Preparation and characterization of SiO₂ nanoparticles doped carbonized *Zygosaccharomyces bailli* for arsenic deduction

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Abstract: The present investigation shows that carbonized yeast doped with silica nanoparticles is an effective adsorbent for the removal of As(V) from aqueous solutions. The doping of carbonized yeast with silica nanoparticles is a new and reliable process which is an emerging aspect of current nanotechnology research. The doping of carbonized yeast which was prepared using the cultural supernatants of a commonly used yeast, *Zygosaccharomyces bailli* (MTCC 8177). The sorption of As(V) and the nature of the adsorbent was characterized by Fourier Transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Scanning electron microscope (SEM), Energy dispersive spectroscopy (EDS), Particle size analyzer and Zeta potential studies, respectively. The application of nanoscale materials and structures, usually ranging from 1 to 100 nanometers, is an emerging area of nanoscience and technology. Nanomaterials may provide solutions to technological and environmental challenges in the area of solar energy conversion, catalysis, medicine and water treatment.

Keywords: Biosorption, *Zygosaccharomyces bailii*, Characterization, Silica nanoparticles, As(V).

Introduction

Arsenic is the 20th abundant element in the earth and its 12th element found in the human body. Dual nature of arsenic was used by Ancient Greeks and Romans as therapeutic and as well as poison. Later the world recognized drinking water was contaminated by arsenic, largely at natural sources this is globally affected by the humanity[1]. The arsenic contamination of groundwater is a major concern and it poses a great threat to human health. The portable water supplied in many countries contains dissolved arsenic in excess of 0.01mg/L, which is the maximum level recommended by the World Health Organization[2]. Numerous water bodies around the world carry soluble arsenic at concentration higher than the standard. The arsenic concentration of many ground waters in the Western United States is found higher than 0.01 mg/L and most tube-wells in South and Southeast Asia do not meet the standard of the World Health Organization.

To meet the stricter standard of 0.01 mg/L a simple approach for efficient arsenic removal at low concentrations from drinking water is required[3]. Millions of people worldwide are exposed to arsenic contaminated groundwater, which they use as their sole source of drinking water. Increased use of groundwater as a source for drinking water has caused serious health problems such as neurological, dermatological, gastrointestinal and cardiorenal diseases; arsenic is also a suspected carcinogen. Furthermore, recent research has suggested that arsenic acts as an endocrine disrupter at extremely low concentrations. The U.S. Environmental Protection Agency has revised the maximum contaminant level (MCL) of arsenic in drinking water from 50 to 10 µg/L[4]. Exposure to arsenic can cause skin, kidney, bladder and lung cancer as well as neurological and cardiovascular problems[2].

It is highly desirable to develop an adsorbent for efficient and cost-effective removal of arsenic without any pretreatment. During the past decades, several techniques have been developed in the removal of arsenic from the waste water including precipitation followed by solid/liquid separation, adsorption and ion exchange, biological removal process, and so forth. Due to the low cost, good performance and easy operation adsorption is considered to be one of the most effective approaches among these technologies[5].

Nanoparticles can be designed and synthesized to act as either separation or reaction media for pollutants. The high surface area to mass ratios of nanoparticles can greatly enhance the adsorption capacities of sorbent materials. Nanotechnology is a deliberate manipulation of matter at size scales of less than 100 nm holds the promise of crating new materials and devices which take advantage of unique phenomena realized at those length scales. In addition to having high specific surface areas, nanoparticles also have unique adsorption properties due to different distributions of reactive surface sites and disordered surface regions[6].

The nanoparticles have extremely small feature size which is of the same scale as the critical size for physical phenomena for example, the radius of the tip of a crack in a material may be in the range 1-100 nm. Fundamental electronic, magnetic, optical, chemical and biological processes are also different at this level. Scientific studies and evidences suggested that adsorption is an efficient method to control the mobility and bioavailability of arsenic. Extensive adsorption studies have been carried out to characterize the reaction of As(III) and As(V) with various solid phases, including pillared clay and iron oxides, amorphous iron hydroxides, basic yttrium carbonates, hardened paste of Portland cement, fly ash, metal loaded polymers and activated alumina[7].

