



Removal of arsenic from aqueous solution using SiO₂ nanoparticles doped carbonized *Zygosaccharomyces bailli*

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Abstract: The present study involves the development of adsorbent containing silica oxide nanoparticles for arsenate removal using the reducing property of a novel yeast strain *Zygosaccharomyces bailli* (MTCC 8177) isolated from a tea fungus consortium. The yeast cells were harvested and subjected to carbonization at 400 °C for 1 hour and doped with silica oxide nanoparticles to improve its adsorbent properties. Batch adsorption studies were carried out using the carbonized yeast doped with silica nanoparticles (CYDSN). As(V) adsorption efficiency of CYDSN was deduced in batch mode by varying parameters like contact time, initial concentration, adsorbent dosage and pH. Equilibrium isotherms were analyzed by Langmuir, Freundlich and Temkin isotherms and the experimental data fitted well into these isotherms. Kinetics of the adsorption process was studied and it was fitted into the Langergren kinetic studies. The results indicated that CYDSN could be used as a viable and cost-effective adsorbent for As(V) removal from aqueous solution.

Keywords: *Zygosaccharomyces bailli*, As(V) removal, Doping, Silica oxide nanoparticles, Adsorption.

Introduction

Arsenic is a chemical element with the symbol As with the atomic number 33. Arsenic is all-pervasive and ranks 20th in natural abundance, comprising about 0.00005% of the earth's crust, 14th in the seawater, and 12th in the human body. It is a silver-grey brittle crystalline solid with atomic weight 74.9; specific gravity 5.73, melting point 817°C (at 28 atm), boiling point 613°C and vapor pressure 1mm Hg at 372°C. Since its isolation in 1250 A.D. by Albertus Magnus, this element has been a continuous center of controversy¹. From both the biological and the toxicological points of view, arsenic compounds can be classified into three major groups. These groups are inorganic arsenic compounds, organic arsenic compounds and arsine gas.

Arsenic exists in the -3, 0, +3 and +5 oxidation states. Environmental forms include arsenious acids, arsenic acids, arsenites, arsenates, methylarsenic acid, dimethylarsinic acid, arsine, etc. Arsenic (III) is a hard acid and preferentially complexes with oxides and nitrogen. Conversely, arsenic (V) behaves like a soft acid, forming complexes with sulfides. Inorganic forms of arsenic most often exist in water supplies². Pentavalent species predominate and are stable in oxygen rich aerobic environments. Trivalent arsenites predominate in moderately reducing anaerobic environments such as groundwater (N.N. Greenwood). It has been established that the toxicity of arsenic is dependent on its chemical form.

Arsenite is more toxic for biological systems than arsenate. As³⁺ is 4 to 10 times more soluble in water than As⁵⁺. However, the trivalent methylated arsenic species have been found to be more toxic than inorganic arsenic because they are more efficient at causing DNA breakdown. Although As⁵⁺ tends to be less toxic

compared to of As^{3+} , it is thermodynamically more stable due to it predominates under normal conditions and becomes the cause of major contaminant in ground water³.

The arsenic contamination of potable groundwater is a worldwide concern and poses a great threat to human health and condition. International concern has also focused on the problem of arsenic in groundwater in Bangladesh and Bengal, India because of the large scale of the population who are affected adversely by high arsenic concentrations. In Bengal, nearly 30 million people in the state are exposed to arsenic in the concentration range of 0.2-2.0 mg/L due to consumption of water for drinking purposes⁴. Clinical evidences of arsenic poisoning begin with various forms of skin disease and proceed via damage to internal organs ultimately to cancer and death. Arsenic contaminated water has led to hyperkeratosis, skin cancers and pigmentation of palm. A long term exposure to arsenic can cause skin, kidney, bladder cancer as well as neurological and cardiovascular problems. Due these clinical manifestations caused by arsenic contaminated water, World Health Organization (WHO) has recommended 0.01mg/L as maximum contaminant (MCL) in drinking water⁵.

