might be because (i) a huge quantity of hydroxyl ions in water try to compete for active sites alkaline pH, or (ii) the above-achieved pH demonstrates a decent concurrence with zero-point surface charge [17].

3.3.4 Effect of Initial Arsenic (Adsorbate) Concentration

The adsorption behaviour of As was analyzed in As concentration limit of 25-100 ppb at pH=7.0. Essentially, the removal percentage of As on ICPG adsorbent was first enhanced with increasing the initial amount of As attaining the optimal level of 95.0% at 50 ppb As concentration. From there, the level of evacuation demonstrated a little decline as shown in Figure 7.

3.4 Study on Real Water Sample (Hala City) for As Expulsion

For the purpose of evaluating the arsenic removal results of the real sample, real sample water (groundwater) was collected from Hala city, Sindh, Pakistan and its arsenic contamination was tested and found to be 200 ppb. After the atomic absorption spectrometer test, the result revealed that As removal is 94% by employing optimized parameters found in the current study.

3.5 Comparison With the Literature

The results obtained in the presented study are also compared with other studies in the literature (Figure 8). While the operating parameters and the type of adsorbent are different in other studies, but the removal
Fig. 7: Effect of initial arsenic concentration on As adsorption by ICPG

Fig. 8: Comparison of current study with the studies presented in literature

efficiency of adsorbent developed in our study is highly efficient compared to others.

4 Conclusions & Recommendations

Iron coated pottery granule has been observed as an effective adsorbent for As removal from drinking water. There are several benefits of ICPG media such as the cost-effective process makes ICPG media a great competent adsorbent for removing As at ordinary pH, and its arsenic adsorption competency utilizing F(0) coated on the sample. The qualitative results from SEM and FTIR assured the As adsorption. Batch adsorption experiments showed that the maximum As removal percentage was 95% under ideal conditions of adsorbent dosage: 0.5 grams/50ml, pH=7 of the solution, agitation time=90 mints and agitation speed = 150 r/min. From this research, it is evidently concluded that ICPG sample can be appropriately used for As expulsion from portable water. This work can be extended by using ICPG as an adsorbent for the expulsion of arsenic and other contaminated minerals from groundwater, and similarly in the removal of heavy metal ions from wastewater. Column studies can also be carried out to determine the efficiency of the adsorbent for commercial and industrial purposes. By keeping in view the current scenario of arsenic-contaminated water problems around the globe, the usage of this adsorbent is not up to that mark. Therefore, more studies and exploration of this adsorbent are needed. By removing other contaminants from potable water, in this way, the scope of this adsorbent can be extended.

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