Treatment of arsenic containing wastewater by activated carbon has been reported as effective technique for the removal of arsenic species. Arsenic adsorption has been investigated with Fe-treated activated carbon, activated carbon impregnated by ferric hydroxide and tartaric acid and copper impregnated coconut husk carbon. The chemically treated activated carbon exhibits higher adsorption capacity for arsenic[8].

Activated carbon produced from conventional raw materials such as bituminous coal, peat, and lignite is expensive. The unaffordable price of commercially activated carbon has always been a limitation for its usage in treatment plants in developing countries like India. Hence, there is a need to find out non-conventional materials for the production of low cost activated carbon for water purification and wastewater treatment[9]. Silica nanoparticles (NPs) are widely applied in many fields, such as chemical industry, medicine, cosmetics, and agriculture. However, the hazardous effects of silica NPs exposure are not completely understood[10].

Silica is encompassed of a honeycomb-like porous structure with hundreds of empty channels. Due to their unique properties such as high surface areas, large pore volumes, tuneable pore sizes with a narrow distribution, and tuneable particle diameters, currently silica nanoparticles have been intensively investigated in materials research. Because of their simple preparation and possible applications in several fields, dispersed, uniform, and amorphous silica nanoparticles have produced specific interest[11]. In the present study, the preparation of activated carbon from *Zygosaccharomyces bailii* was doped with silica nanoparticles in order to increase its adsorption potentiality, to adsorb arsenate. The characterization study of the doped silica was also performed.

Experimental

Silica dioxide

Silicon dioxide, also known as silica, is a chemical compound that is a dioxide of silicon with the chemical formula SiO_2. It has been known since ancient times and it is most commonly found in nature as quartz, as well as in various living organisms. Silica is one of the most complex and most abundant families of materials, existing both as minerals and also being produced synthetically. Applications range from structural materials to microelectronics to components used in the food industry.

Broth preparation

The biomass for the preparation of carbonized yeast (*Zygosacchromyces 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

Harvesting the biomass

After 72 hours of incubation, the biomass was harvested by centrifugation at 8,000 rpm at 4°C. Pellets were collected and were washed twice with milli Q water. The washed pellets serves as the biomass which has to be doped with the silicon oxide. The harvested biomass was then dried and kept in the muffle furnace at 400ºC for one hour.

Doping of the carbonized yeast with silica nanoparticles

0.05M silica dioxide was added to a flask containing 0.5g of carbonized yeast dissolved in 100mL of distilled water. This flask was kept in the orbital shaker at 150 rpm, at room temperature for 24 hours. The solution was then filtered using the Watt Man filter paper. The filtrate was washed with distilled water and dried on the hot plate. The filtrate, thus obtained, is the *Z. bailii* doped silica dioxide.

The biosorption study of arsenic with the doped biomass was performed and estimated using the method[12]. In brief, a known quantity of ammonium molybdate was added to 9 mol/L sulphuric acid and made upto 100mL with distilled water (Reagent A). 10% ascorbic acid was prepared daily before use. As(V) estimation was carried out using a known quantity of ascorbic acid solution and 2mL reagent A and successively added to a 40mL sample aliquot in a 50 mL volumetric flask. The volume was completed by deionized water. A blank was prepared according to the same procedure using the appropriate volume of deionized water. The minimum detection limit of As(V) determination by this method is $20\mu g/L$.

Characterization of carbonized *Z.bailii* doped silica nanoparticles (CZDSN)

To understand the potential of nanoparticles, a deeper knowledge of their synthesis and applications is needed. Characterization is done by using a variety of different techniques, mainly drawn from materials science. CYDS before and after the removal of As(V) were characterized using FTIR, XRD, SEM attached with EDAX, particle size analyzer and zeta potential.

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range[13]. A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with high energy beam of electrons in a particular scan pattern[14]. X-ray diffraction yields the atomic structure of materials and is based on the elastic scattering of X-rays from the electron clouds of the individual atoms in the system. The most comprehensive description of scattering from crystals is given by the dynamical theory of diffraction[15].

