

Removal of As (III) ion using Syzygium cumini seeds (SCS) biomass from ground water and waste water

Jyoti Shah, Indu Sharma, Om Silakari, Rajeev Sharma

Abstract— Arsenic (As) contamination in drinking water is a serious environmental and health problem all over the India. Since biosorption is a less consuming, cheap and easy handling technique to remove As from ground water and waste water, so in present work biosorptive behaviour of Syzygium cumini seeds (SCS) biomass in a batch system has been investigated successfully to remove As (III) from ground water and waste water. Maximum percent removal of 69.30 % of As (III) was achieved at pH - 5, adsorbent dose of 0.3 gm, As (III) concentration of 0.2 mg/l, time of 135 minutes, temperature of 40°C and agitation speed of 180 rpm. Percent removal after chemical pretreatment was in the order of FeCl₃ (75.75) > NaOH (73.70) > HCHO (67.25) > H₂SO₄ (69.35) > HCl (64.40). Fourier Transmission Infrared Spectroscopy (FTIR) studies of SCS was done before and after biosorption process to establish the functional groups responsible for As (III) adsorption. In case of ground water the % removal by native, FeCl₃, and NaOH pretreated biomass was 83.6 %, 88 % and 86 % respectively, while in case of waste water the % removal was 75.26 %, 79.47 %, and 79.47 % respectively. It is concluded that SCS biomass can be effectively used to remove As (III) ion from aqueous solution. Scanning Electron Microscopy (SEM) of SCS biomass before and after biosorption was also done to understand the morphological changes in biomass.

Index Terms— Adsorption, arsenic (As), biosorption, FTIR, ICP-MS, Syzygium cumini seeds, SEM.

I. INTRODUCTION

Contamination of ground water and drinking water with As is a global problem. It is a naturally occurring, highly toxic metalloid in its inorganic form. Release of As in ground water as well as in marine water is due to the natural process of rocks weathering, volcanic emissions, geological leaching and so the concentration of As is higher in ground water than that of surface water [1]. Inorganic As is found as arsenite, As (III) and arsenate, As (V) species [2]. The toxicity of As is due to its oxidation states [3]. Anthropogenic activities adding As to environment are industrial activities and waste produced by them as wood preservatives, pharmaceutical products, farming chemicals including arsenical pesticides, insecticides herbicides, burning fossil fuels, coals, production of metals and deliberate mining [4]. The Maximum Contaminant level (MCL) of 10 µg/l of As recommended in drinking water [5],

[6]. Prolonged As exposure can damage the Central Nervous System (CNS), liver, skin and results in the appearance of various types of cancers such as lung, skin, internal, bladder, liver and prostate cancers [7]. There are various conventional methods for the removal of heavy metals from ground water and waste water including chemical precipitation, reduction or oxidation, reverse osmosis, ion exchange, electrochemical treatment and filtration etc. [8]. But these methods have some disadvantages e.g. produce secondary sludge which pose disposal problem, causing the environment to be polluted, poor efficiency, sensitive operating parameters, and high running cost [9]. Agricultural wastes, pharmaceutical waste, household waste or kitchen waste and microorganisms (live or dead) may be used in the biosorption process. Syzygium cumini (SCS) used in the present investigation which also called as jamun, black berry, black plum and java plum etc., belongs to myrtaceae family. The objective of this research is to understand the absorptive capacity of SCS biomass for the removal of As (III) ion from synthetic solution, real ground and waste water.

II. MATERIAL AND METHODS

A. Preparation of SCS biomass

SCS were washed repeatedly with tap water as well as double distilled water (DDW), dried in sunlight and then in an oven at 60°C until the constant weight obtained. The dried seeds grinded in an electric grinder to get the uniform SCS powder which was stored in an airtight container for further use [10], [11].