Keeping in mind its clinical significance, extensive studies have been carried out for As(V) removal using various methods like precipitation, ion exchange and adsorption. Scientific evidences suggested that adsorption is an efficient method to control the mobility and the bioavailability of arsenic when compared to other methods. In recent times, plant and fungal biomass has been viewed as a potential biosorbent for removal of arsenic. The effect of physical and chemical pretreatment processes appeared to enhance the metal biosorption capacity of biosorbents⁶. Treatment of arsenic containing wastewater by activated carbon has been reported as effective technique for the removal of arsenic species. Activated carbon produced from conventional raw materials such as bituminous coal, peat and lignite is expensive. The commercially affordable carbon has a limited usage due to its expensiveness. This is a limitation for its usage in developing countries like India. Hence, there is a dire need in current times to find out a low non-conventional material for production of low cost activated carbon for water purification and wastewater treatment.

A novel effort was made in this present study, to dope silica nanoparticles with carbonized yeast, keeping all the above mentioned points in mind. The interaction of Si with yeast (*Zygosacchomycesbailli*) is directly related to the size and shape of the nanoparticles. Depending on the size of the nanoparticles, their applications branch out. The yeast culture, *Zygosacchomycesbailli*, was retrieved from Institute of Microbial Technology (IMTECH), Chandigarh, India where it has been identified and deposited as MTCC8177. MTCC is an affiliate member of the World Federation for Culture Collections (WFCC) and is registered with the World Data Centre for Microorganisms (WDCM).

Experiment chemical compound and organism used

Silica dioxide

Silicon dioxide, also known as silica, is a chemical compound that is a dioxide of silicon with the chemical formula SiO_2 .

Zygosacchomyces bailli

The yeast culture, *Zygosacchomyces bailli*, was retrieved from Institute of Microbial Technology (IMTECH), Chandigarh, India where it has been identified and deposited as MTCC8177. It has been isolated from a tea fungus consortium at Vadavalli, Coimbatore. MTCC is an affiliate member of the World Federation for Culture Collections (WFCC) and is registered with the World Data Centre for Microorganisms (WDCM).

Broth preparation

The biomass for the preparation of carbonized yeast (*Zygosacchomyces bailli*) was grown in the Yeast peptone dextrose (YPD) broth. Based on literature study, YPD was optimized and used for the biomass growth. The yeast strain (MTCC 8177) was retrieved and subcultured in the YPD broth.

Doping of carbonized yeast

The doping of carbonized yeast with silica nanoparticles was carried out⁷. In brief, a known quantity of carbonized yeast was treated with 100mL of 0.1M silica oxide solution and agitated in an orbital shaker at 125 rpm for 24 hours at room temperature. The silica oxide doped biosorbent was filtered and washed with distilled water and dried using a hot plate oven. The silica oxide doped carbonized yeast was stored and used for further analysis.

Batch adsorption studies

Batch biosorption experiments were carried out by agitating 1.0 g of the biosorbent with 50mL of As(V) solution of 1-5 mg/L concentration and pH at 125 rpm at room temperature. The samples were withdrawn at predetermined time intervals, the supernatant solution was separated from the adsorbent by centrifugation and the residual As(V) concentration was analyzed.

Adsorption isotherms

The prediction of the sorption rate of the pollutants onto the sorbent materials under various conditions is carried out by adsorption isotherms. From the data obtained in the batch mode studies the adsorption isotherms were determined. Isotherm studies were carried out to calculate the adsorption capacity, adsorption rate and type of adsorption. The Langmuir⁹, Freundlich¹⁰, Temkin isotherms, Lagergren first and second order kinetics were studied and the type of adsorption was determined.

Results and Discussion

Effect of contact time and initial ion concentration

Arsenic uptake increased with time and at some point of time reached a constant value where no more adsorbate was removed from the solution and the system was in a state of dynamic equilibrium. The equilibrium time increased with the increase in the initial concentration of the adsorbates studied.

