

Synthesis and application of alumina supported nano zero valent zinc as adsorbent for the removal of arsenic and nitrate

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Abstract—Arsenic and nitrate are ill-famed environmental pollutants that are responsible for various lethal diseases. Their removal from drinking water is very essential. In present study, newly synthesized alumina supported nano zero-valent zinc (Alumina-nZvZ) has been tested to remove arsenic and nitrate. Quantitative analyses of arsenic have been performed spectrophotometrically and while that of nitrates ions colorimetrically. After optimization of time and amount of adsorbent, Langmuir, Freundlich and D-R isotherms were applied to determine different parameters for the assessment of adsorption. Synthesized samples were characterized by scanning electron microscopy (SEM) to evaluate porosity and void size. Alumina coated with reduced $ZnCl_2$ showed better efficiency for removal of arsenic and nitrate ions. Kinetics of adsorption was evaluated by using pseudo first-order and pseudo second-order rate equations.

Keywords: Adsorption, Alumina, SEM, Arsenic, Nitrates

INTRODUCTION

Arsenic and nitrates pollute the environment and cause different chronic diseases in human beings and animals. So their detection, quantification and removal are a matter of great concern. In 1986, the World Health Organization (WHO) developed some standard permissible limits for nitrate, (10 ppm) and arsenic (0.05 ppm) concentration in drinking water for Pakistan. WHO has claimed that approximately 50% of the population of developing countries faces health problems linked with lack of uncontaminated water [1] and more than 60% of the population has no access to pure drinking water [2]. There rapid increase in population size, climate change and rapid increase of human activities to meet the challenges of energy, food, households etc., ultimately pollutes water with toxic chemical species. Physical storage of massive water is quite impossible on our earth. The water covers 70% of the globe and 97% water of world is salty and not drinkable. The 2% of the total water is captured into glaciers, polar ice caps etc., resultantly 1% is left for human needs [3]. Contamination of drinking water by nitrate may cause blue-body syndrome (methaemoglobinemia) in babies of age less than six months due to oxygen deficiency [4]. Basically in the intestine of infants, *Escherichia coli* bacteria reduce nitrate (NO_3^-) ions into nitrite (NO_2^-) ions. The reduced ions are then absorbed in blood where they oxidize iron (II) of haemoglobin to iron (III) in methaemoglobin. Thus, oxygen carrying capacity of blood is reduced. High level of nitrate ions causes the formation of carcinogenic nitrosamines and diabetes [5-7]. After ingestion of plants with high concentration of nitrate ions, poisoning may occur within 30 min to 4 hours

in cattle, and affected cattle may die after 24 hours [8]. Symptoms may be salivation followed by the frequent urination, high respiratory rate, difficulty in breathing, chocolate colored blood and mucous membrane [9]. Pregnant cattle, if receiving a dose which is not somewhat deadly, may abort very soon after recovering such amount [9].

Contamination of drinking water caused by high concentration of arsenic for the longer period of time may seriously cause cancer to skin, lungs, urinary bladder and kidney. It may change in the pigmentation and thickening of the skin, disordering of nervous systems, weakening of tissues, loss of hunger etc. High concentration of arsenic in underground drinking water is a big issue [10] which may result in abdominal tract pain, vomiting, “rice water” diarrhea etc. The increasing concentration of nitrates and arsenic in ground and stream water is due to heavy use of nitrogenous fertilizers, pesticides, poor sanitary activities, effluents of dyes and drugs industries [11-14]. The level of nitrate concentration and turbidity rises during heavy rain episodes [15].

Some technologies are available which are being used for nitrate removal from water, including biological denitrification [16], electro dialysis [17], reverse osmosis [18], ion exchange [19-21], zero-valent magnesium [22] and zero-valent iron [23]. The use of zero-valent iron (ZVI) is the most common for nitrate and arsenic removal from drinking water [24,25-29]. None of above cited processes is widely acknowledged, due to high original and maintenance costs [30]. High level of nitrates and arsenic contamination of drinking water is reported in China, USA, Bangladesh, Mexico, Argentina, Poland, India, Canada, Taiwan, New Zealand, Japan and Hungary [31].

Application of nanoparticles for removal of pollutants from drinking water is an interesting area of research. Nanoparticles, due to their high surface area and dramatic unique properties, are providing unprecedented opportunities for removal of hazardous materials

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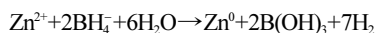
from water with high efficiency [32,33-40]. Alumina nanoparticles are a novel material as adsorbent because of high adsorption capacity, large surface area, mechanical strength and low temperature modification [41-43]. In the present work, novel adsorbents have been synthesized by coating alumina with zero valent zinc (alumina-ZnZ) nanoparticles. Newly synthesized adsorbents are used for the adsorption of nitrates and arsenic from contaminated drinking water. Experimental conditions for removal process were studied in detail and optimized. The synthesized adsorbents have several advantages such as high surface area and removing capacity, easy availability, low cost, environment friendliness and possibility to be used on industrial scale in the future.