B. Biosorption experiment

All the chemicals used were of Analytical Grade (AG). 1000 mg/l stock solution of As (III) was prepared by dissolving 0.173 gm As₂O₃ in 100 ml DDW in 100 ml volumetric flask and working solution was prepared freshly from stock solution to the desired concentrations each time. Particular quantity of SCS biomass was added in As (III) ion solution followed by shaking and filtration using Whatmann filter paper No. 42 and analyzed for final As (III) concentration by ICP-MS. The percent removal (% R) and uptake capacity i.e. $q_e = (\text{mg/g})$ - the amount of metal ion adsorbed/unit mass of adsorbent was calculated as:

$$R (\%) = (C_i - C_f)/C_i \times 100$$

$$q_e (\text{mg/g}) = (C_i - C_f)/W \times V$$

where, C_i is initial concentration of As (III) in the solution in mg/L, C_f , final concentration of As (III) in the solution in mg/L, q_e , equilibrium uptake of As (III) ions in mg/g, V , volume of As (III) solution in liters (l), and W , weight of adsorbent in grams (g).

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III. RESULTS AND DISCUSSION

A. Physical Characterization of SCS biomass

In physical characterization, SCS biomass has pH of 6.37, moisture content of 7.83 % and ash content of 8.53 % was obtained in the present investigation which are in accordance the study reported by [12], [13].

B. Chemical Characterization (FTIR analysis) of SCS biomass

FTIR analysis involves the chemical characterization of SCS biomass before and after the biosorption process presented in Fig. 1 and Fig. 2 respectively. It was done using FTIR-8021PC (Shimadzu), with working range of 650-4000 cm⁻¹ used in KBr phase to determine the functional groups present. Absorption peak ranges from 3281.88 cm⁻¹ to 3284.92 cm⁻¹, 2919.90 cm⁻¹ to 2917.88 cm⁻¹, 2850.92 cm⁻¹ to 2849.90 cm⁻¹ shows the presence of O-H (alcohol), C-H (alkane), =C-H (aldehyde) functional groups respectively. After absorption of As (III) ion to the SCS biomass, there is the addition of new absorption peak i.e. 1732.95 cm⁻¹ shows the involvement of C=O (carbonyl) functional group. Absorption peaks from 1618.89 cm⁻¹ to 1617.92 cm⁻¹, 1448.93 cm⁻¹ to 1462.94 cm⁻¹, 1325.92 cm⁻¹ to 1331.94 cm⁻¹ shows the presence of N-H (amide), -C-H (alkane) and C=C (aromatic), C-F (alkyl halide) and C-N (amine) group respectively are functional group which are found to be involved in biosorption process.

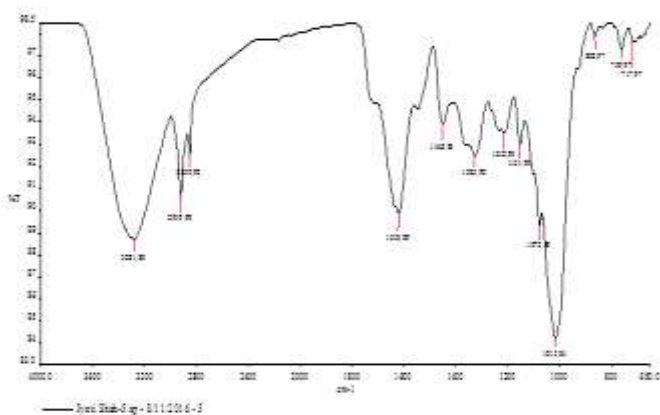


Fig. 1 FTIR spectrum of unmodified SCS biomass before adsorption of As (III)