Results and Discussion

The central findings of these studies indicate that the biological effect of silicon oxide particles depends on the particle structure and particle shape. These observations have been based on very high particle concentrations that are not realistic in real life. They are relevant nevertheless, since the biological effects produced contribute to the understanding of basic effect of silica when in contact with the cells. Silica ingested orally is essentially nontoxic, with an LD_{50} of 5000 mg/kg. The inexpensiveness and the non-toxic nature of silica dioxide make it a favorable compound to be used for Arsenic removal from water. Also, the yeast strain used *Zygosaccharomyces bailli* are adaptable and promising due to their potential metabolic fluxes. It is said that the capabilities of this benevolent microbe have not been taken into full use in terms of modifying the properties of silica oxide through doping for the purpose of arsenic removal.
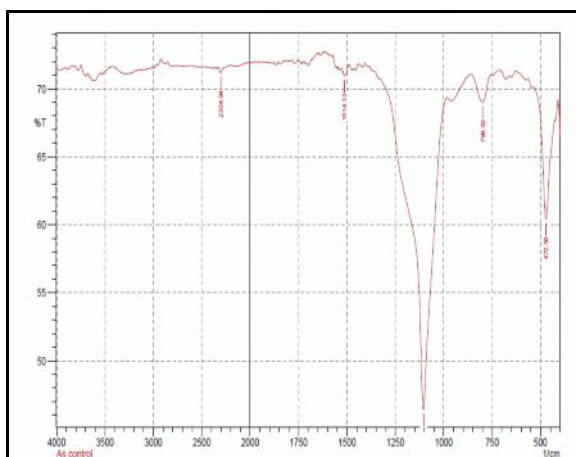
FTIR analysis

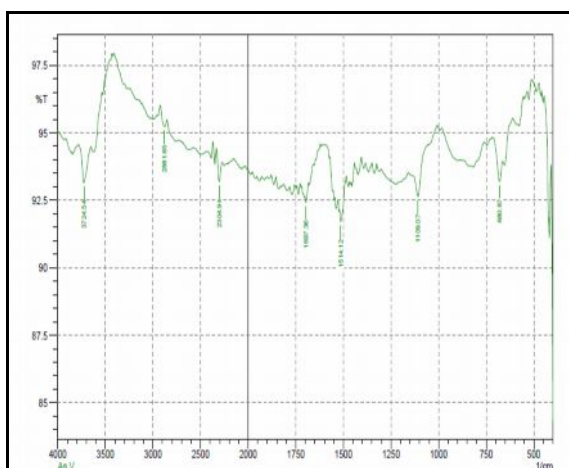**Figure 1: Before removal of As(V)**   **Figure 2: After removal of As(V)**

The FTIR analysis permits spectrophotometric observation of the CZDSN surface in the range of 400-4000 cm^{-1} and serves as the direct means for the identification of functional groups on the surface. The CZDSN before adsorption had peaks at 472.56 cm^{-1} which indicates the binding to the metal oxides, 798.53 cm^{-1} which shows the presence of the C-H bend, which shifted to 680.87 cm^{-1} after adsorption. The peak at 1105.21cm^{-1} shows the presence of H-O-H group, shifted to 1109.07 cm^{-1} after adsorption. A peak was also formed at 1514.12 cm^{-1} which can attribute to the presence of the C-H deformation of cyclic CH_2 groups, which remained the same even after adsorption. The peak which was formed at 2304.94 cm^{-1}, indicates the presence of COOH group, which also remained same after adsorption. Two new peaks were obtained at 2881.65 cm^{-1} and 3724.54 cm^{-1}, which shows the presence of aliphatic OH stretching and OH stretching vibration mode of hydroxyl functional groups including hydrogen bond[16].