EXPERIMENTAL

All the chemicals used in this study were of analytical grade and were used for synthesis and quantitative analysis without any further purification. Synthesis of novel adsorbent has been carried using by the reduction of Zn (II) chloride by Na-borohydride (NaBH₄). Then optimization of time and concentration for maximum adsorption of nitrate and arsenic ions was taken into account with the help of double beam spectrophotometer and Multy colorimeter (Spectroquant).

1. Preparation of Alumina Supported Nano Zero Valent Zinc Particles (Alumina-nZVZ)

The synthesis of nano zero valent zinc (nZVZ) material is based on reduction of Zn (II) chloride with sodium borohydride. The proposed chemical reaction for the preparation of nZVZ is as follows:



For the synthesis of nZVZ, ZnCl₂ (3.127 g) was dissolved in a of ethanol and deionized water, with ratio of 4/1 (v/v), and the mixture was kept on a hot magnetic stirrer for absolute mixing at 40 °C. Sodium borohydride (1 M, 100 mL) was poured dropwise from a burette. Brownish black tiny particles appeared instantly by the addition of sodium borohydride. The solution was further stirred for ten minutes. Alumina (10 g) was then added to nZVZ solution and stirred vigorously for one hour. The alumina supported nZVZ was separated using Whatman filter papers. For complete removal of water from nZVZ, the mixture was washed three times with methanol (3×25 mL) and dried in oven at 60 °C.

2. Determination of Arsenic Ions

The optimization of time and concentration of solution for the maximum adsorption was determined spectrophotometrically. NaAsO₃ (0.17320 g) was dissolved in deionized water (100 mL) to prepare stock solution of As (III). Further dilutions were made from this stock solution. All the remaining solutions were prepared following the standard method using analytical grade chemicals.

Arsenic solutions of different known concentrations were treated with Y.A-3 (Alumina-nZvZ). For the determination of optimum removal, arsenic samples of known concentrations (0.005-0.025 M) were treated with self-prepared adsorbent (25.0 mL As solution+ 0.6 g adsorbent) at moderate speed using a magnetic stirrer. Arsenic solutions were transferred to series of 10 mL clean, sterilized and dried flasks. Potassium iodate (2%, 1.0 mL) and hydrochloric acid (0.4 M, 1.0 mL) were added to each flask and the mixtures were shaken thoroughly. Then variamine blue (0.05%, 1 mL) and sodium

acetate (2 M, 2 mL) were added to the above solution and saved for further use. Resultant solution was kept for 5 minutes at room temperature and volume was made up to the mark with deionized water. Absorbance of colored species was determined at 570 nm.

3. Determination of Nitrate Ions

The optimum conditions for time and concentration for maximum adsorption of nitrate ions were measured with a colorimeter. Stock solution of nitrate was prepared by using potassium nitrate (1.63 g) in deionized water (1,000 mL). Further dilutions were made from the stock solution.

Sample solutions of known concentration of nitrate were treated with Y.A-3 (25 mL of solution and 0.60 g of adsorbents) in order to determine nitrate removing capacity. The mixture was stirred by magnetic stirrer at moderate speed for 40 minutes and then filtered. Concentration of nitrate in the filtrate was determined using method 321, given in the manual, supplied with colorimeter (Spectroquant).

RESULTS AND DISCUSSION

Nano zerovalent zinc particles were adsorbed on alumina to improve the morphology of latter. Such efforts are present in literature for activated carbon which increased the micro-porosity of adsorbent [44].

1. Effect of Time and Concentration

To study the effect of time and concentration, optimized data was collected for maximum adsorption of arsenic and nitrate ions using a spectrophotometer (λ_{max} =570 nm) and colorimeter. The optimized amount of adsorbent (0.6 g) and the optimized time (40 minutes) were used in all the subsequent studies.

2. Characterization of Alumina-nZVZ Using SEM Analysis

To investigate the morphology and porosity of the sample, SEM was performed at different zoom level. Pore size and interstices were seen at high resolution. Different SEM images were taken at 50 kv and different zoom levels shown in Fig. 1. This sample was highly porous having micro, meso and macro pores. Crystal size was found greater than 100 μm . Porosity of this sample was totally different from its parent adsorbent. This sample followed two different mechanisms for adsorption of adsorbate: adsorption into pores and adsorption in between voids, thus increasing the adsorption capacity.