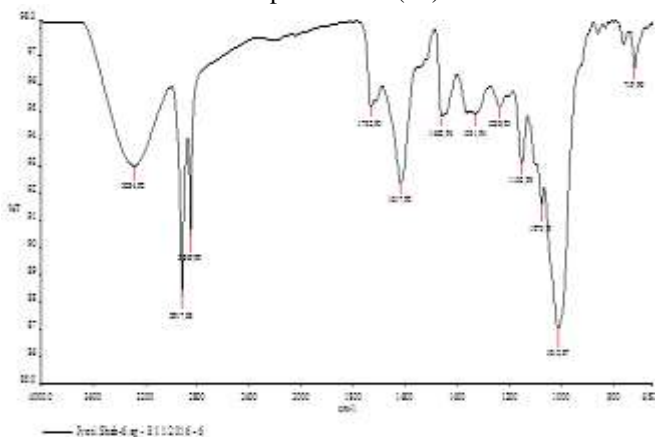


Fig. 2 FTIR Spectrum of unmodified SCS biomass after adsorption of As (III)

C. SEM micrograph

The structure and geometry of SCS biomass was determined by SEM micrograph shown in Fig. 3 (a and b). The micrograph pictures showed the effect of As (III) ion to the biomass of SCS which revealed that changes or deformation occurred in the morphology or structure of the biomass due to the adsorption of metal ions by the biomass. The control i.e. the biomass not treated with As (III) ion was also used to know the effect of As (III) on the morphology of the biomass showed intact structure and shape.

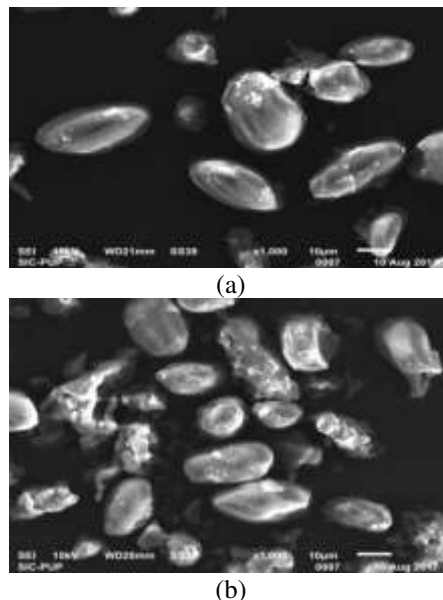


Fig. 3 SEM micrograph of *S. cumini* seed biomass before biosorption (a) at X1000 magnification and after biosorption (b) at X1000 magnification.

D. Effect of pH

pH is an important parameter which affects the surface charge of biomass, degree of ionization, speciation and solubility of the metal ion in the aqueous solution [14], [15]. The % removal increased when pH increased from 3 to 5 and then decreased after that presented in Fig 4. Acidic pH lowers biosorption of As (III) because there is a competition between H⁺ ions and As (III) ions for active sites present on SCS biomass surface. However when pH increases, this competition lowers and As (III) ions replaces H⁺ ions on SCS biomass [16], [17]. As (III) ions adsorbed more strongly at pH 5 having the removal percent of 48.15 % on SCS biomass surface which possess negatively charged active sites which were in accordance with the results of [18].

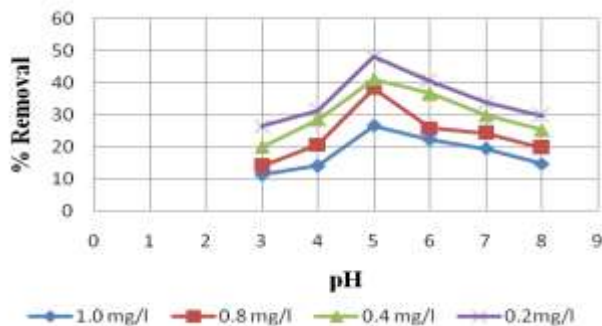


Fig. 4 Effect of pH on As (III) ions removal efficiency of SCS biomass

E. Effect of Adsorbent dose

When adsorbent dose increases from 0.1 gm to 0.35 gm, % removal of As (III) was increased from 38.93 % to 64 % at 0.2 mg/l (Fig 5). This behavior is due to the increase in number of binding sites resulting in increase in surface area on the biomass, with increase in adsorbent dose concentration [19]. Once the equilibrium state was achieved, further addition of biomass did not result in increase in % removal. This occurs because binding sites on the biomass were progressively saturated as the adsorbent dose was increased resulting in low % removal [20].