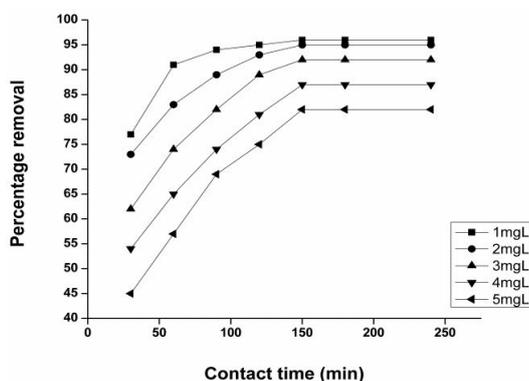


Figure 1: Effect of contact time and initial ion concentration on removal of As(V) from aqueous solution by CYDSN

Equilibrium time and adsorbate uptake varied with adsorbate concentration and adsorbent dosage. The adsorption of arsenic on CYDSN was also studied as a function of contact time in order to find out the equilibrium time for maximum adsorption. The results showed that equilibrium time required for the adsorption of arsenic ranged from 150 to 240 minutes.

Effect of adsorbent dosage

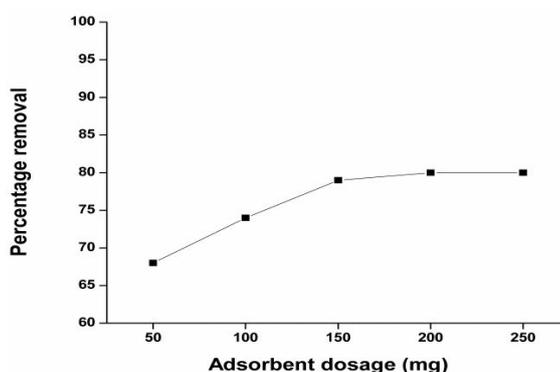


Figure 2: Effect of adsorbent dosage on removal of As(V) from aqueous solution by CYDSN pH:7; Temperature: 30 °C

The As(V) solutions were treated with different dosages of adsorbent (50 to 250mg/50 mL of adsorbate). The results revealed that increase in adsorbent dosage increased the percent removal and either reached a constant value or showed a very low removal after a particular dosage level. The optimum dosage level was fixed and used for further studies. The optimum adsorbent dosage for As(V) was 100mg/50 mL. Availability of more surface area of the adsorbent could be the reason for increase in percent removal of adsorbate with the increase in adsorbent dosage. Similar results were obtained¹¹ in batch adsorption studies.

Effect of pH

The pH of the solution has a significant influence on the adsorption of the released charged groups onto the adsorbent surface¹². In any adsorbate-adsorbent system, pH effects the nature of the surface charge of the adsorbent and speciation of adsorbate and hence the extent of adsorption¹³. The pH of the dye solution plays an important role in the adsorption process, particularly on adsorption capacity. The q_e was found to be maximum at the natural pH of the arsenic solution (pH=7).

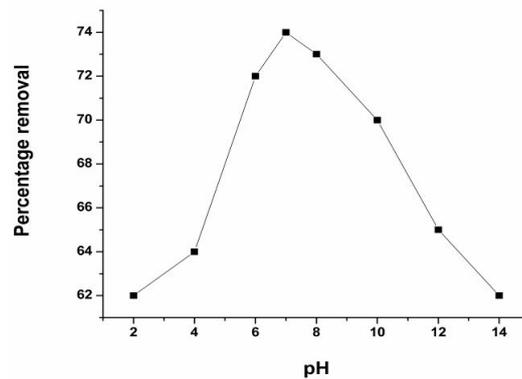


Figure 3: Effect of pH on removal of As (V) from aqueous solution by CYDSN Adsorbent dosage: 100mg/50mL; Temperature: 30 °C

The observed low adsorption rate of arsenic on the CYDSN at pH<9 may be because the surface charge becomes positively charged, thus making (H^+) ions compete effectively with As(V) causing a decrease in the amount of adsorbate adsorbed. The electrical charge of surface of the surface group may also enhance or hinder the adsorption of the target molecules on the nanoparticle surface. The As(V) percentage removal versus time curve is single and continuous leading to saturation, suggesting the possibility of monolayer coverage of arsenic on the outer surface of the adsorbent. Although the percentage removal decreased with an increase in initial adsorbate concentration, the actual amount of adsorbate adsorbed per unit mass of adsorbent increased with increase in adsorbate concentration in aqueous solution.

