Sindh Univ. Res. Jour. (Sci. Ser.) Vol.43 (1) 97-104 (2011)

SINDH UNIVERSITY RESEARCH JOURNAL (SCIENCE SERIES)

Utilization Of Tea Waste For The Removal Of Arsenic (III) From Aqueous Solution

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Received 22nd April 2011 and Revised 30th May 2011

Abstract: Water contaminated with arsenic causes severe health hazard. Arsenic is found in the ground water of various provinces of Pakistan including Sindh and Punjab. Arsenic containing more than tolerable limits in ground water requires proper treatment before use. In the present study tea waste was used as adsorbents for removing arsenic from aqueous solution and found successful. Various parameters i-e shaking time, pH, shaking speed, temperature, adsorbent dose, adsorbate concentration were studied. The maximum sorption percentage 92.5 % of arsenic onto the tea waste was found at pH 7.0, shaking time 100 minutes, shaking speed 150 rpm, temperature 25 ^{0}C, adsorbent dose 1.0 gm and adsorbate concentration 10 ppm. Tea waste showed good efficiency when compared to other various biosorbents already used for arsenic removal.

Keywords: tea waste, isotherms, arsenic (III)

INTRODUCTION

The arsenic discovery in ground waters from many parts of the world has warned the use as a source of drinking water. Different factors such as man made activities, geochemical reactions; biological actions facilitate to activate arsenic into ground waters. There are also some non anthropogenic conditions which cause arsenic problem in drinking water. Fossil fuels combustion, activities of mining practices, pesticides containing arsenic, herbicides and arsenic use in the feed of livestock and other uses give birth to various effects (Dinesh Mohan *et al.,* 2007). Arsenic occurs in the oxidation state of -3, 0, +3 and + 5. Arsenic occurs in ground water mostly in the form As (III) which is called as arsenite and As (V) which is called as arsenate. Under oxidizing conditions (aerated surface water), the arsenite can be converted into arsenate and under reducing conditions (anaerobic ground water); the arsenate can be converted into arsenite. (Malana, *et al.,* 2011).

In Pakistan, especially in the province of Punjab and Sindh, the presence of arsenic in drinking water systems and subsurface aquifers is potentially dangerous human health hazards. Various subsurface aquifers and tube wells are polluted with intolerable limits of arsenic. The tolerable limit of arsenic is 10 ppb as recommended by WHO. It is reported by PCRWR and UNICEF that arsenic contamination level lies in the range between 10 to 200 µg/Litre especially in ground water of different regions of Punjab province which poses serious threats to the people of the Punjab. In Sindh, the arsenic contaminated water is reported in various districts including Sukkur, Khairpur, Jacobabad, Dadu, Thatta, Sanghar, Tando Allahyar, and Jamshoro. The concentration of arsenic in these districts is more than the prescribed value.

The exposure of arsenic to human body may be the consumption of arsenic contaminated waters, inhalation and skin absorption of arsenic at work such as mining and other industrial activities.Various diseases are caused by consuming arsenic contaminated water such as cancers, internal malignancies, non malignant skin alterations, vascular diseases (Zhang *et al.,* 2003). Other serious health effects of arsenic are disturbances in skin, heart disruptions, and damage of brain, damage of DNA, nerve injury and skin pigmentation. Many scientists and researchers have worked in this area such as preparation of adsorbents from various waste materials such as rice husk (Ranjan *et al.,* 2009), iron ores (Zhang *et al.,* 2004) and waste tea leaves. (Mamisahebei, *et al.,* 2007).

In the present study, for arsenic removal, an economical adsorbent was prepared by using waste tea and optimizing operating parameters such as pH, shaking time, shaking speed, adsorbent dose and adsorbate concentration. The adsorbents were investigated in order to check As (III) sorption. Adsorption isotherms such as Langmuir and Freundlich were also applied.