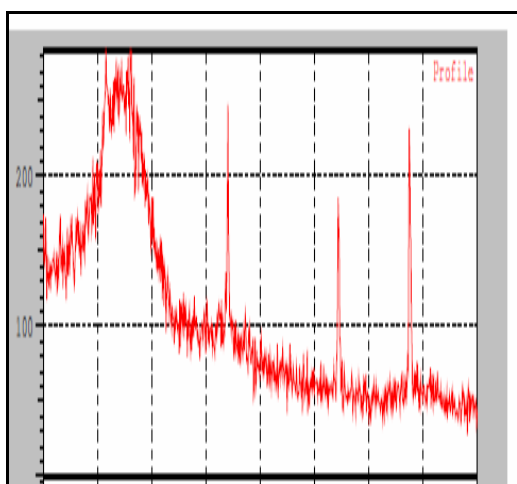**XRD analysis**

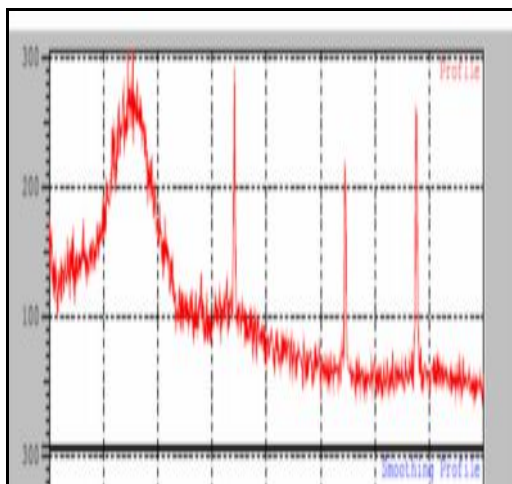**Figure 3: Before removal of As(V)**   **Figure 4: After removal of As(V)**

X-ray diffraction technique is a powerful tool to analyze the nature of the materials. If the material under investigation is crystalline, well-defined peaks are observed while noncrystalline or amorphous system show hallow instead of well defined peak. Adsorption reaction may lead to change in structure of adsorbent and hence an understanding of the adsorbent and resulting changes thereof would provide valuable information regarding the adsorption reaction[16]. In this study the XRD analysis, showed the presence of well defined peaks before and after adsorption, thus indicating the crystalline nature of the CZDSN.
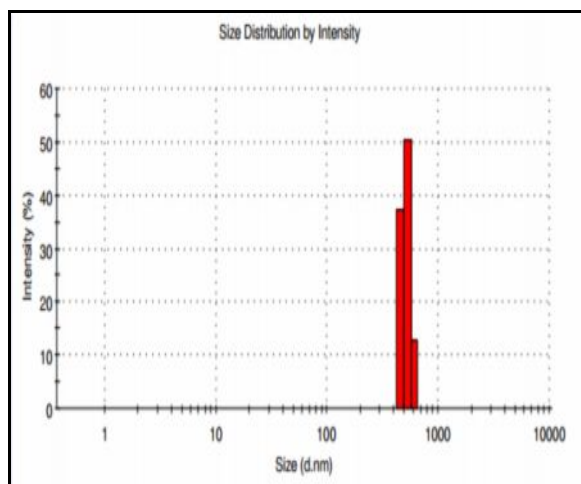
Particle size analysis

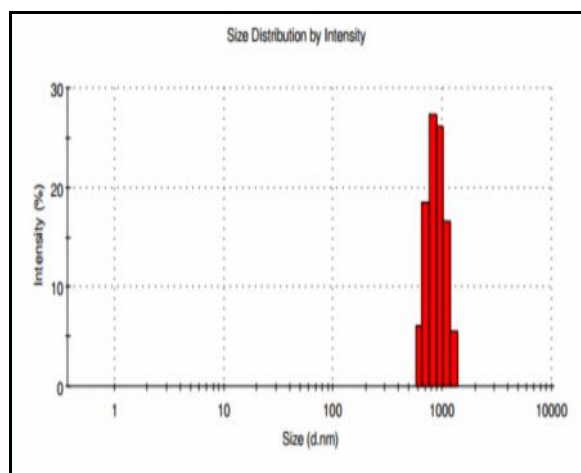**Figure 5: Before removal of As(V)**   **Figure 6: After removal of As(V)**

