SURFACE ADSORPTION STUDY OF SAPONIFIED ORANGE WASTE GEL FOR ARSENIC (III) REMOVAL

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ABSTRACT

Arsenic is mostly present in Sindh and Punjab provinces of Pakistan. In some districts of Punjab and Sindh arsenic concentration has reached up to the level of 906 ppb and 200 ppb respectively. Since 1993, the World Health Organization has recommended a maximum contaminant level for arsenic in drinking water of 10 ppb (except for a few countries) and the water treatment system must comply with this standard. Orange juice waste was used to prepare adsorbent gel by loading iron oxide. The iron oxide loaded SOW gel was used to remove As (III) from water. Batch experiments conditions were conducted to optimize the adsorbent dose, shaking time, adsorbate concentration for maximum 96% removal of arsenic (III) from aqueous solution.

1. INTRODUCTION

The rapid growth of population in Pakistan the available water resources are about to exhaust and there is strong need to treat the underground water making it safe for use. Arsenic is mostly present in Sindh and Punjab provinces of Pakistan. Pakistan council for research and water resources (PCRWR) conducted survey under UNICEF arsenic monitoring program in 2005, it was found that ground water collected from 60 locations in four districts of Sindh contained arsenic from 100 to 500 ppb [1]. Arsenic problem is also identified as a result of field testing in ground water of various districts of Punjab like Attock and Rawalpindi (year 2000), and also in Muzzafargarh concentrations of As reached up to 906 ppb Arsenic (As). It was reported that arsenic contamination exceeded 200 ppb in some districts of Sindh like Khairpur, Dadu, Nawabshah, Nausheroferoz, and Thatta [1], and 170 ppb in Tando Allahyar. It was identified as one of the major issue in some areas of both provinces of Pakistan i.e. Southern Punjab and Central Sindh. It is one of the most toxic contaminants found in the environment and can exist as various complex forms or species in the aquatic environment. Arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}), referred to as As (III) and As (V), respectively, are common in natural waters [7]. The presence of arsenic in ground water has been reported in many countries like Bangladesh China Iran Nepal Pakistan hence it is a global issue. In Pakistan the underground and tube wells are contaminated with arsenic reported to be above the recommended USEPA arsenic level of 10ppb. In order to overcome the drawbacks of these traditional treatment processes, attempts have been made regarding the removal of As (V) and As (III) by using Fe (III)-loaded chelating ion exchange resins having either an acidic or basic moiety as the functional group. However, treatment with such resins is rather expensive for the recovery of arsenic. At this juncture adsorption of arsenic using natural products and biomass has emerged as an option for developing economic and eco-friendly wastewater treatment processes [5]. Pakistan is the largest producer of 'Citrus Reticula' variety (Kinow) [2], this unique variety of citrus is indigenous to this part of the world. In the present research the Natural adsorbent was prepared from orange waste, which is totally bio nature and safe for human being, as well as more effective and economic for our country because Pakistan produces about 133600 tons of mandarins orange predominantly Kinnow. Which is about 95% of world kinnow production [2].

2. MATERIAL AND METHODS

The first phase of work was preparation of saponified orange waste gel (SOW gel) from orange juice waste along with loading of iron oxide. The second phase of the work was optimization of adsorption parameters such as adsorbent dose, shaking time, and adsorbate concentration for the use of SOW gel for the removal of Arsenic from aqueous solution.

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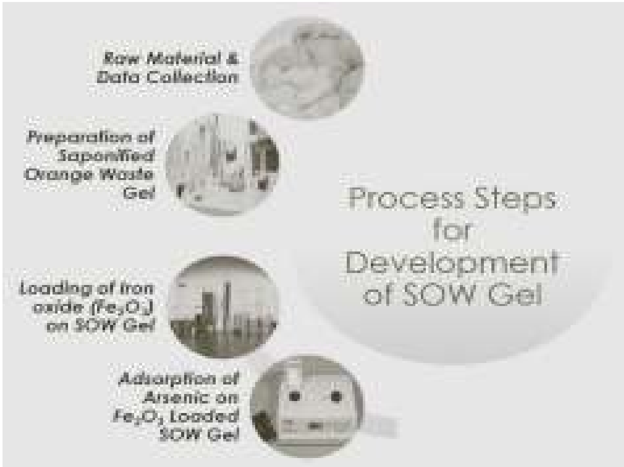

Fig-1: Schematic of the Experimental Benchmark

2.1 Raw Material Collection

Maximum percentage of orange production (70%) is utilized to produce derivative products and approximately 50–60% of the processed fruit is transformed into citrus peel waste i.e. peel, seeds and membrane residues (Wilkins et al., 2007a). Approximately 20.17% represents the solid material existence in the orange fruit which has a potential to be used as adsorbent for arsenic removal converting approximately 4 million tons of orange waste into useful product and eliminating an environmental waste. The orange juice waste was collected from local juice shop, and iron oxide was purchased of analytical grade from local market.