MATERIALS AND METHOD

Adsorbent prepared from tea waste:

After preparation of tea, the waste is discarded, the waste of Lipton brand was used for the preparation of adsorbent as **(Fig.1)**.

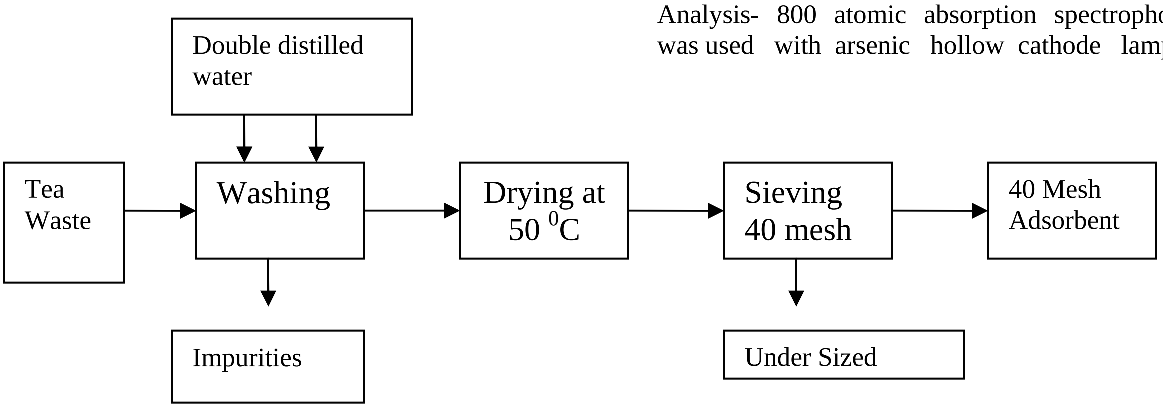

Fig. 1: Preparation of adsorbent from Tea waste

The waste tea distilled water up to three times in order to remove the foreign materials and colors. The washed waste tea was oven dried at 50 ^{0}C for 24 hours. The sample was sieved and retained on the mesh 40 and used for the sorption process.

Standards and reagents Preparation

In this study all analytical grade chemicals were used. For preparation of standards deionised double distilled water was used. Stock solution 1000 mg/ litre of As (III) was made for the experiments. 1.320 grams of As_2O_3 (Sigma Aldrich) was dissolved in approximately 10 mL of NaOH solution of 5 M, then nitric acid was used to neutralize the solution and finally the 1000 mL volumetric bottle filled up to 1000 ml with deionised double distilled water to give 1000 mg/L of stock solution of arsenic. 2.5 grams NaOH and 2.0 grams of $NaBH_4$ were dissolved in deionised distilled water to make 500 ml $NaBH_4$ solution. 5 M HCl was made with 208.33 ml of concentrated HCl diluted to 500 ml. The different pH buffers were made, those include pH (2-3), (4-6) and (7-10). These were made by mixing appropriate volume of 0.1 M solution of HCl- KCl, CH_3COONa and H_3BO_3-NaOH respectively.

Batch sorption experiments

Experiments of adsorption were done for investigating tea waste potential for arsenic removal, initially, pH(1-10) effect on the removal percentage was checked, then more experiments were done to analyze the effect of shaking time, shaking speed, temperature, adsorbent dose and adsorbate concentration by using the optimized pH.

Analysis of arsenic in aqueous system

For analysis of samples, Perkin Elmer A Analysis- 800 atomic absorption spectrophotometer was used with arsenic hollow cathode lamp set on m, with current of 18 mA and slit lene 98 % instrument grade was used and maintained at 2.2 Liters/minute, for generation of flame in atomic absorption spectrophotometer, 0.9 kg/cm^2 pressure was set simultaneously, air (compressed) was used and flow maintained at 17.0 Liter/minute and pressure at 3.5 kg/cm^2. For hydride generation, a continuous hydride generator unit was linked with AAS. Nitrogen gas was used as sample carrier. The calibration of instrument was made of 1, 5, 10 and 15ppm. For further investigation of samples, dilution of samples was done till calibration range results were achieved. Every sample was tested three times and the results were obtained in averages.

