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Comparative study on biosorption of arsenite ions onto raw and chemically activated orange peel powder in batch reactor

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Abstract

In present work, comparative study of sorption potential of raw and chemically activated orange peel powder has been explored for the removal of arsenite ions (As III) from wastewater. Several operating parameters such as contact time, adsorbent dose, adsorbate ion concentration, solution pH as well as temperature were studied in batch reactor. Surface as well as physicochemical analysis of orange peel was done by using FTIR (Fourier Transform Infrared Spectroscopy), SEM (Scanning Electron Microscopy), proximate and ultimate analysis. Maximum removal of As (III) 86.3% and 87% was obtained at initial metal ion concentration 20 mg/l and 25 mg/L, optimum pH 2 and 2.8, temperature 30˚C and 25˚C, contact time 120 and 150 minutes as well as the adsorbent dose 4g for raw and chemically activated orange peel respectively. Modeling of experimental data showed that Freundlich model (R^2 = 97.45) had a better fit over Langmuir isotherm (R^2 = 96.33) for raw orange peel and the Freundlich model (R^2 =99.8%) in comparison to Langmuir model (R^2 =94.5%) shows better fit. The present comparative study depicts that the chemically activated orange peel powder are more effective than raw orange peel powder. Thus, orange peel is found to be promising simple material for removal of arsenite ions (As III) ions.

Keywords: Biosorption, Sodium Arsenite, Orange peel powder, chemically activated orange peel

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1. Introduction

With an increase in the industrial activities and several emerging technologies, the arsenic contamination in the surrounding receives a considerable attention. Arsenic exposure cause many hazardous diseases such as skin, lung, liver, bladder cancer (Peng *et al,* 2013) and may also affects thrombocytes that play a key role in cardiovascular diseases (Hong *et al,* 2014). The surface water as well as groundwater contamination with an elevated arsenic concentration has been emerged as a worldwide health as well as environmental issue. Both geogenic processes and anthropogenic activities like smelting and mining, coal combustion and leather tanning operations causes contamination to water resources with arsenic (Abid *et al,* 2016). Low cost adsorbent is considered to be an (ideal) alternative to the recent expensive techniques for the removal of arsenic from wastewater. The term orange peel has diverse flavonoids, including a lot of flavanone and C-glycosides and flavone O- , and the polymethoxylated flavones (PMFs). It was reported that orange peel is considered to be adsorbent as it has larger surface area as well as greater potential for adsorbing toxic contaminants like heavy metals form industrial effluents as well as from wastewaters (Ajmal *et al*, 2000).

Arsenic determination is considered to be a critical importance in saving living beings from different health issues it poses (Pasha *et al*, 2008). Orange peel is considered to be a essential biomass as in world orange take up 75% of the total citrus fruits. The carboxyl group as well as the hydroxyl group results in higher affinity to the metal ions (Peng *et al*, 2013). The ranking of arsenic in human body and the earth's crust is 20th and in seawater is 14th .Arsenic abundance in continental crust of earth is 1.5-2 ppm and according to ASTDR the ranking of arsenic holds 1st ranking that's why arsenic is relatively scarce (Shakoor *et al*, 2016). In 1980's it was reported that the arsenic is considered as carcinogenic substance that was also registered with IARC (International Agency for Research on Cancer).

2. Material and methods

Preparation of orange peel powder

Orange peel has been taken from Limbdi corner at IIT (BHU) Varanasi then the biosorbent was washed with double distilled water to remove complete dirt from its surface then it was dried for about one day in sunlight then miling of the peel was done to get powdered form and then sieved at 210-300 micron size. Finally the biosorbent was ready to use.

Activation of orange peel powder (OPP) with HCl

5g of raw orange peel powder (210-300 micron) was chemically treated in a 1M HCl. The mixtures were transferred to the beaker. After addition of required amount of water (deionized), stirring of was done for about 4h at room temperature. The sample was filtered and washed with 20% of isopryl alcohol no color was shown in filtrate. Then at 55°C washed sample was dried in an oven for 24h then it was used as chemically activated adsorbent.

Raw orange peel

5g of raw orange peel (210-300 micron) with stock solution (prepared by 0.1734g Na_3AsO_4 in 1000 ppm) is taken along with distilled water. The mixtures were transferred to the beaker. And after the addition of required amount of distilled water, the stirring of suspension is done for about 4h at room temperature. After vaccum filtered the sample were repeatedly washed by the help of a 20% of isopropyl alcohol until no color was shown in filtrate. Then sample (washed) was dried in an oven at 55°C for about 24h so that it can be used as raw adsorbent.

Batch adsorption experiment

In a 250ml conical flask add 0.5ml As (III) ions with 45ml distilled water and 0.5g of chemically activated orange peel. The above mixture is taken on shaker at 150rpm for 120 minute at temperature 25°C. After attaining equilibrium, contents in flasks were filtered and analysis of residual concentration of As (III) ions is done by the help of Atomic Absorption Spectrophotometer. The effect of pH on As (III) adsorption has been studied at several pH like 2, 4, 6, 8, 10 and 12. The adjustment of pH was done by addition of 0.1mol L^{-1} HCl / 0.1mol L^{-1} NaOH. In same way adsorption capacity of untreated orange peel were performed from 100ml (10µgmL^{-1}). The rate of metal adsorbed on was determined by analyzing supernatant after a contact period of 30, 60, 90, 120, 150 and 180, 210 minute and the rate of adsorption were also analyzed at different temperature such as 10 ˚C, 20˚C, 30˚C, 40˚C and 50˚C. The of pH analysis of the solution were measured with the help of pH meter.