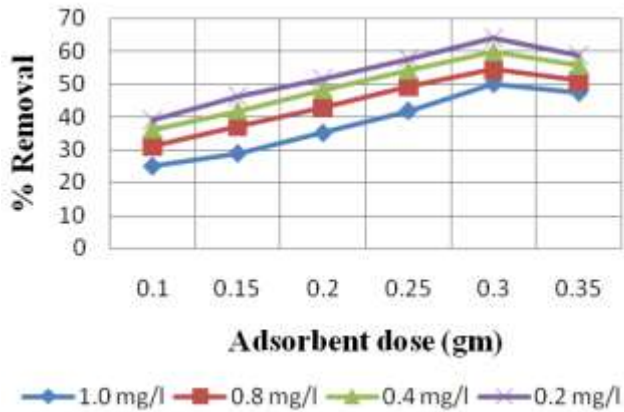


Fig. 5 Effect of adsorbent dose on As (III) ion removal efficiency of SCS biomass

F. Effect of initial metal concentration

As the initial concentration of As (III) ions increased, there is decrease in As (III) ion removal, because of saturation of binding sites and decrease in sufficient surface area on the SCS biomass in the aqueous solution shown in Fig. 6 [21]. Percent removal of As (III) decreased from 65.25% - 50.05% as the initial concentration increased from 0.20 mg/l to 1 mg/l. At initial As (III) (0.2 mg/l) concentration, most of the ions in aqueous solution would interact strongly with the binding sites on SCS biomass resulting in higher % removal as compared to higher As (III) concentration (1 mg/l).

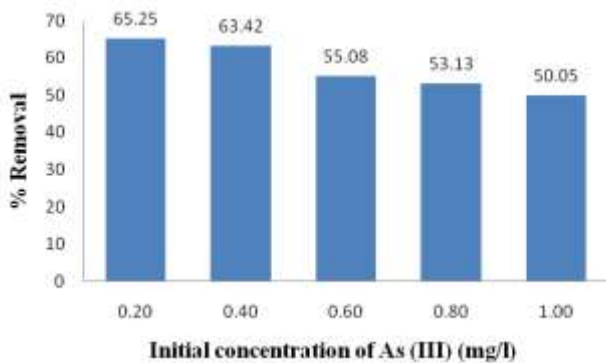


Fig. 6 Effect of metal ion concentration on As (III) removal efficiency of SCS biomass.

G. Effect of temperature

Effect of temperature was studied by varying the temperature ranges from 25, 30, 40, 50 and 60°C while keeping other parameters constant presented in Fig. 7. Since biosorption of As (III) ion is an endothermic process so adsorption increases with increase in temperature (Fan et al., 2008). The optimum temperature was 40°C (69.30 %) for the removal of As (III) using SCS biomass was used for the further experiment

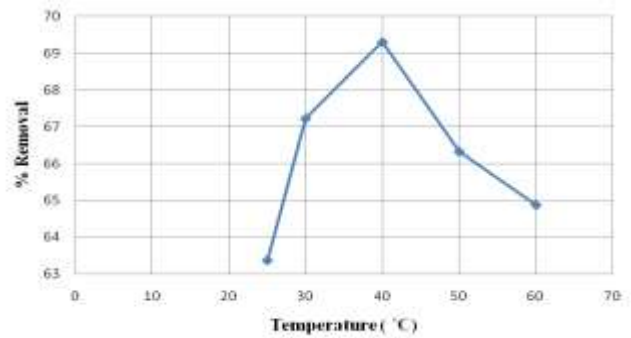


Fig. 7 Effect of temperature on As (III) ion removal efficiency of SCS biomass.