3. Freundlich Isotherm

The different parameters during adsorption of arsenic at 40 minutes dosage time are given in Table 1. The Freundlich Isotherm assumes that the adsorption phenomena occur on heterogeneous surface of adsorbent, and non-linear distribution of heat of adsorption takes place on the surface of the adsorbent as well. The linear transformation of the Freundlich Isotherm is given as:

$$\ln(q_e) = \ln K_f + \frac{1}{n} \ln C_e \quad (1)$$

Where q_e gives concentration of As that is adsorbed at equilibrium (mg/g) and C_e represents the equilibrium concentrations of As (III) in solution (mg/L). A plot of $\ln C_e$ against $\ln (q_e)$ for adsorbent, represented as Y.A-3 is shown in Fig. 2. Values of n and K_f parameters are calculated from slope and intercept of these graphs (Table 2).

K_f is the adsorption capacity and parameter n shows adsorption intensity. Higher values of n (greater than unity) indicate that adsorption of As (III) on newly synthesized adsorbents is favorable.

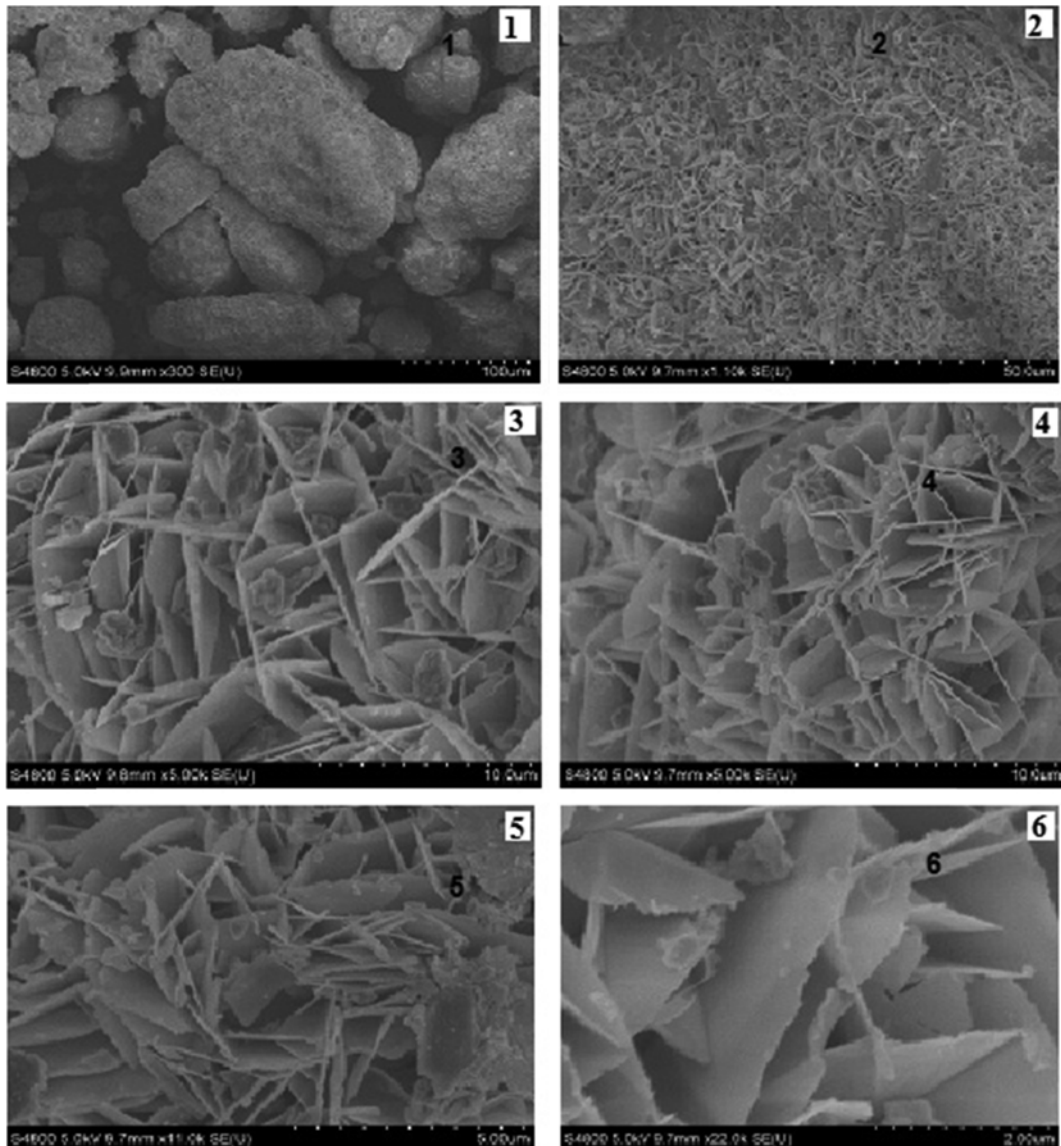


Fig. 1. SEM images of synthesized adsorbent at six different resolutions.