Theoretical development

The percentage of arsenite removal was estimated by using following equation.

$$R\% = Ci\text{-}Ce/Ci*100 \tag{1}$$

where, C_e = equilibrium concentration d after adsorption (mg/L)
C_i = Initial concentration of adsorbate (mg/L)

Thus the equilibrium adsorption amount (qe) in mg/g were calculated by the formula

$$Qe = ((Ci\text{-}Ce)*V)/m \tag{2}$$

where, V= volume of the solution (L)
m = adsorbent mass (g)

3. Characterization of biosorbent

SEM analysis:

Surface morphology like porosity of the raw biosorbent were determined by using Scanning Electron Microscopy (SEM).

FTIR analysis:

To ascertain the functional group on orange peel, Fourier Transformed Infrared Spectra were obtained from raw and treated adsorbent i.e. Orange peel.

Proximate analysis:

For the determination of moisture content, ash content, volatile content as well as fixed carbon here we used proximate analysis.

Ultimate Analysis:

To determine the nitrogen, oxygen, sulphur and hydrogen content ultimate analysis were done.

4. Results and discussions

Table.1. depicts the proximate analysis of orange peel as we come to know the moisture content (8.9%), ash content (6.5%), volatile content (53.9%) as well as fixed carbon (30.2%) of the sample content with the help of this analysis.

Table 1: Proximate analysis of orange peel:

Moisture	8.9%	105˚C
Ash	6.5%	800˚C
Volatile	53.9%	925˚C
Fixed carbon	30.2%	This can be determined by deducting volatile matter, moisture as well as ash from original weight of sample

Table.2 depicts the ultimate analysis of orange peel as here we come to know that how much N% (3.143), C% (0.87), H% (NA), S% (NA), O% (NA) were present in the sample through this analysis.

Table 2: Ultimate Analysis of Orange Peel:

N%	**C%**	**H%**	**S%**	**O%**	**Weight (mg)**
3.143	0.87	NA	NA	NA	1.249

NA= Not Available

FTIR analysis

To ascertain the functional group on orange peel, Fourier Transformed Infrared Spectra were obtained from the pretreated adsorbent i.e. Orange peel. Little amount of KBr along with adsorbent (orange peel) was taken for further FTIR analysis. The spectra of FTIR were identified by obtaining the result graphically.