H. Effect of time

The effect of time used, ranged from 15-210 minutes, using the As (III) concentration ranges from 0.2, 0.4, 0.8 and 1mg/l was used (Fig. 8) revealed that maximum % removal of 65.75 % at As (III) ion concentration of 0.2 mg/l was occurred at 135 minutes of contact time. The increase in adsorption occurs relatively at slow speed until the equilibrium attained i.e. 135 minutes. After attaining the equilibrium further increase in contact time has no effect on % removal. This may be attributed to the presence of large number of vacant surface sites on the biomass [22].

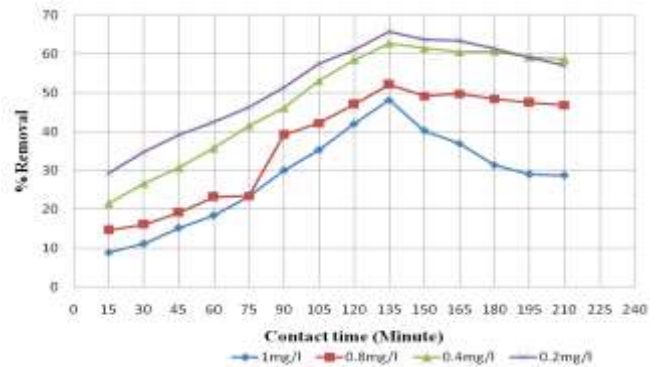


Fig. 8 Effect of time on As (III) ion removal efficiency by SCS biomass.

I. Agitation speed

Agitation speed range selected was 100, 150, 180, 200, 250, 300 and 350 rpm (Fig. 9). With an increase in an agitation speed, there is an increase in removal efficiency and maximum percent removal was 69.30 % at 180 rpm, It may be explained by the fact that at 180 rpm speed the entire active sites on the biomass was available for As (III) uptake.

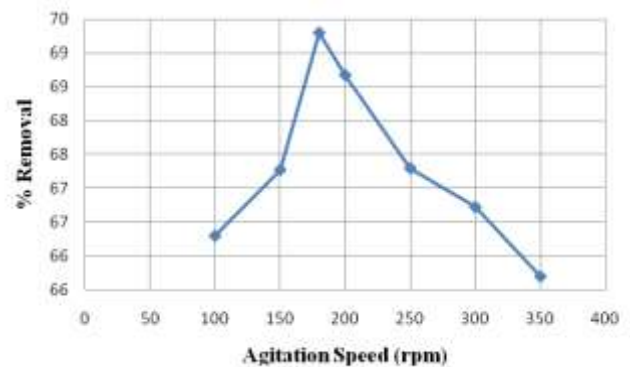


Fig. 9 Effect of agitation speed on As (III) ion removal efficiency by SCS biomass.

J. Effect of chemical pretreatment

SCS biomass was pretreated with two acids i.e. H₂SO₄ and HCl (0.1 M) showing a little increase in % removal from 69.30 % to 69.35% and decrease from 69.30 % to 64.40 % respectively presented in (Fig. 10). This may be explained by the fact that after certain concentration of acidic pretreatment of biomass there is a decrease in electronegativity of biomass causes the decrease in the remaining H⁺ ions (protons) on the pretreated biomass, resulting in decrease in biosorption [23]. Pretreatment of SCS with HCHO (formaldehyde, 0.1 M) results in decrease in % removal from 69.30 % to 67.25 %. This may be due to the reason that methylation of amine group in the cell wall of biomass causes enhancement or decline in % removal, which indicate that there is important role of amine group in biosorption [24]. Pretreatment of SCS biomass with NaOH (Fig. 10) increases the removal efficiency from 69.30 % to 73.70% and hence increases the biosorption capacity, which is in accordance with the results given by [25]. According to [24], this improvement in % removal may be because of surface impurity removal, expose of binding sites due to the cell membrane rupturing. Cell components may be chemically modified or exposes the binding sites buried in the inner layer of the cell wall by alkali treatment. Biosorption of As increases due to FeCl₃ pretreatment of fungal mat and according to [26], FeCl₃ pretreated fungal mats efficiently remove 79% of As (III) and As (V).