RESULTS AND DISCUSSION

Effect of pH

This parameter is very important because it influences electrostatic binding of ions to corresponding metal groups. It provides a suitable adsorbent surface charge for the sorption to take place. The pH effect on As (III) sorption by tea waste was

i-e non-ionic (H_3AsO_3) in the range of pH 2 to 9 and anionic ($H_2AsO_3^-$) from10 to 12 respectively. As (III) adsorption onto the waste tea was observed continuously increasing from pH range between 2 to 5 and there after the increment in removal occurs quickly ultimately reached at greatest point when pH 7.0 is kept and then consequently in adsorption density quick reduction occurred. When pH was 7 then optimum removal occurred because at this stage there is presence of neutral species H_3AsO_3 only and in the adsorption process there may be possibility of different unspecified reaction products endorsed. When the alkaline medium is kept, the surface is liable to attain negative charges and domination of negative charged $H_2AsO_3^-$ group starts. Adsorbent surface and adsorbate species affinity of this kind would increase continuously by pH increase resulting in slow but sure repulsive forces increment among the sorbate species and the surface which ultimately results the decrement of the As (III) adsorption.

0.1 gm of tea waste adsorbent was agitated with 50 ml of 10 ppm sorbate at 100 rpm for 50 minutes, temperature was kept at 25 ^{0}C. It was observed that more sorption occurred at neutral conditions. Maximum sorption % of 74.7 was achieved at pH7, which is similar to previous work by researchers (Yan-Hua Xu *et al.*, 2002, Ranjan *et al.*, 200, C.H Niu *et al.*, 2007, Abbas Razaee *et al.*, 2008). In other experiments the pH7 was maintained.

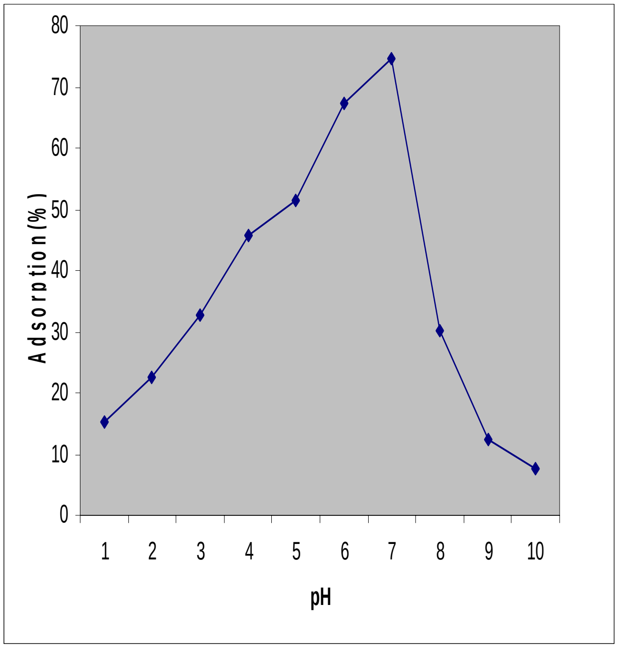

Fig. 2: Effect of pH on sorption of Arsenic onto the Tea Waste

Effect of Shaking Time

Shaking time in the adsorption process is also an essential. To optimize this parameter, various shaking times effect (25-175 minutes) was studied in order to check the arsenic sorption **(Fig. 3)** . In observations, the rate of adsorption of As (III) was noted to be improved when shaking time increased. The sharp rise is noted in amount of As (III) adsorbed by escalating the time from 25 minutes to 100 minutes, showing readily accessible sites presence in favor of rising of sorption of As (III) rate onto the sorbent. Finally, when time increased beyond 100 minutes, sorption removal remained nearly same. A maximum of 75.03% at 100 minutes was reported which meets with previous work (Mamisahebei *et al.*, 2007). After attaining the maximum level of adsorption, when the shaking time was further increased, rate of adsorption became constant up to end of experiments. This indicates that the adsorbent sites have become saturated and no more sorption would take place.