2.2 Preparation of Saponified Orange Waste Gel

The orange juice waste was treated with calcium hydro oxide to carry out the saponification reaction to form saponified orange waste gel as shown in fig: 2a.

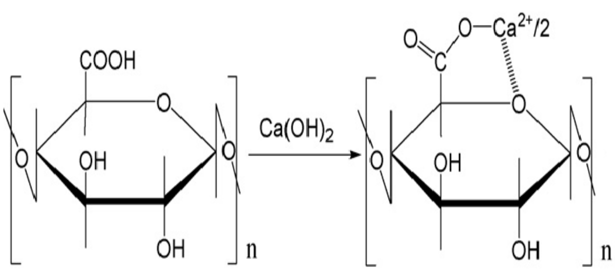

Fig-2a: Saponification of orange juice waste

In fig: 2a H^+ in the –COOH functional group has been replaced by calcium forming saponified orange waste and yielding H_2O as by product. In order to carry out the reaction orange waste was processed through various unit operations including crushing, washing, drying and mixing. Series of operations were carried out including Mixing, washing, drying and grinding etc. to produce SOW gel for arsenic removal.

The SOW gel achieved was repeatedly washed with deionized water by means of decantation process until neutral pH; acquired Wet gel then shifted into a china dish and left for 48 hours in a forced convection oven (FC-42D) at 70 C to produce dry SOW gel. Dried Gel further grinded in a pistil morter up to the favorable size for the loading process.

2.3 Loading of Iron oxide (Fe_2O_3) on SOW Gel

SOW gel being a cation exchanger cannot adsorb arsenic species and it is necessary to load metal ion [19]. The extent of adsorption largely depends on the kind of metal ion loaded onto the gel, moreover in aqueous solution, iron gives $[Fe(OH)(H_2O)5]^{2+}$ ion [26], which facilitates ligand exchange and can alter the properties of SOW gel to be suitable for the arsenic removal [21]. The loading of metal ion on the saponified orange waste gel results in the elimination of calcium and it is replaced by metal ion suitable for the ligand exchange.

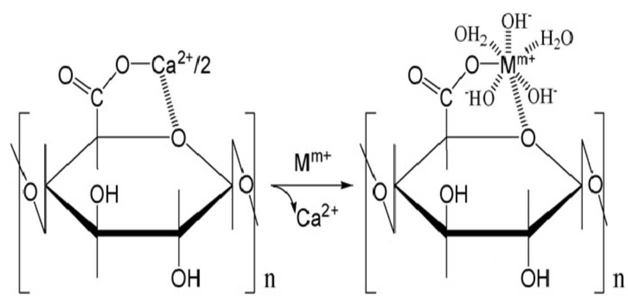

Fig-2 b: Loading of iron oxide (Fe_2O_3) on SOW gel

In order to load iron oxide onto the saponified orange waste SOW gel 3 grams of the SOW gel were equilibrated with 500 ml of 0.1M iron oxide solution at pH 2 for 24 hours and then filtered from iron oxide solution by a filter paper. Subsequently gel was achieved after filtration was characterized as iron oxide (Fe_2O_3) loaded SOW gel**.** The (Fe_2O_3) loaded SOW gel obtained was than repeatedly washed with deionized water until neutral pH. After neutralization of iron oxide loaded saponified orange waste gel, it was dried in (FC-42D) oven until constant weight, the temperature of oven was raised to 110 C. The surface area of the adsorbent for the removal of arsenic from aqueous solutions was increased by further grinding of dried (Fe_2O_3) loaded SOW gel. The grinded (Fe_2O_3) loaded SOW gel was sieved to obtain a uniform particle size fraction of between 75 and 150 µm for the adsorption tests.