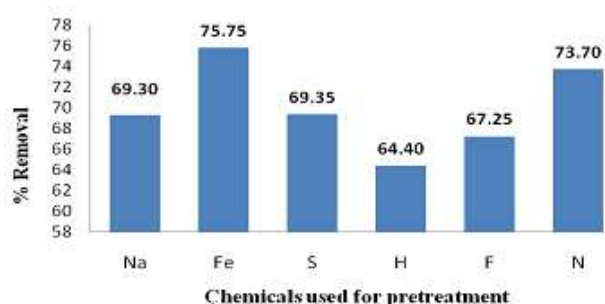


Fig. 10 Effect of chemical pretreatment of As (III) removal by SCS (Na: native, Fe: FeCl₃, S: H₂SO₄, H: HCl, F: HCHO, N: NaOH).

IV. APPLICATION OF INVESTIGATED METHOD TO REMOVE AS (III) FROM REAL WATER

In order to test the applicability of biosorption method, it was applied on the real ground water and waste water. The results obtained by batch experimental studies indicate that SCS biomass can be used as an adsorbent material to remove toxic As (III) ion from ground water and waste water. The results obtained are showing that the concentration of As (III) reduced the permissible limit or below the permissible limit (in ground water) encouraging to apply the technique on the industrial level (i.e. industrial application) that reduced the concentration of As (III) below the concentration given by industrial waste water standard [27]. SCS biomass was pretreated with FeCl₃, increased in percent removal from 83.6 % to 88 % was achieved (Table. 1). Whereas in case of waste water, native SCS biomass showed the percent removal of 75.6 %, representing that this is a good adsorbent for removal of As (III) from aqueous solution. While pretreatment of SCS biomass with FeCl₃ in case of waste

water also increases the percent removal by 79.47 %. Again when SCS biomass was pretreated with NaOH, percent removal achieved was 86 % and 79.47 % when it was used to treat the ground water and waste water respectively.

V. CONCLUSION

It is concluded from the batch experimental studies that maximum As (III) removal of 69.30 % was achieved by using SCS biomass. The application part of this method is that it was applied on the real ground water and waste water. In case of ground water the % removal by native, FeCl₃, and NaOH pretreated biomass was 83.6 %, 88 % and 86 % respectively

Table 1: Biosorption studies on removal of As (III) uptake capacity (mg/g) from real ground water (NFL, Bathinda - hand pump) and waste water (TDS, Bathinda).

Adsorbent	Optimized pH	Water sample pH	C _i (mg/l)	C _f (mg/l)	R (%)	Uptake capacity (mg/g)
GW - SCS (Native)	5	7.73 ±0.12	0.05	0.008	83.6	0.084
GW - SCS (FeCl ₃)	5	7.73 ±0.12	0.05	0.006	88	0.088
GW - SCS (NaOH)	5	7.73 ±0.12	0.05	0.007	86	0.086
WW - SCS (Native)	5	5.80 ±0.72	0.19	0.047	75.26	0.29
WW - SCS (FeCl ₃)	5	5.80 ±0.72	0.19	0.039	79.47	0.3
WW - SCS (NaOH)	5	5.80 ±0.72	0.19	0.04	79.47	0.3

Gw: Ground water, WW: Waste water, *NFL: National Fertilizer limited, *TDS:Textile Dyes Shop

While in case of waste water the % removal was 75.26 %, 79.47 %, and 79.47 % respectively. This experimental research on SCS biomass would be useful in removal of As and other heavy metals from ground water and waste water, which will be useful in developing less expensive, easily handling technologies for decontamination of water.

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