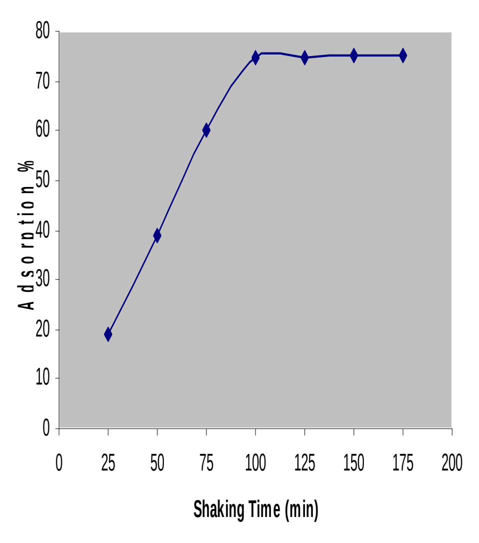

Fig. .3: Effect of shaking time on sorption of Arsenic onto the tea waste

Effect of Shaking Speed

Low, medium and high shaking speeds (50-300 rpm) were investigated to study the effect of shaking speed on sorption efficiency as shown in **(Fig .4.).** Noticeable and rapid increase in rate of sorption was noted when speed of shaking enhanced from 50 to 100 rpm. The justification of this fact may be given in a way that when shaking speed is increased then boundary layer resistance to mass transfer in bulk declines as well as for As (III) ions driving force increased. Therefore, film diffusion does not principally control an adsorption process overall. It was observed in addition that no major increment is noted in adsorption with further increase in shaking speed. The maximum sorption of 76.24 % was achieved at 150 rpm which is same as previously reported (Mamisahebei *et al.*, 2007, Razaee *et al.*, 2008).

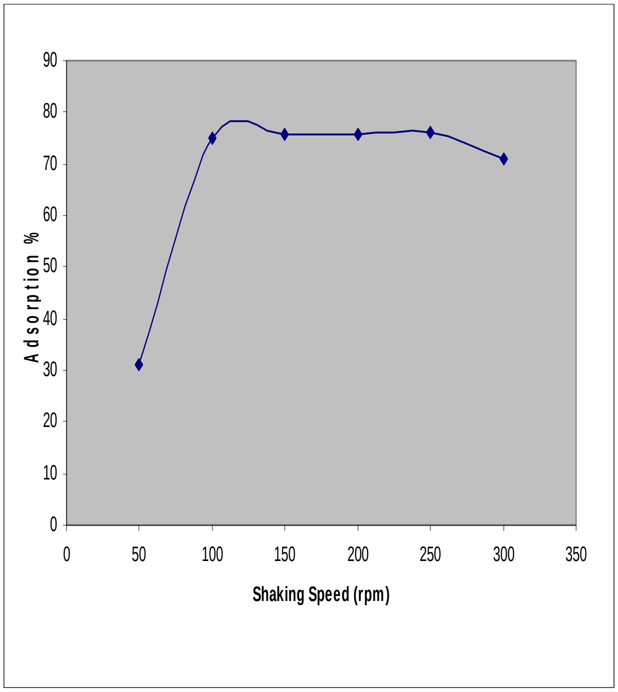

Fig. 4: Effect of shaking speed on sorption of Arsenic onto the tea waste

Temperature Effect

The temperatures effect (20, 25 and 30 ^{0}C) on sorption of arsenic onto the tea waste was studied at optimized conditions **(Fig. 5),** Rapid increment in sorption was observed as the rise of temperature from 20 ^{0}C and reached at maximum at 25 ^{0}C. When the temperature increases, the rate of adsorption decreased rapidly. This trend shows the nature of As (III) adsorption is an exothermic process. The maximum sorption of 76.24 % was achieved at 25 ^{0}C. Results obtained in this studies matches the previous work in which the maximum sorption of arsenic is achieved at the temperature range of 25 to 30 ^{0}C (Ranjan *et al.*, 2009, Abbas Razaee *et al.*, 2008).