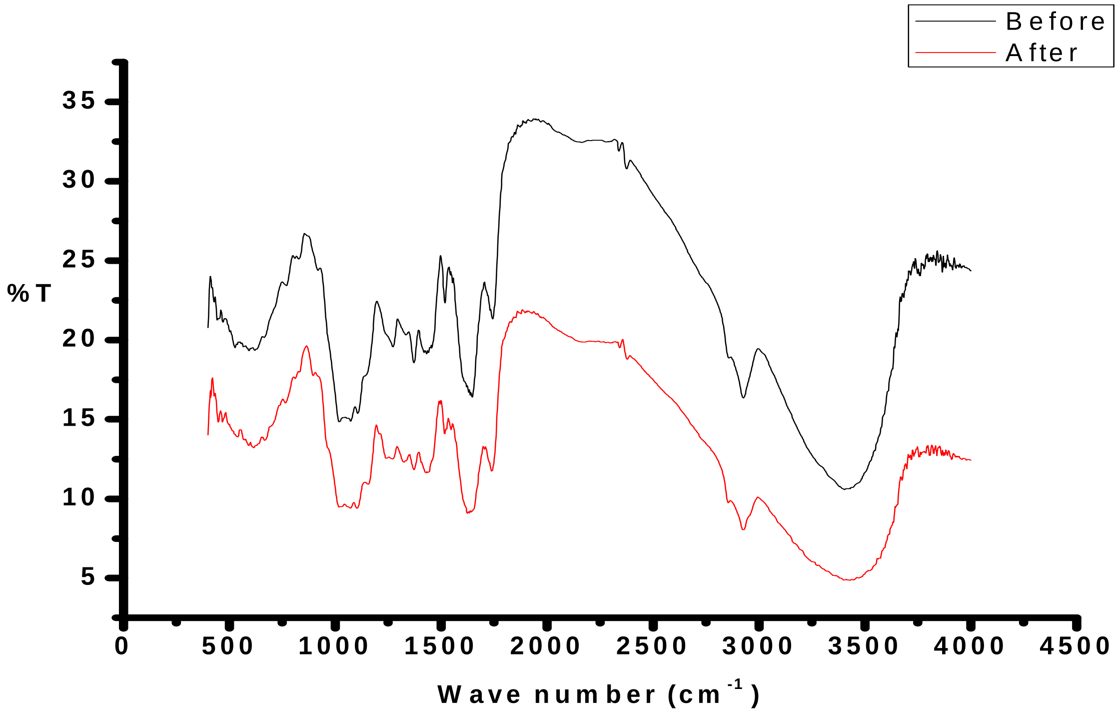

Fig. 1: FTIR result for raw orange peel before and after adsorption

Table 3:FTIR readings of raw orange peel before and after adsorption

Raw (before biosorption)	Functional groups	Raw (after biosorption)	Functional groups
3404.47	N-H asymmetric stretch	3524.06	-
2926.11	C-H stretch	3468.13	O-H stretch (Carboxylic acid)
2858.60	C-H stretch	3352.13	O-H stretch (Carboxylic acid)
2374.45	-	3248.23	O-H stretch (Carboxylic acid)
2164.20	-	2924.18	O-H stretch (Carboxylic acid)
2144.91	-	2854.74	O-H stretch (Carboxylic acid)
2048.47	C=O stretch	2378.31	-
1743.71	C=O stretch (Esters)	2154.56	-
1647.26	C=c stretch (Alkenes)	1739.85	C=O stretch (Esters)
1518.03	N-H bend(Amides)	1624.12	-
1371.43	CH_3 , C-H bend (Alkanes and alkyls)	1438.94	-
1332.80	C-F stretch (alkyl halides)	1371.43	CH_3, C-H bend (Alkanes and alkyls)
1271.13	=C-O-C Asymmetric stretch (Ethers)	1323.21	C-F stretch(Alkyl halides)
1105.25	C-F stretch(Alkyl halides)	1242.20	C-F stretch(Alkyl halides)
1072.45	C-F stretch(Alkyl halides)	1555.40	N-H bend(Amides)
1018.45	C-F stretch(Alkyl halides)	1103.32	C-O stretch (Alcohols)
920.08		1072.46	C-F stretch (Alkyl halides)
827.49	C-H bend(Aromatic compounds)	1018.45	C-F stretch (Alkyl halides)
709.62		765.77	C-H bend(Aromatic compounds)
663.53	=C-H bend(Alkynes)	685.46	=C-H bend(Alkynes)
328.51	C-I stretch(Alkyl halides)	615.31	C-Br stretch (Alkyl halides)

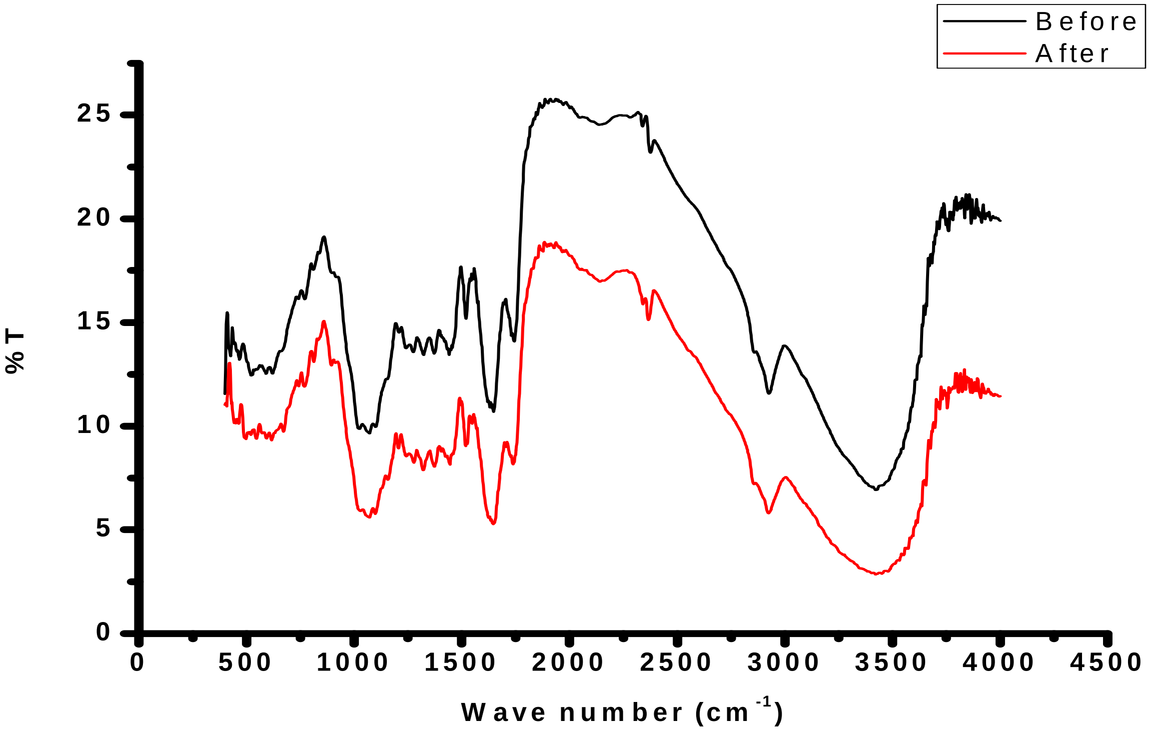

Fig. 2: FTIR result for activated orange peel before and after adsorption

Table 4: FTIR readings of raw orange peel before and after adsorption

Activated (before biosorption)	Functional groups	Activated (after biosorption)	Functional groups
3421.83	O-H stretch (Carboxylic acid)	3477.77	O-H stretch (Carboxylic acid)
3377.47	O-H stretch (Carboxylic acid)	3421.83	O-H stretch (Carboxylic acid)
2137.20	C=C stretch (Alkynes)	3350.46	O-H stretch (Carboxylic acid)
1743.71	C=O asymmetric stretch (Anhydrides)	3273.31	C=O stretch (Esters)
1647.26	N-H bends(Amines)	2924.18	O-H stretch (Carboxylic acid)
1620.26	N-H bends(Amides)	2856.67	O-H stretch (Carboxylic acid)
1519.96	N-H bends(Amides)	2553.66	O-H stretch (Carboxylic acid)
1448.59	-	2141.06	-
1371.43	CH_3 C-H bend(Alkanes and alkyls)	1737.92	C=0 stretch(Esters)
1321.28	C-F stretch (alkyl halides)	1645.33	N-H bend (Amines)
1273.06	C-F stretch (alkyl halides)	1624.12	N-H bend (Amines)
1099.46	C-F stretch (alkyl halides)	1521.89	N-H bends(Amides)
1070.53	C-F stretch (alkyl halides)	1452.45	_
1024.24	C-F stretch (alkyl halides)	1371.45	CH_3 C-H bend (Alkanes and alkyls)
619.17	=C-H bend (Alkynes)	1321.28	C-F stretch (alkyl halides)