According to the parcticle size analysis (Malvern instruments), the size of the silica nanoparticles in the control (before the adsorption of arsenic), ranges from 712 nm to 1281nm in diameter. The maximum intensity is at 825 nm, which is 27%, therefore, the average size of the nanopaticles before adsorption is 825 nm. After the adsorption of As(V), the size of the silica nanoparticles ranges from 458.7 nm to 615.1nm in diameter. The maximum intensity is at 458.7 nm, which is 37.2%, therefore, the average size of the nanoparticles after adsorption is 458.7 nm.
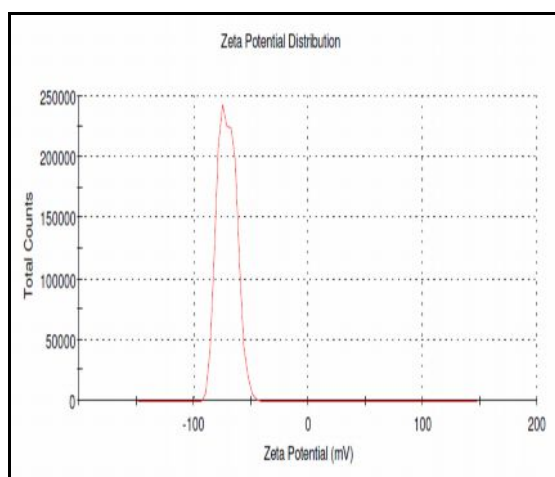
Zeta potential analysis

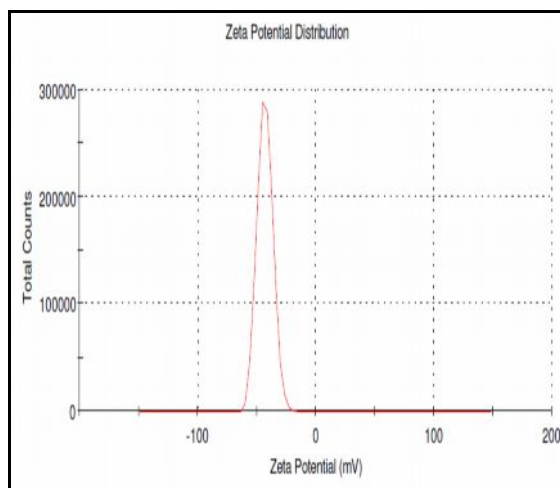**Figure 7: Before removal of As(V)**   **Figure 8: After removal of As(V)**

The zeta potential analysis (using Malvern instruments) of the silica nanoparticles in the control (before the adsorption of arsenate), shows a peak at -70.8 which indicates the high electronegativity of the paticles and its ability to attract positively charged particles, it also indicates its moderate stability. Whereas, the zeta potential analysis of the silica nanoparticles after the adsorption of As(V), shows a peak at -42.9, which indicates that the electronegativity has decreased and it also indicates better stability of the particles after adsorption.
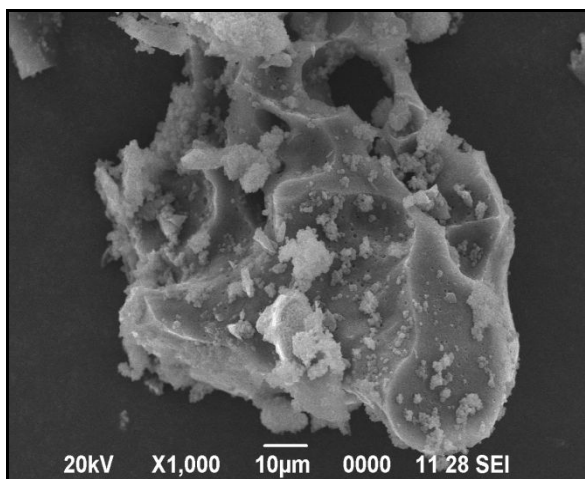
SEM-EDS analysis
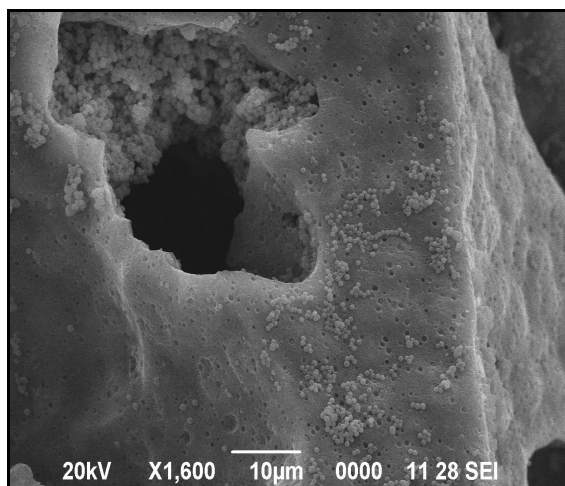