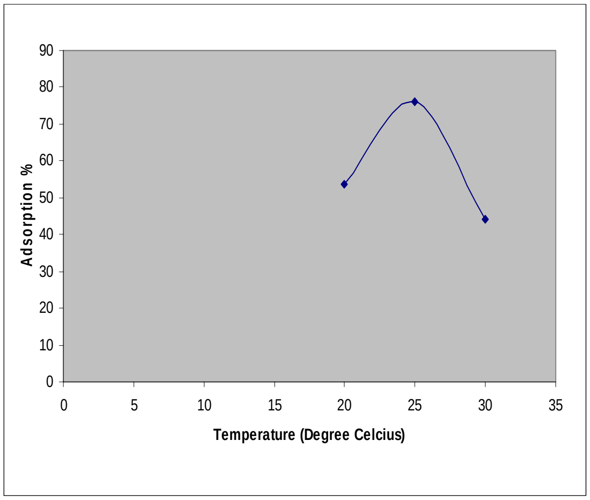

Fig..5: Temperature Effect on sorption of Arsenic on to Tea Waste

Effect of Adsorbent Dosage

For the effective sorption, the amount of sorbent is very important factor to be considered. **(Fig.6)** shows adsorbent dosage effect on arsenic sorption % onto tea waste. Varying adsorbent amount ranging from 0.1, 0.25, 0.50, 0.75 and 1.0 gm were used for the sorption of arsenic. Initially increment in As (III) sorption % was observed rapidly as the adsorbent dosage increased. As dosage of adsorbent rises, adsorbent speck number raise as well, and which for adsorption to take place create larger accessibility of exchangeable spot. Other investigators have as well found similar observations (Yan-Hua Xu *et al.*, 2002, Mamisahebei *et al.*, 2007, Razaee *et al.*, 2008). Maximum sorption of arsenic 92.5% was achieved when 1 gm of adsorbent was used.

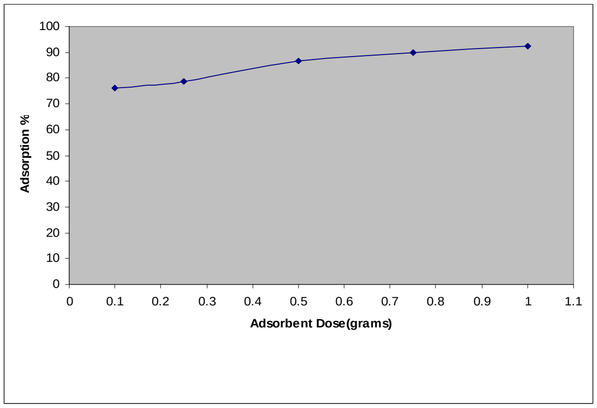

Fig. .6: Adsorbent Dosage Effect on Arsenic sorption onto the Waste Tea

Effect of Adsorbate Concentration

Sorbate concentrations of 1, 5, 10 and 15 ppm was shaked with 1.0 gm sorbent to see the sorption efficiency as shown in **(Fig.7).**

With increment of initial metal ion concentration, As (III) uptake onto tea waste was noted to be increased. Reason of this is, from solutions of higher concentrations, quantity of ions adsorbed is more than removed from solution of less concentration. It is shown in figure 7 that as sorbate concentration increased the percentage removal of arsenic increased rapidly and the highest sorption of 92.5% was achieved at 10 ppm concentrations of sorbate. As compared to previous research, the result obtained is slightly matching with earlier work conducted by researchers (Ranjan, *et al.*, 2009).