Table 4 (Cont'd): FTIR readings of raw orange peel before and after adsorption

Activated (before biosorption)	**Functional groups**	**Activated (after biosorption)**	**Functional groups**
520.80	C-Br stretch (Alkyl halides)	1155.40	C-O stretch (Alcohols)
		1097.53	C-F stretch (alkyl halides)
		1070.53	C-F stretch (alkyl halides)
		1030.02	C-F stretch (alkyl halides)
		893.07	=C-H stretch (Alkenes
		767.69	C-H bend (Aromatic Compounds)
		671.25	=C-H bend (Alkynes)
		592.17	C-Br stretch (Alkyl halides)
		545.87	C-Br stretch (Alkyl halides)

FTIR graph shows different peaks of functional groups like alkanes and alkyls, alcohols, carboxylic acid, amides, aldehydes as well as ketone groups present in the raw and activated orange peel which are responsible for holding the heavy metal ions onto the surface of biosorbent. Shifting of peaks was observed after adsorption process. On comparing table 1 and 4 we found that there was more functional groups were detected in activated biosorbent as compared to the raw one.

SEM analysis

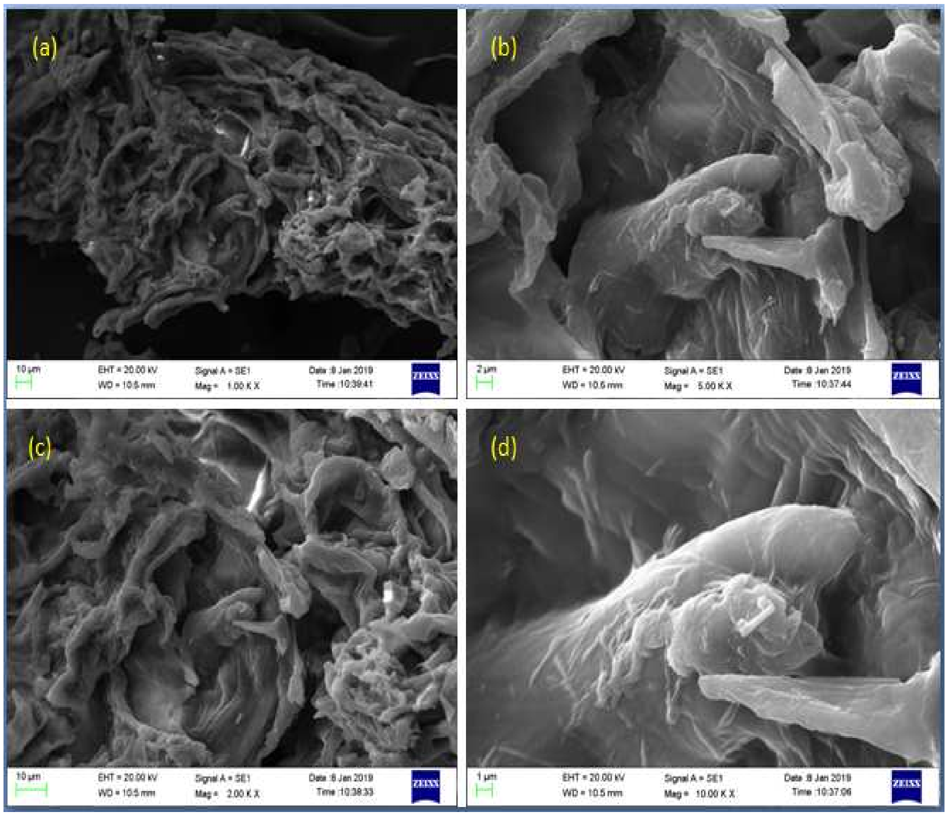

Fig.3: SEM Analysis of orange peel

Figure 3 depicts the SEM analysis of orange peel before adsorption at different resolution which depicts that the surface of orange peel is highly mesoporous and the biomass surface is seen to be irregular and porous empowering large interface for the biosorption.