Adsorption Isotherm study

Langmuir isotherm

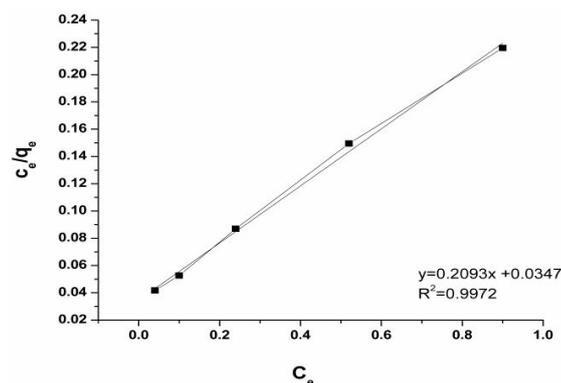


Figure 4: Langmuir plot for arsenic removal from aqueous solution: Adsorbent dosage: 100mg/50mL pH:7; Temperature: 30 °C

The Langmuir model is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. The Langmuir isotherm is given by: $C_e/q_e = 1/(Q_0*b) + C_e/Q_0$

The constants in the Langmuir isotherm are Q_0 and b . Q_0 indicates the maximum adsorption capacity of the adsorbent and b is the binding energy between the adsorbent and adsorbate. From the graph $Q_0 = 4.77$ mg/g and $b = 6.03$ L/mg. from the plot we observe that the isotherm data fits the Langmuir equation well ($R^2=0.9972$). In the present study it was observed that R_L values ranged from 0.01 to 0.15. The R_L values of the adsorbent used in the present study were always less than one and more than zero indicating the favorable adsorption of arsenic by the adsorbent.

Freundlich isotherm

The Freundlich isotherm model is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved. The logarithmic form of the equation is: $\ln q_e = \ln K_f + (1/n)\ln C_e$

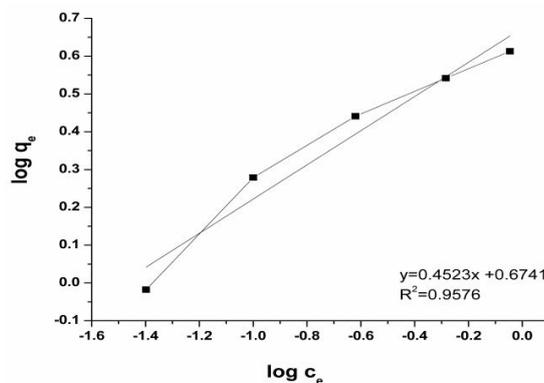


Figure 5: Freundlich plot for arsenic removal from aqueous solution: Adsorbent dosage: 100mg/50mL pH:7; Temperature: 30 °C

where K_f and n are the Freundlich constants, the characteristics of the system. K_f and n are the indicators of the adsorption capacity and adsorption intensity, respectively. The ability of Freundlich model to fit the experimental data was examined. The Freundlich constants K_f and n were found to be 1.96 and 2.21 respectively. The n value was found high enough for separation ($1 < n < 10$). The Freundlich isotherm is more widely used but provides no information on the monolayer adsorption capacity in contrast to the Langmuir model. Freundlich isotherm fitted well with the correlation coefficient of 0.9576.

Temkin isotherm

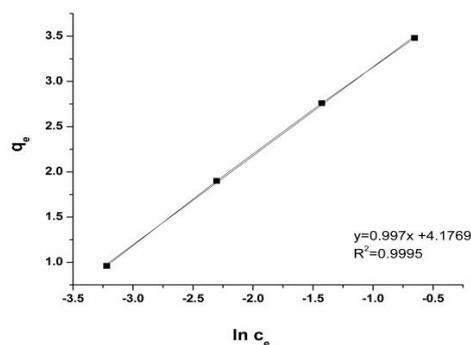


Figure 6: Temkin plot for arsenic removal from aqueous solution: Adsorbent dosage: 100mg/50mL pH:7; Temperature: 30 °C

A linear form of the Temkin isotherm can be expressed as: $q_e = (RT/b) \ln A + (RT/b) \ln C_e$

where A and B are the Temkin constants. Therefore a plot of q_e versus $\ln C_e$ enables one to determine the constants A and B. The isotherm model and its linear form are shown. The A and B constants were determined to be 3.11 and 0.997 kJ/mol. Temkin isotherm fitted well with the correlation coefficient of 0.9995.