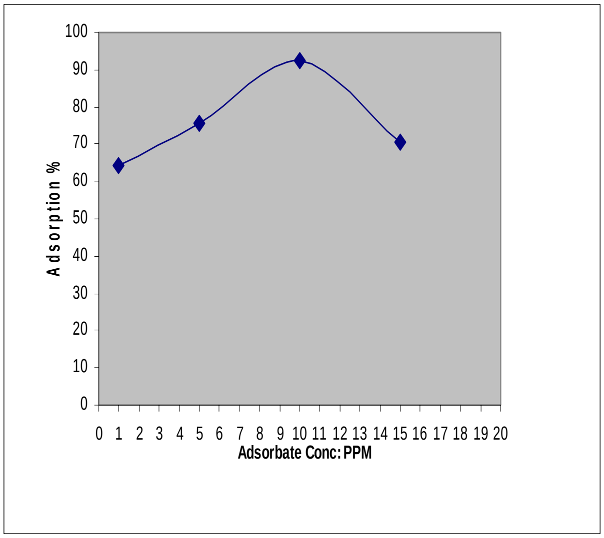

Fig .7: Effect of Adsorbate Concentration on sorption of Arsenic onto the Tea Waste

Adsorption Isotherms

Many different isotherms of adsorption are there but the most important are freundlich and Langmuir. These isotherms are very essential to study the bond between the ions of metal and adsorbent. These two isotherms are analyzed in present study. The equation of Langmuir for this study is selected as under:

$$\frac{1}{qe} = \left(\frac{1}{Qob}\right)\frac{1}{Ce} + \frac{1}{Qo}$$

Where qe is called as metal ions quantity adsorbed per unit mass of adsorbent (mg/g), Ce is the arsenic concentration at equilibrium (mg/l), Qo is measure of adsorbent capacity (mg/g), b is constant of Langmuir.

The data which was obtained by experimentation were fitted in the equation of Langmuir in order to plot Ce/qe against Ce. The value of Qo is calculated as 6.402 mg/g and that of b is 0.1562. The value of R^2 was also found which is **0**.9636. This value of R^2 indicates that adsorption is monolayer on tea waste. The values of R_L which is called as separation factor were also calculated by using equation as below:

$$R_L = \frac{1}{1+bCo}$$

Where, Ce is the concentration in mg/l of arsenic initially, b is constant of Langmuir.

The factor of separation is calculated in this study at various concentrations of arsenic. The obtained values of $R_L$are in the range of 0.2991 to 0.8649. These values of factor of separation show that adsorption is of favorable. So far as Freundlich isotherm is concerned, it gives the adsorption of multilayer which is appropriate for the surfaces of heterogeneous. The equation of Freundlich used in this study is as below:

$$\log qe = logkf + \frac{1}{n}\ logCe$$

In above equation, kf is called adsorption capacity while 1/n is known as the intensity of adsorption. All the data obtained in the experimentation were fitted in the model. The value of R_2 is found as 0.9797. The values of 1/n and k_f were calculated from the slope and intercept. 1/n value is 0.2593 while the value of k_f is 4.7424.

The value of 1/n is less than 1, indicates more adsorption. In figure .8 and .9 these two models are shown. It was noted that the data obtained from sorption experimentation fitted as satisfactory in both the models. But the calculated values of coefficient of regression show that Freundlich is better fitted with data as compared to Langmuir.

