REMOVAL OF As(III) WITH (CYNODON DACTYLON) GREEN DUB AND ORANGE PEEL FROM AQUEOUS MEDIUM

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ABSTRACT

In the present study, Cynodondactylon (green dub) and orange peel powder have been utilized for remediation of As(III) ion from an aqueous medium. Different weights of Cynodondactylon have been treated with 2ppm As(III) solution up to a fixed time interval and again fixed weight of Cynodondactylon has been treated up to different intervals of time at a pH range of 2-6.5. Similar experiments have been repeated with orange peel powder at different pH values to know the adsorption isotherm, remediation efficiency, and adsorption rate. Results show that percentage removal in 30 minutes is 99.5% and agitation time for equilibrium is 30 minutes, with orange peel powder whereas maximum percentage removal with Cynodondactylon is 98.5% at pH 2. Thus orange peel and Cynodondactylon both could be used as a potential adsorbent for removal As(III) from an aqueous medium.

Keywords: Adsorption, Orange Peel, As(III), Remediation, CynodonDactylon.

RASĀYAN J. Chem., Vol. 14, No.2, 2021

INTRODUCTION

Arsenic contamination in groundwater samples of the Gangetic plain has been reported in India in general and in Bhagalpur district in particular causing a detrimental effect to the health of the inhabitants of the district.^{1,2} When arsenic-contaminated water enters the human body, it attacks the DNA as a result of which various types of cancer takes place. Early symptoms are hyperpigmentation of skin and prolonged use of arsenic-contaminated water may lead to even death.³⁻⁶ The cause of arsenic-contaminated water may be attributed to the sedimentary rocks which come in contact with the aquifer.^{7,8} Newer Alluvium having grey to black colored argillaceous sediments have emerged as a source of arsenic.

In addition to natural sources, arsenic enters water bodies through anthropogenic sources i.e., metal extraction, anticorrosive agent, steel industries, and industrial effluents. Amongst different oxidation states of 0, +3, and +5, Arsenic (III) has been found most common in an aqueous medium. Inorganic arsenic, redox conditions, and pH values affect the toxicity of arsenic in soils. Humus present in soil has also the capacity to bind with arsenic. Thus arsenic (III) is being released primarily from sediments. Arsenic contaminated groundwater is generally found in newer alluvium from shallow aquifers.⁹ Older alluvium aquifer has rarely arsenic contamination. Arsenic in an aqueous medium can be remediated by some of the methods e.g. adsorption by active charcoal, coagulation, membranes, clay, or clay derivatives.¹⁰⁻¹² Activated alumina and iron coated sand have also the ability to remove arsenic (III) from an aqueous medium. Soil rich in ferric salts combines with arsenate to give Fe (III)-arsenate and so it has been established that soil rich in ferric salt has a lesser probability of arsenic contamination.¹³⁻¹⁵

Amongst a series of removal methods, bioremediation may be a better option for selecting appropriate biomass from a wide spectrum of plants, agricultural by-products. Some of the bacterial biomass effective for arsenic removal may be mentioned here as *Agrobacterium tumefaciens*, *Bacillus indicus*, *Bacillus subtilis*.^{16,17} but here Cynodondactylon and orange peel have been selected for study keeping in mind the

abundance of *Cynodondactylon* and orange peel. This method of adsorptive removal has gained an edge over the existing traditional methods e.g. ion exchange, ultrafiltration, liquid-liquid extraction. Due to its low cost and eco-friendly nature, this method has been adopted under suitable laboratory conditions. In most of the traditional methods, it becomes very difficult to mitigate the arsenic concentration below the permissible limit of 0.05 ppm. Ion exchange also is not very effective due to the interference of some associated ions. Orange peel contains cellulose, fibers, and protein in its cell wall. Pectin, a carboxylated polysaccharide acts as an intercellular material. *Cynodondactylon* acts as a phytoremediator of arsenic. Alkaloids, B-Carotene and Vitamin C are commonly known chemical constituents of *Cynodondactylon*. Also, docosanoic acid hexadecenoic acid, furfural alcohol, lignin, and flavon are present in *Cynodondactylon*, a perennial herb widely available with rapid growth. As pH controls the adsorption of arsenic, the experiment has been carried out at different pH values.¹⁸⁻²⁰ Obtained data of adsorption is explained based on Freundlich and Langmuir adsorption isotherms. Freundlich isotherm represents multilayer adsorption whereas Langmuir adsorption isotherm explains monolayer adsorption.²¹ Freundlich isotherm may be represented as $x/m = kc^{1/n}$ where x/m is the mass of adsorbate per unit adsorbent and c is the concentration.²² Adsorption kinetics of arsenic may be seen with the Lagergren rate equation given as:

$$\log(q_e - q_t) = \log q_e - k/2.303t$$

Where q_e stands for the amount of arsenic adsorbed at equilibrium and q at any time t . If the plot of $\log(q_e - q_t)$ vs t gives the straight line, first-order kinetics is followed. Surface functional groups may be known by conducting FTIR tests before and after adsorption.²³

EXPERIMENTAL

Cynodondactylon is collected from the field as this is widespread and abundant. It is washed with deionized water again and again. After repeated washing, the fixed mass of green dub is put in 100ml 2ppm sodium arsenite solution up to different intervals of time and different masses of green dub up to fixed time. The kinetics is studied at different time intervals. Another experiment is done with orange peel, a waste after the use of orange. This peel is dried and powdered after repeated washing with double distilled water. This fine powder is mixed with 100 ml 2ppm solution and the residual concentration is known at different intervals of time. Residual concentrations of arsenic are determined from mercoquant arsenic kit and further confirmed by Atomic Absorption Spectrophotometer.