Figure 9: Before removal of As(V)

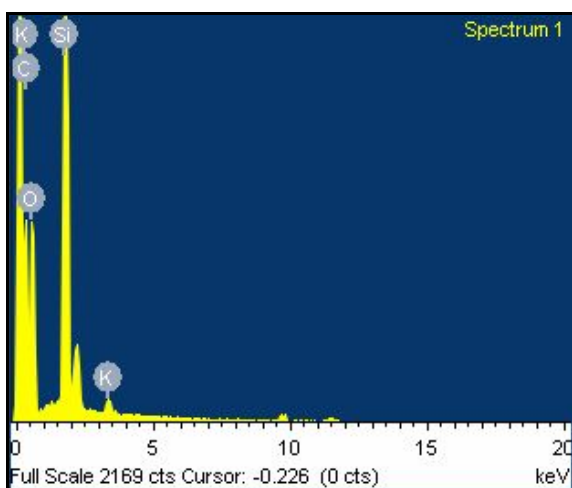**Figure 10: After removal of As(V)**

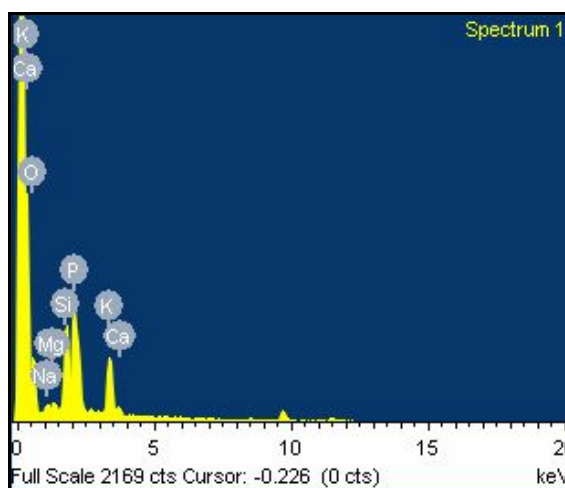**Figure 11: Before removal of As(V)**

Figure 12: After removal of As(V)

The surface morphology of the adsorbent was clearly understood with the help of SEM. The SEM images revealed the presence of multiple pores in the CZDSN formed due to thermal activation. Similar pores are observed on CZDSN before and after adsorption. Energy dispersive analysis of X-ray (EDAX) was employed to analyze the chemical constituents of Wattle humus before and after adsorption of arsenic ions. The EDS spectrum of the SEM images confirmed the presence of silica, potassium and oxygen on CZDSN before adsorption. This clearly indicated that the carbonized yeast was successfully doped with silica dioxide nanoparticles. The EDS spectrum of the SEM images confirmed the presence of potassium, phosphorous, magnesium and oxygen.

Conclusion

The present investigation shows that carbonized yeast doped with silica nanoparticles is an effective adsorbent for the removal of As(V) from aqueous solutions. The doping of carbonized yeast with silica nanoparticles is a new and reliable process which is an emerging aspect of current nanotechnology research. The doping of carbonized yeast which was prepared using the cultural supernatants of commonly used yeast, *Zygosaccharomyces bailli* (MTCC 8177). The CZDNS exhibited multiple pores with silica oxide on its surface when observed under SEM attached with EDAX. It was further characterized using FTIR, XRD, Particle size analyzer and zeta potential. The high porosity could be the possible reason of As(V) adsorption onto the CZDSN. The application of nanoscale materials and structures, usually ranging from 1 to 100 nanometers, is an

emerging area of nanoscience and technology. Nanomaterials may provide solutions to technological and environmental challenges in the area of water purification.