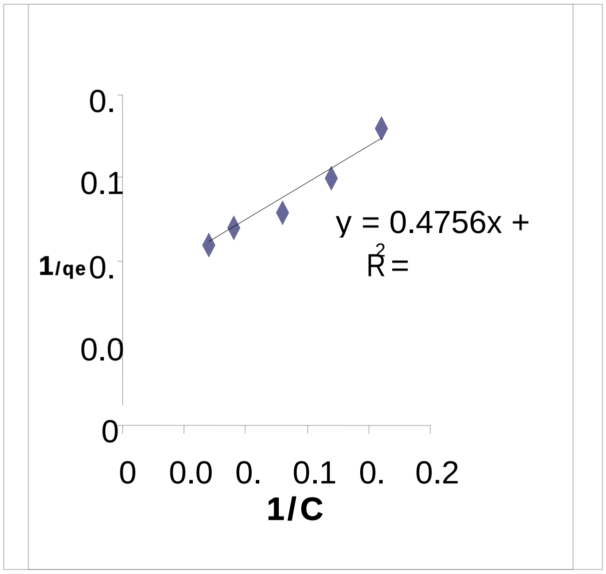

Fig.: 8 Langmuir Isotherm Model Graph of 1/Ce vs 1/qe

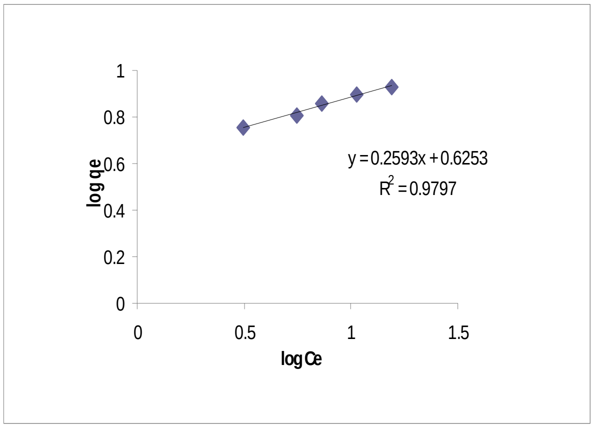

Fig.: .9 Freundlich Isotherm Model Graph of log Ce vs log qe

Table: .1 Langmuir and Freundlich constants and coefficients

Tempe rature ºC	Q_o mg/g	b	R^2	k_f mg/g	1/n	R^2
25	6.402	0. 1562	0.9636	4.7424	0.2593	0.9797

Comparison with other Adsorbents

In **(Table .2)**, the capacities of different adsorbents are shown. When the comparison of capacities is made between various adsorbents for remediation of arsenic, it was noted that present adsorbent has more capacity than some other adsorbents.

CONCLUSION

It was concluded that adsorbent prepared from tea waste has good potential for the arsenic removal when the comparison is made with adsorbents. It was noticed that arsenic adsorption onto the tea waste adsorbent is highly dependent on pH. From the observations, it was noted, as increment in adsorbate concentration increased arsenic sorption, and it reduces when the temperature is increased. The optimum arsenic removal was noted as 92.5 % at pH 7, shaking time 100 minutes, shaking speed 150 rpm, temperature 25^{0}C, adsorbent dose 1.0 gm and 50 ml adsorbate concentration 10 ppm. The data of equilibrium sorption was feasible to both Langmuir as well as Freundlich isotherms, reporting capacities of 6.402 mg/g and 4.7424 mg/g correspondingly.

Table .2 Comparison of adsorption capacities of different adsorbents for Arsenic

Adsorbents	**Adsorption capacity Q_0(mg/g)**	**References**
Stem of Acacia nilotica	50.8 mg /g	Jameel A. Baig et al (2010)
Rice polish	0.138 mg/g	D. Ranjan et al (2009)
Saw dust of Picea abies	9.259 mg/g	M. Urik et al (2009)
Siderite-hematite filter	0.013 mg/g 16.2 mg/g	Huaming Guo et al (2008)
Macro fungus biomass (Inonotus hispidus).	51.9 mg/g	Ahmet Sari et al (2009)
Nanocrystalline TiO_2	3.93 mg/g	Chuanyong Jing et al (2009)
Orange waste get loaded with zirconium (IV)	130 mg/g	Biplob Kumar Biswas et al (2008)
Adsorbent made from Tea waste	**6.402 mg/g**	**Present Study**

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