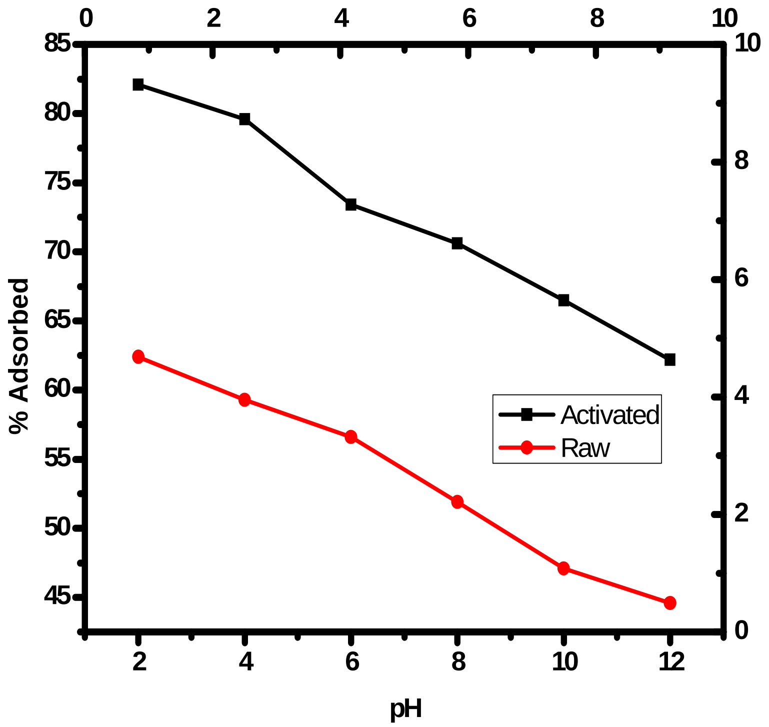

Fig.4: Effect of pH on biosorption of arsenic (III) with untreated and treated orange peel

Fig.4 represents the effect of pH on treated and untreated biomass which shows that the acid treated shows better result in comparison to raw biosorbent. Because of the presence of the larger number of sorption sites at onset of process, a rapid uptake rate of As(III) ions was found at the initial stage.

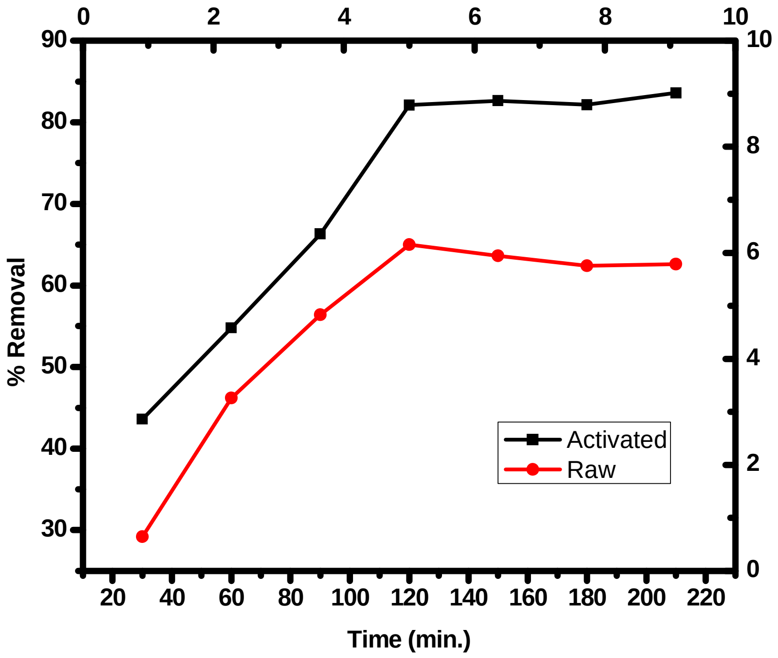

Fig.5: Effect of contact time on biosorption of arsenic (III) with untreated and treated orange peel

Figure 5 depicts the effect of contact time on treated as well as on untreated biomass which shows that the acid treated shows better result than untreated biomass. Contact time plays a major role in biosorption phenomenon. Initially the biosorption was rapid from 30 to 120 minutes and after 120 minutes equilibrium was achieved due to saturation of active sites.

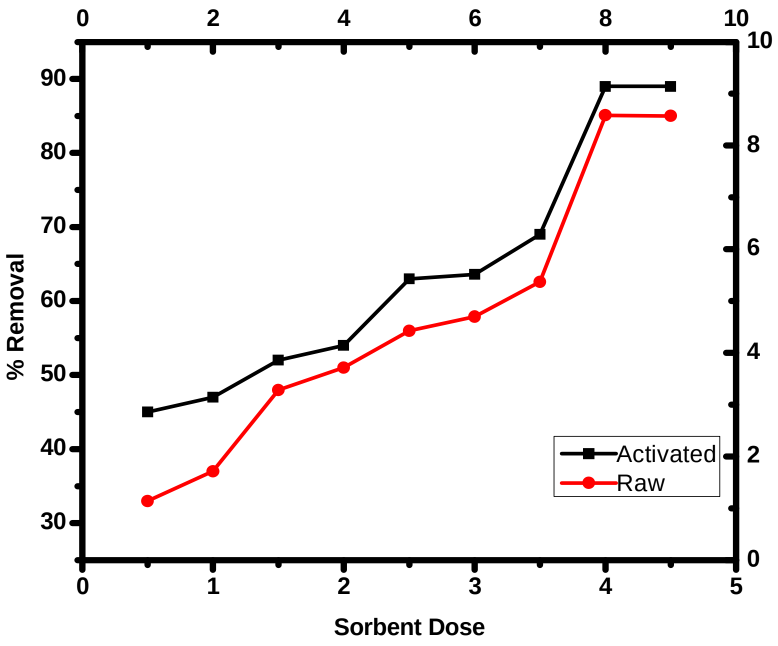

Fig.6: Effect of sorbent dose on biosorption of arsenic (III) with untreated and treated orange peel

Figure 6 represents the effects of sorbent dose on biosorption of As (III) with chemically treated as well as untreated orange peel. Finally the better result was obtained at 4g due to filling of active sites.