RESULTS AND DISCUSSION

SEM is an important analysis for knowing the surface morphology of orange peel powder before and after adsorption at different magnifications. Comparison of SEM images before and after adsorption clearly showed that adsorption took place on the surface of the adsorbent due to the presence of active sites.^{24,25}

Fig.-1: SEM Image of Orange Peel Powder at a magnification of 1.00K X before Adsorption.

Fig.-2: SEM Image of Orange Peel Powder at a magnification of 1.00K X after Adsorption

Fig.-3: SEM Image of Orange Peel Powder at a magnification of 2.00K X before Adsorption

Fig.-4: SEM Image of Orange Peel Powder at a magnification of 2.00K X after Adsorption.

Fig.-5: SEM Image of Orange Peel Powder at a magnification of 5.00K X before Adsorption.

Fig.-6: SEM Image of Orange Peel Powder at a magnification of 5.00K X after Adsorption

Fig.-7: SEM Image of Orange Peel Powder at a magnification of 10.00 KX before Adsorption.

Effect of Time on Percentage Removal with Orange Peel Powder

Effect of time on percentage removal shown in Fig.-9 and Table-1 describes the residual concentration of As(III) in 10 minutes, 15 minutes, 30 minutes, 60 minutes, 120 minutes, 180 minutes. From table 1 it is clear that an equilibrium concentration of 0.03 ppm is attained in 60 minutes or percentage removal of 98.5% takes place.

The percentage removal of As(III) is known by the formula:

$$\text{Percentage removal} = (C_i - C_t) / C_i \times 100.$$

Where, C_i is the initial concentration and C_t is the concentration at time t . Fig.- 9: shows a graph of percentage removal versus time with orange peel powder.

Fig.-8: SEM Image of Orange Peel Powder at a magnification of 10.00K X after Adsorption

Table-1: Residual Concentration of As(III) with Orange Peel Powder at a Different Time Interval at pH 6.5

S.No.	Initial concentration (ppm)	Mass of Orange Powder (gram)	Time (min.)	Residual Concentration	% Removal	q_t	$\log q_t$	$\log C_t$	C_t/q_t
1	2 ppm	1 gm	10	0.1	95	0.19	-0.72	-1	0.53
2	2 ppm	1 gm	15	0.06	97	0.194	-0.71	-1.2	0.3
3	2 ppm	1 gm	30	0.05	97.5	0.195	-0.7	-1.3	0.2564
4	2 ppm	1 gm	60	0.03	98.5	0.197	-0.7	-1.5	0.15
5	2 ppm	1 gm	120	0.03	98.5	0.197	-0.7	-1.5	0.15
6	2 ppm	1 gm	180	0.03	98.5	0.197	-0.7	-1.5	0.15

Fig.-9: Percentage Removal of As (III) Vs Time with 1 gm of Orange Peel Powder at 26°C and pH 6.5

Table-2: Residual Concentration of 100 ml 2 ppm As(III) Solution after Treatment with Cynodon dactylon at pH 6.5

S.No.	Initial concentration	Mass of Cynodon dactylon	Time (hour)	Residual Concentration	% Removal	q_t	$\log q_t$	$\log C_t$	C_t/q_t
1	2 ppm	10 gm	24	1.3 ppm	35	0.007	-2.154	-0.1139	185.71
2	2 ppm	10 gm	48	0.2 ppm	90	0.018	-1.744	-0.6989	11.11
3	2 ppm	10 gm	72	0.12 ppm	94	0.0188	-1.725	-0.9208	6.382
4	2 ppm	20 gm	24	0.8 ppm	60	0.006	-2.221	-0.969	133.33
5	2 ppm	30 gm	24	0.6 ppm	70	0.0046	-2.337	-0.2218	130.43

Adsorption Isotherm

Freundlich and Langmuir adsorption isotherms have been represented by Figs.-10 and 11 respectively for adsorption of As(III) on orange peel powder. Freundlich Isotherm is obtained by plotting $\log q_t$ versus $\log c_t$ and Langmuir adsorption isotherm is obtained by plotting c_t/q_t versus c_t .^{26, 27} q_t can be expressed as:

$$q_t = (c_i - c_t)/m \times v$$

Where,

C_i is the initial concentration of As(III) solution

C_t is the concentration of As(III) at time t

m = mass of adsorbent in grams

v = volume of As(III) solution

Fig.-10: $\log q_t$ Vs $\log c_t$ (Freundlich Isotherm of As(III)-Orange Peel Powder System) at 26°C and pH 6.5

Fig.-11: C_t/q_t Vs C_t (Langmuir Isotherm of As(III)- Orange Peel Powder System) at 26°C and pH 6.5

Adsorption isotherms have been studied at pH 6.5 for Cynodondactylon at 26°C. Langmuir and Freundlich isotherms have been explained by Figs.-12 and 13 respectively. At pH 6.5 a graph of $\log q_t$ versus $\log c_t$ has been plotted which shows that Freundlich adsorption is obeyed (Fig.-12).