References

1. Kang, M., Kawasaki, M., Tamada, S., Kamei, T. and Magara, Y., Effect of pH on the removal of arsenic and antimony using reverse osmosis membranes, Desalination, 2000, 131, 293–298.
2. Selvakumar, R., Arul Jothi, N., Jayavignesh, V., Kathikaiselvi, K., Geny Immanual Antony., Sharmila, P.R., Kavitha, S. and Swaminathan, K., As(V) removal using carbonized yeast cells containing silver nanoparticles, Wat. Res., 2010, 45, 583-592.
3. Wang, N.X., Li, Y., Deng, X.H., Miao, A.J., Ji, R. and Yang, L.Y., Toxicity and bioaccumulation kinetics of arsenate in two freshwater green algae under different phosphate regimes, Wat. Res., 2013, 47, 2497-2506.
4. Mallikarjuna, M.N. and Darren, A. L., Microwave-assisted combustion synthesis of nano iron oxide/iron-coated activated carbon, anthracite, cellulose fiber, and silica, with arsenic adsorption studies, J. Nanotech., 2011, 8, 1-8.
5. Yang, J., Zhang, H., Yu, M., Irene, E., Jin, Z., Zhiguo, Y. and Yu,C., High-content, well-dispersed γ – Fe_2O_3 nanoparticle encapsulated in macroporous silica with superior arsenic removal performance, Adv. Func. Mat., 2013, 5, 178-183.
6. Cigdem, O. M., Jimmie, R. B. and Quoc, P. N., Adsorption of surface functionalized silica nanoparticles onto mineral surfaces and decane/water interface, J. Nanopart. Res., 2012, 14, 1246.
7. Vitela-Rodriguez, A.V. and Rangel-Mendez, J.R., Arsenic removal by modified activated carbons with iron hydro (oxide) nanoparticles J. Environ. Manag., 2013, 114, 225–231.
8. Selvakumar, R., Kavitha, S. and Swaminathan, K., Adsorption of As(V) from aqueous solution by chemically doped coir pith carbon, Ind. J. Chem. Tech., 2007, 14, 276-282.
9. Mitrovic, J., Radovic, M., Bojic, D., Ambelkovic, T., Purenovic, M. and Bojic, A., Decolorization of the textile azo dye reactive orange 16 by the UV/H_2O_2 process, J. Serb. Chem. Soc., 2012, 77, 465–481.
10. Hamsa, J. and Biana, G., Biocompatibility Assessment of Si-based Nano- and Micro-particles, Adv. Drug. Deliv. Rev. 2012, 64, 1800-1819.
11. Chitra, K. and Annadurai, G., Fluorescent silica nanoparticles in the detection and control of the growth of pathogen, J. Nanotech., 2013, 2, 1-6.
12. Lenoble, V., Veronique, D., Bernard, S. and Bollinger, J., Arsenite oxidation and arsenate determination by the molybdene blue method, Talanta, 2003, 61, 267-276.
13. Elizarova, T.E., Shtyleva, S.V. and Pleteneva, J.V., Using near infrared spectrophotometry for the identification of pharmaceuticals and drugs, Pharm. Chem. J., 2008, 42,432-434.
14. Goldstein, J., Newbury, D.E., Joy, D.C., Lyman, C.E., Echlin, P., Lifshin, E., Sawyer, L. and Michael, J.R., Scanning Electron Microscopy and X-ray Microanalysis, Springer, 2003.
15. Raymond, B., Johnston, P.R., Wright, D.J.,Ellis, R.J., Crickmore, N. and Bonsall, M.B.https://www.imperial.ac.uk/people/b.raymond/publications.html, A mid-gut microbiota is not required for the pathogenicity of *Bacillus thuringiensis* to diamondback moth larvae, Environ. Microbio., 2009, 11, 2556-2563.
16. Selvakumar, R., Kavitha,S. and Swaminathan, K., Adsorption of As(V) from aaqueous solution by chemically doped coir pith carbon, Ind. J. Chem. Tech., 2007, 14, 276-282.

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