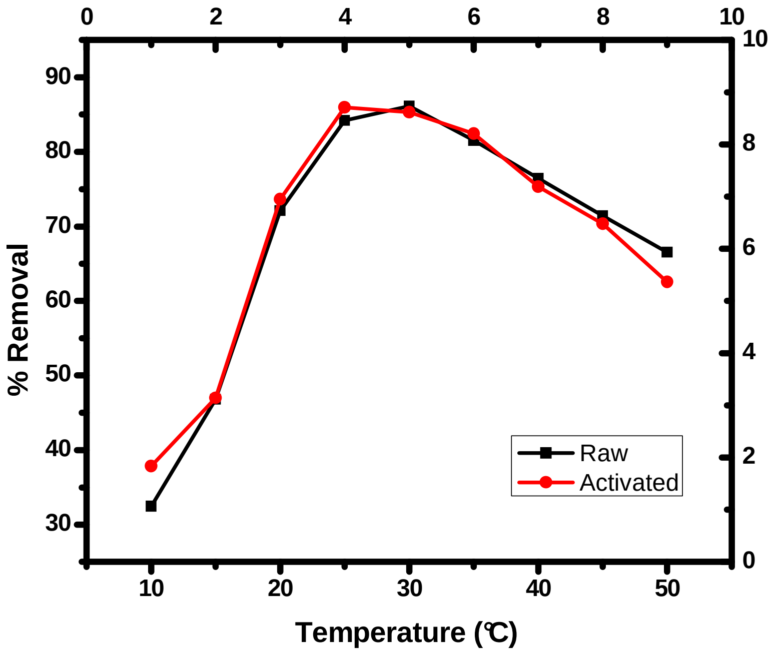

Fig.7 Effect of Temperature

By evaluating the temperature at different temperatures we are going to know what changes occurs during biosorption. With increment in the temperature, the removal of As (III) increases upto 30˚C as well as after 30˚C it starts decreasing because of the breaking down of As (III) ion bond on biomass surface (orange peel) at high temperature for raw orange peel and the maximum removal were shown at 25˚C for activated orange peel. The temperature of sorption medium is very essential for an energy dependent mechanism in the field of biosorption.

Adsorption Isotherms:
The isotherm studies were done at temperature 30, 40 and 50 ˚C by varying the initial arsenic concentration from 50 to 200ppm as well as the experimental data were utilized for fitting into commonly used Freundlich and Langmuir Isotherms to fit the suitable model for the better approximation of adsorption mechanism which can be used in designing the field applications.

Langmuir Isotherm: This isotherm is used to describe gas-solid phase adsorption as well as is also used to quantify and contrast the adsorptive capacity of different adsorbents. Langmuir isotherm accounts for the surface coverage by balancing the relative rates of adsorption and desorption (dynamic equilibrium). Adsorption is proportional to the fraction of the surface of the adsorbent that is open while desorption is proportional to the fraction of the adsorbent surface that is covered [9]. The linear form of this isotherm can be represented as

$$Ce/qe = 1/Q^0 b + Ce/ Q^0 \quad (3)$$

where Q^0 and b = Isotherm constant

The value of constant Q^0 as well as b were obtained from calculating the slope and intercept of plot Ce/qe vs Ce.