Figure-11 shows that Langmuir adsorption isotherm is obeyed in case of adsorption of As(III) by orange peel powder. Experimental data explains well Freundlich and Langmuir adsorption isotherms. Experimental data for adsorption of As(III) by Cynodondactylon fit Freundlich and Langmuir adsorption isotherm.²⁸ Figure-12 shows that Langmuir isotherm is obeyed in case of adsorption of As(III) by Cynodondactylon and Fig.-13 shows that Freundlich adsorption isotherm is obeyed in case of adsorption of As(III) by Cynodondactylon.

Effect of pH on Adsorption of As(III)

Cynodondactylon and orange peel powder has been found good adsorbents of As(III) like bentonites.²⁹ Effect of pH has been studied on adsorption as pH controls the process of adsorption. Here the

experiments have been done at pH 2, 4, and 6.5 with Cynodondactylon and orange peel powder both. At pH 6.5, the maximum percentage of removal with 10 g of Cynodondactylon on treatment with 100 ml 2 ppm As(III) solution is up to 72 hours is 94%. Removal percentage at pH 2 with similar conditions ranges from 94% to 98.5%. So maximum percentage removal of As(III) by Cynodondactylon is 98.5% at pH 2. For pH varying from 2 to 4, an increase in percentage removal is not significant. The optimum temperature is 26°C and pH is 2 for maximum adsorption of As(III) by Cynodondactylon(Fig.-15, Table-4).

Fig.-12: ct/qt Vs ct (Langmuir isotherm of As(III)-Cynodondactylon System) at 26°C and pH 6.5.

Fig.-13: $\log qt$ Vs $\log ct$ (Freundlich Isotherm of As(III)-Cynodondactylon System) at 26°C and pH 6.5

The effect of pH changes has also been studied for adsorption of As(III) on orange peel powder. Studies have revealed that the maximum percentage of removal at pH 6.5 is 98.5% and at pH 4 maximum percentage of removal is 99.5%. There is no change in removal percentage on varying the pH from 4 to 2. So maximum adsorption takes place at pH 4 or 2(Fig.-14, Table-3). But the effect of pH change on adsorption of As(III) by orange peel powder does not make any considerable change.³⁰⁻³³

Table-3: Percentage Removal by Orange Peel at Different pH

Time(minutes)	Percentage Removal at pH 2	%Removal at pH 4	%Removal at pH 6.5
10	95	98.5	95
15	97.5	99.0	97
30	99.5	99.5	97.5
60	99.5	99.5	98.5
120	99.5	99.5	98.5

Table-4: Percentage Removal by Cyanodon Dactylon at Different pH

Time(Hours)	% Removal at pH2	% Removal at pH 4	% Removal at pH 6.5
24	94	90	35
48	96	92.5	90
72	98.5	97.5	94

Fig.-14: Percentage Removal of As(III) by Orange Peel at Different pH

Fig.-15: % Removal of As(III) by Cynodon Dactylon at Different pH

Effect of Adsorbent Dosage

The removal of As(III) from aqueous medium increases with an increase in adsorbent dosage. With 10 g of Cynodondactylon at pH 4 removal percentage is 90%. As the dosage is increased from 10 g to 20 g, the removal percentage increases from 90 to 94%. When the dosage is further increased to 30 g, percentage removal increases to 96%. This increase in removal percentage may be explained as an increased number of active sites for adsorption due to an increase in adsorbent dose.³⁴ But maximum percentage removal is obtained by increasing contact time with a fixed mass of adsorbent.

CONCLUSION

Potential adsorbents for removal of As(III) from aqueous medium have been utilized and the effect of pH, adsorbent dose, and adsorption isotherms have been studied. The pH studies revealed that maximum removal of As(III) by Cynodondactylon and orange peel powder took place at pH 2 to 4 but no considerable variation in percentage removal was marked with variation in pH. An increase in masses of adsorbent increased the percentage removal due to the availability of more active sites on the surface. Isotherm studies clearly showed that Freundlich and Langmuir adsorption isotherms were followed. Cynodondactylon, a perennial weed, and orange peel powder both could be utilized for arsenic mitigation. This low-cost and eco-friendly adsorbent has been established as a potential remover of As(III) from an aqueous medium.

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[DOI:10.31788/RJC.2020.1335725](https://doi.org/10.31788/RJC.2020.1335725)

[RJC-6178/2020]