2.4 Adsorption of Arsenic on Fe2O3 Loaded SOW Gel

Adsorption of arsenic onto Fe_2O_3 loaded SOW gel is governed by ligand exchange as shown in fig-3.

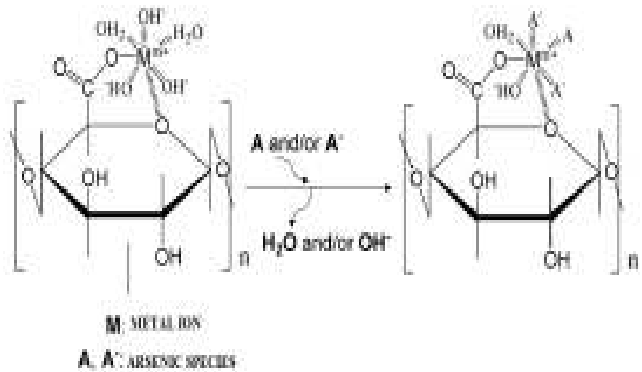

Fig-3: Adsorption of arsenic on the (Fe_2O_3) loaded SOW gel

Batch-wise adsorption tests for arsenic were carried out to examine the adsorption behavior of arsenic on the (Fe_2O_3) loaded SOW gel.

3. RESULTS AND DISCUSSION

The adsorption tests were carried out in the concentration range of 1ppm to 10 ppm. First of all adsorption of arsenic as a function of adsorbent concentration (adsorbent dose) was examined in a series of experiments where the initial concentration of arsenic was maintained constant at 1 ppm (mg/l) and thus the optimum adsorbent concentration was determined. These experiments were carried out at pH 10 on the basis of previous studies. All batch adsorption experiments were carried out in a 50 ml conical flask by taking 15 ml of arsenic solution and varying concentration of adsorbent. Than these samples were put in to a thermo shaker at 180 rpm for 100 minutes and then filtered to investigate the removal efficiency. Further operating parameters such as adsorbent dose(0.25g, 0.5g, 0.75g, 1g, 1.25g) shaking time (25 min, 50 min, 100 min, 125min) and metal concentration (1ppm, 5ppm, 10ppm, 20ppm) were optimized through batch type adsorption tests by keeping following parameters constant Temperature, pH, and shaking speed.

3.1 Optimization of Operating Parameters

In order to optimize operating parameters batch type adsorption tests were carried out by keeping following parameters constant Temperature, pH, shaking speed and adsorption parameters such as adsorbent dose(0.25g, 0.5g, 0.75g, 1g, 1.25g) shaking time (25 min, 50 min, 100 min, 125 min) and metal concentration (1ppm, 5ppm, 10ppm, 20ppm) were investigated.

3.2 Effect of adsorbent dose on Arsenic III removal

Batch type experiments were carried out in a 50 ml conical flask by keeping following parameters constant Temperature 30 ^{0}C, pH10, shaking speed 180 rpm, shaking time 100 minutes and adsorbate concentration 1ppm in order to examine the sorption efficiency of the Fe_2O_3 Loaded SOW gel for the removal of arsenic as a function of adsorbent dose . fig: 5.1 shows the sorption efficiency of Fe_2O_3 loaded SOW gel, maximum sorption efficiency is achieved at 1 gram adsorbent dose which is 86% removal efficiency and at 0.75 gram adsorbent dose sorption efficiency is 85% which is almost same for the 1 gram dose hence the optimum dose for the batch experiments was decided as 0.75 gram adsorbent which is about 50 g/L.

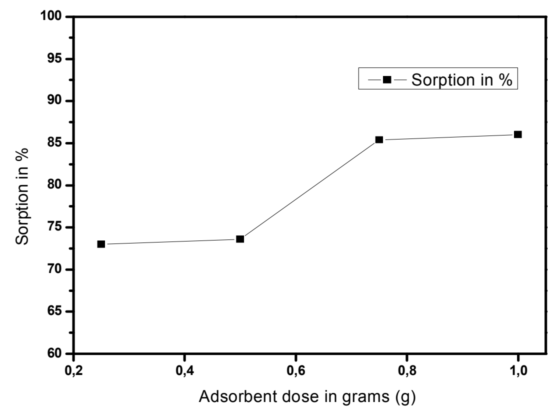

Fig-4: Effect of adsorbent dose on Arsenic III removal

In previous research adsorbent dose of 0.25 gm have been reported while using red mud as an adsorbent [27]. However more than 70% removal can be achieved at 17 g/L adsorbent dose.