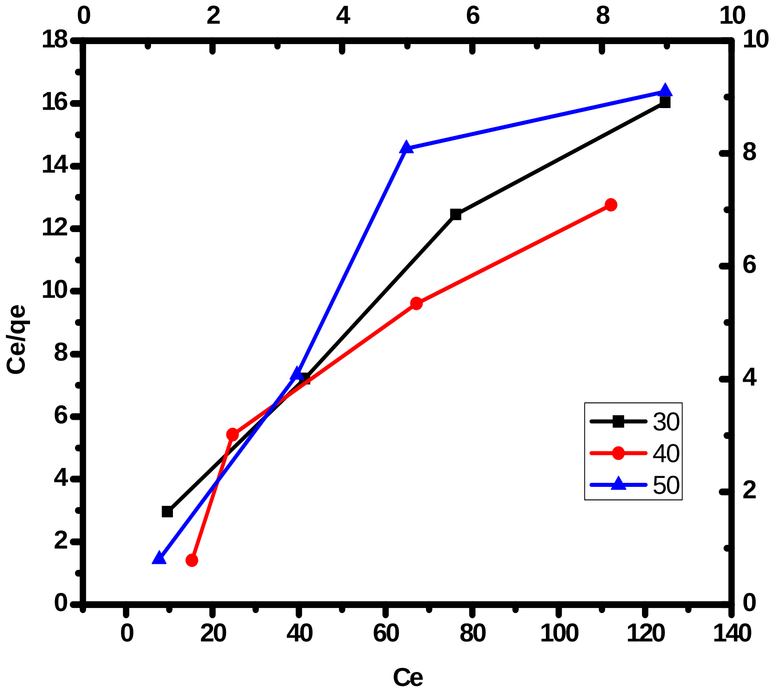

Fig.8: Langmuir Isotherm for raw orange peel

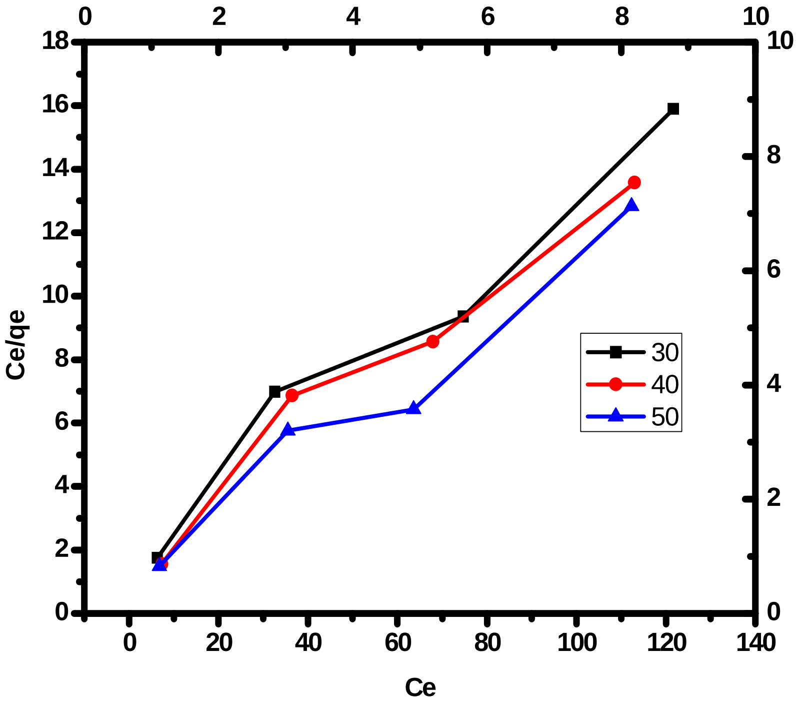

Fig.9: Langmuir Isotherm for activated orange peel

Table 5: Different values of Langmuir Isotherm

Isotherm	**Temperature**	**Intercept**	**Slope**	**R^2**
Langmuir (raw)	30	2.41308	0.11516	0.96
Langmuir (raw)	40	1.44583	0.10681	0.87
Langmuir (raw)	50	2.4058	0.12719	0.76
Langmuir (activated)	30	1.78457	0.1141	0.945
Langmuir (activated)	40	1.59348	0.10707	0.943
Langmuir (activated)	50	1.06058	0.10208	0.91

From the above table it was found that maximum R^2 value was found to be 0.96 and 0.945 for raw and activated biosorbent at 30 ° C .

Freundlich Isotherm. This isotherm can explain adsorption at heterogeneous surface. The linear plot of Freundlich isotherm at different temperature for adsorption of As (III) onto orange peel is shown in the figure below. Freundlich parameters n and kf were calculated from the slope and intercept respectively [8]. Linear form if this isotherm were written as

$$Ce/qe= \log k_f +1/n \log Ce \qquad (4)$$

where, k_f and n= Isotherm constant

The value of constant k_f as well as n were obtained from calculating the slope and intercept of plot log Ce vs log qe.