Kinetic studies

1. First order rate kinetics

The integrated pseudo first order equation is represented by

$$\log (q_e - q_t) = \log q_e - (k_1 * t) / 2.303$$

where q_e and q_t are the adsorption capacities at equilibrium and at time t respectively and k_1 is the pseudo first order rate constant.

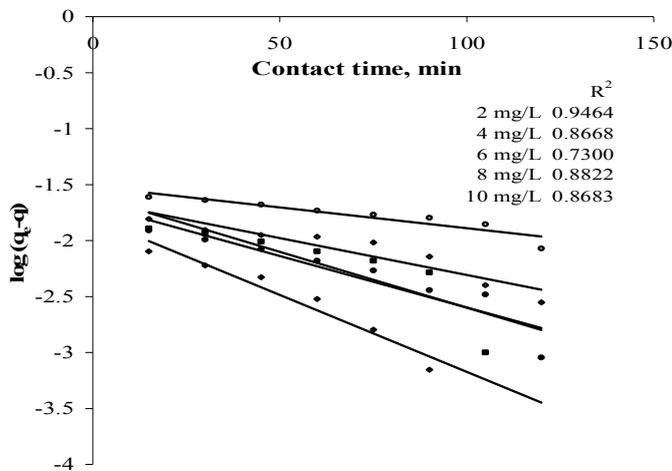


Figure 7: Lagergren first order kinetics

The linear plot of $\log (q_e - q_t)$ versus t was found not to be suitable as the calculated q_e value was different from the experimental q_e values obtained. The adsorption kinetics do not follow the Lagergren model.

2. Second order rate kinetics

The integrated form of pseudo second order kinetic rate equation is expressed as:

$$t / q_t = (1 / q_e^2 k_2) + t / q_e$$

where k_2 is the rate constant of pseudo second order adsorption.

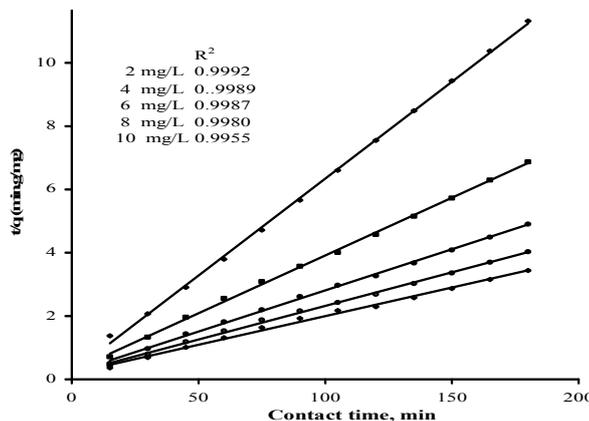


Figure 8: Pseudo second order kinetics

The plot of (t/q_e) versus t gave a linear relationship from which q_e has been determined from the plot which has been presented in the above table. The theoretical q_e as calculated using the second order rate equation were fitted perfectly with the experimental q_e values as determined by the kinetic plots having R^2 value near 0.99.

Hence, the adsorption kinetics for this experiment follows pseudo second order kinetics.

Conclusion

The doping of carbonized yeast was prepared using the cultural supernatants of a commonly used yeast, *Zygosaccharomyces bailli* (MTCC 8177). From the kinetic studies, it is observed that adsorption of As(III) is very rapid in the initial stage and decreases while approaching equilibrium. The equilibrium time increased with initial As(V) concentration. The percentage removal of As(V) increases with the increased in adsorbent dosage and decreased with increase in initial As(V) concentration. Experimental results are in good agreement with Langmuir, Freundlich and Temkin adsorption isotherm models, and have shown a good fitting to the experimental data. Adsorption of As(V) obeys pseudo-second order equation with good correlation and fails to obey the first order. Nanomaterials may provide solutions to technological and environmental challenges in the area of water treatment.

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