3.3 Effect of shaking time on Arsenic III removal

Fig: 5 shows the optimum time required for the removal of arsenic III by Fe_2O_3 Loaded SOW gel by keeping 0.75 gram of adsorbent dose and all other parameters like temperature pH and rpm constant.

Different shaking times ranging from 0 min to 150 min were investigated as a function of arsenic removal

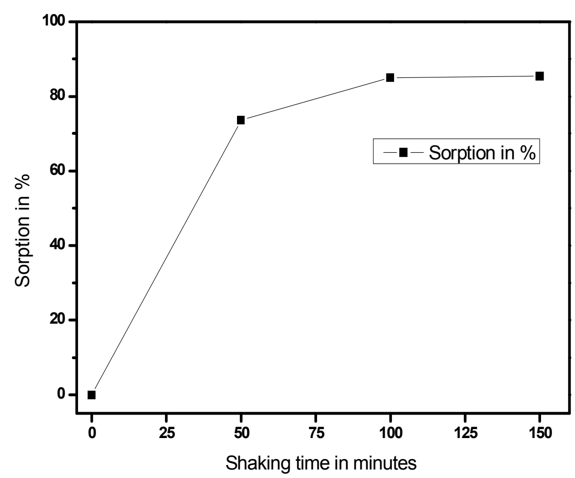

Fig-5: Effect of shaking time on Arsenic III removal efficiency from aqueous medium. The maximum removal efficiency is achieved at 150 minutes which is 85.4% arsenic removal although a significant increase in sorption efficiency is observed from 79.6% to 85% in the shaking time ranging from 50 minutes to 100 minutes.

After 100 minutes the increase in sorption efficiency is insignificant hence the shaking time is optimized at 100 minutes for the batch experiments to remove arsenic from aqueous solution which is less when compared with previous research 92 % efficiency was achieved at 240 minutes [28].

3.4 Effect of adsorbate concentration on Arsenic removal

Different adsorbate concentrations were treated with Fe_2O_3 Loaded SOW gel in order to examine the efficiency of adsorbent in high concentration solutions. All the parameters including temperature, pH, shaking speed were kept constant as in earlier experiments and the remaining optimized parameters were maintained however adsorbate concentration used was in the range of 1 ppm to 20 ppm, as reported in previous studies [29, 30]. Above figure shows the efficiency of the Fe_2O_3 Loaded

SOW gel increases with increase in adsorbate concentration it reaches up to the maximum sorption efficiency of 96% at 20 ppm and more than 85% arsenic removal is possible at adsorbate concentration of 1 ppm,

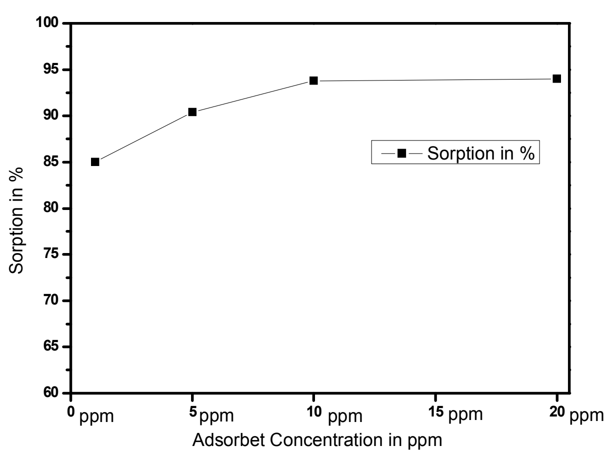

Fig-6: Effect of adsorbate concentration on Arsenic removal

Moreover it also provides knowledge that the same gel could be used repeatedly for the adsorption of arsenic onto it in a low adsorbate concentration.

4. CONCLUSION

The Iron loaded saponified orange waste gel has an intensive potential to replace the presently used expensive methods for removal of arsenic and other heavy metals from ground water in Pakistan. The optimum conditions at which maximum removal efficiency was obtained was 96% at adsorbent dose 0.75 g/L, shaking time 100 minutes, adsorbate concentration 20 ppm. It was found that in alkaline conditions the maximum arsenic removal was achieved. Furthermore Fe_2O_3 loaded saponified orange waste gel can be implied on continuous scale for commercial water filters to remove arsenic.

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