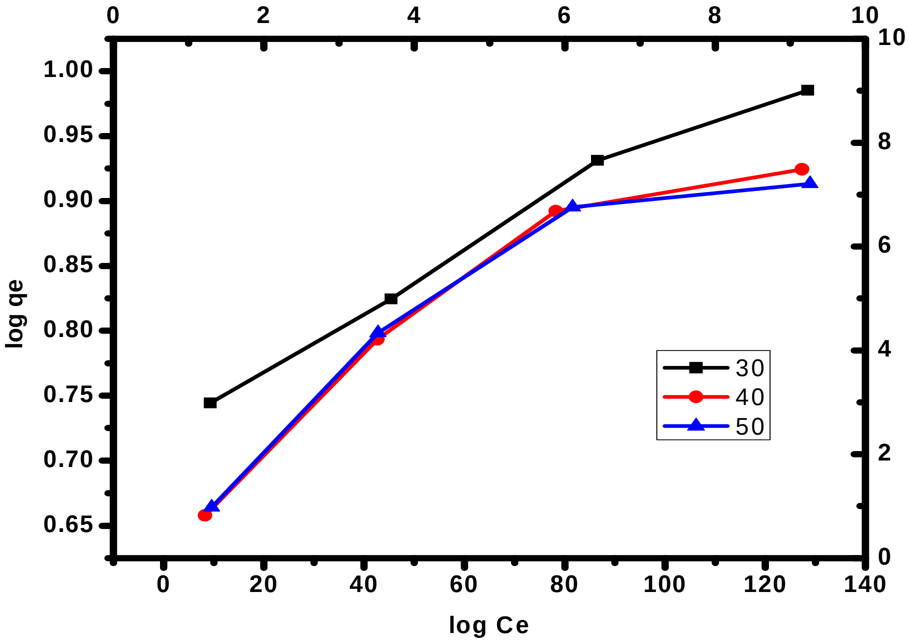

Fig.10: Freundlich Isotherm for raw orange peel

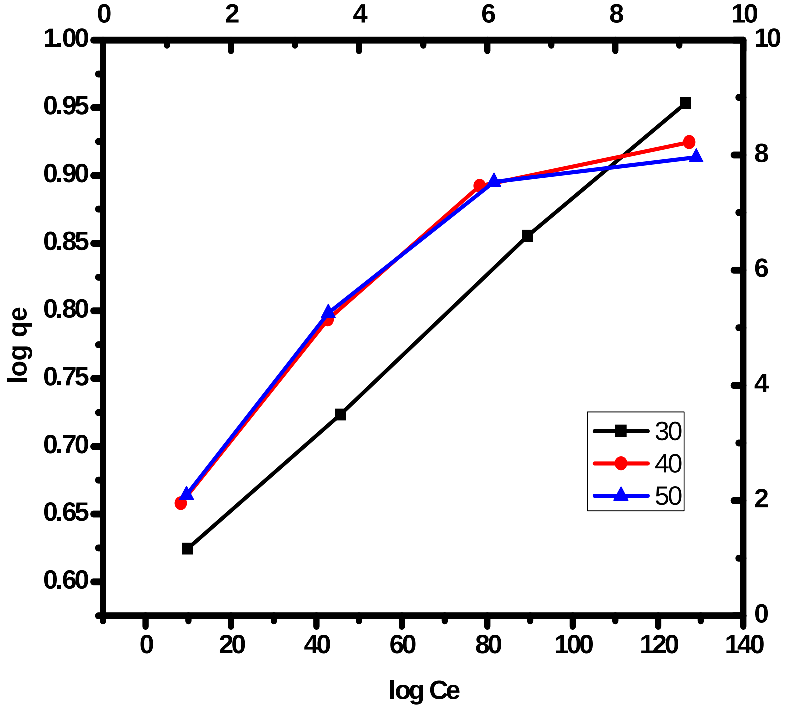

Fig.11:Freundlich Isotherm for activated orange peel

Table 6: Different values of Freundlich Isotherm

Isotherm	Temperature	Intercept	Slope	R^2
Freundlich (raw)	30	0.73156	0.00207	0.97
Freundlich (raw)	40	0.67479	0.00222	0.88
Freundlich (raw)	50	0.68247	0.00206	0.83
Freundlich (activated)	30	0.59614	0.00284	0.99
Freundlich (activated)	40	0.67479	0.00222	0.83
Freundlich (activated)	50	0.68247	0.00206	0.79

From the above table it was found that maximum R^2 value was found to be 0.97 and 0.99 for raw and activated peel at 30 ˚ C.

Table.7: Thermodynamic study of orange peel powder at temperature 30˚C, 40˚C, 50˚C at same ppm i.e 50ppm.

Temperature	**ΔG**	**ΔH**	**ΔS**
30˚	855.42	2.587	-8.870
40˚	1551.547		
50˚	2332.271		

ΔH= 2.587 is positive and the reaction is endothermic in nature.
ΔS= -8.870 is negative which reveals that the randomness decreases at the solid/liquid interface during the adsorption onto the orange peel.
ΔG= 855.42, 1551.547, 2332.271 as well as the reaction is non-spontaneous in nature.

5. Conclusion

From the above comparative study we concluded that the use of activated orange peel shows better result as compared to the raw peel. The Fourier Transformed Infrared Spectroscopy depicts that the surface of biosorbent holds more functional groups on activated peel as compared to the raw peel. The removal efficiency was found to be 86.3% and 87% for raw and activated peel. The Freundlich Isotherm (R^2 =97.45 and 99.8) was found to be better fit over Langmuir Isotherm (R^2 =96.33 and 94.5) for raw and chemically activated orange peel. Thus chemically activated orange peel was found to be an effective as well as efficient for the removal of arsenite from wastewater.

Acknowledgement

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Biographical notes

Priyanka Yadav received B. Tech and M. Tech.from NIET Gr. Noida and ILM CET, Gr. Noida, India in 2017 and 2020 respectively. During her graduation, she carried her project from Delhi Technological University with the project entitled "Synthesis and characterization of pectin based natural hydroge"l and she had done her masters project from IIT BHU Varanasi with project entitled “Biosorption of arsenite with raw and chemically activated orange peel”. She was selected for a post of research assistant at IIT BHU Varanasi with the UPCST funded project entitled "Flow and Segregation of Granular materials out of hoppers with two and three-dimensional devices." She had individually filed a patent on "Hoppers with repulsion tubes". She was awarded 1st position in National Seminar on recent advances in chemical sciences with reference to energy security and environmental safety held in Kanpur. She is also a member of BRSI (Biological Research Society, India).

Mr. Vikas Chandra Gupta is currently working as Assistant Professor (Biotechnology) at IILM-CET, Greater Noida. He graduated in Biotechnology engineering with distinction in his M.Tech- Biotechnology (Major in Industrial Waste Management) and B.Tech-Biotechnology (Specialization in Microbial Process Engineering) and is currently pursuing his doctoral studies (from AKTU, Lucknow) on various agricultural biomass for its potential to be used as a feedstock for ethanol production. Apart from his doctoral research Mr. Gupta has also established his industrial research interest in the domain of soilless (Hydroponics) cultivation of pollution-free agriculture produce at the Department of Biotechnology and has been actively working on a various government-funded research project in the hydroponics and lignocellulosic biofuels research domain at present. Mr. Gupta has been appointed as Member (Reviewer) of the editorial board of the Journal of Agricultural Research recently. Along with his academic and research credential he is also involved in various administrative roles such as Coordinator-M.Tech. (BT), Lab I/c-Microbiology and Fermentation Technology, In-charge- NBA-SAR Criterion 6, Member of organizing committee of BIOGENESIS, Member-Disciplinary committee, Techfest, and Sports fest, etc.