Table 1. Adsorption of arsenic on Y.A-3 from different concentration of As_2O_3 solution Y.A-3=0.6 g

| Sr. no | C_i^a | C_e^b | X_m | q_e^c | $\ln C_e$ | $\ln q_e$ | 2 | C_e/q_e |
|--------|---------|---------|----------|----------|-----------|-----------|----------|-----------|
| 1 | 0.005 | 0.0007 | 0.005488 | 0.179167 | -7.26443 | -1.71944 | 31555.6 | 0.003907 |
| 2 | 0.010 | 0.0060 | 0.04707 | 0.166667 | -5.116 | -1.79176 | 15684.3 | 0.036 |
| 3 | 0.015 | 0.0111 | 0.087024 | 0.1625 | -4.50081 | -1.81708 | 12170.23 | 0.068308 |
| 4 | 0.020 | 0.0161 | 0.126224 | 0.1625 | -4.12894 | -1.81708 | 10271.16 | 0.099077 |
| 5 | 0.025 | 0.0212 | 0.166208 | 0.158333 | -3.85375 | -1.84305 | 8975.8 | 0.133895 |

^aInitial concentration of As (III)

^bEquilibrium concentration of As (III)

^cConcentration of As (III) adsorbed at equilibrium

4. Langmuir Isotherm

The Langmuir isotherm has been tested to determine the mono-layer and multi-layer adsorption on to the surface of synthesized adsorbent. Linear representation of Langmuir isotherm is shown as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L + a_L} \cdot \frac{C_e}{K_L} \quad (2)$$

where, K_L and a_L are Langmuir constants which were calculated from slope and intercept of the graphs of C_e versus C_e/q_e (Fig. 3),

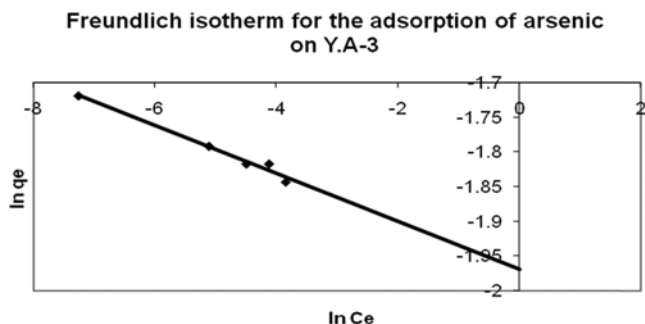


Fig. 2. Freundlich isotherm for the adsorption of As(III) on Y.A-3.

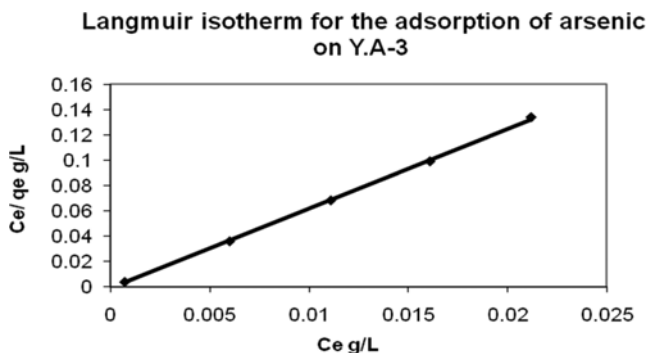


Fig. 3. Langmuir isotherm for the adsorption of As (III) on Y.A-3.

(Table 2). Adsorption capacity can be calculated from inverse of slope (Eq. (3))

$$q_m = \frac{q_L}{K_L} \quad (3)$$

5. Dubinin Radushkevich (D-R) Isotherm

D-R isotherms are plotted using the following equations:

$$\ln q_e = \ln X_m - K_{DR} \varepsilon^2 \quad (4)$$

$$\varepsilon^2 = RT \ln \left[1 + \frac{1}{C_e} \right] \quad (5)$$

Absolute values of K_{DR} and X_m are determined by plotting $\ln q_e$ versus

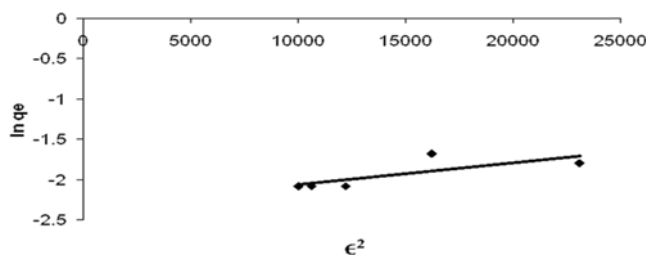


Fig. 4. Rudshkevich isotherm for the adsorption of As (III) on Y.A-3.

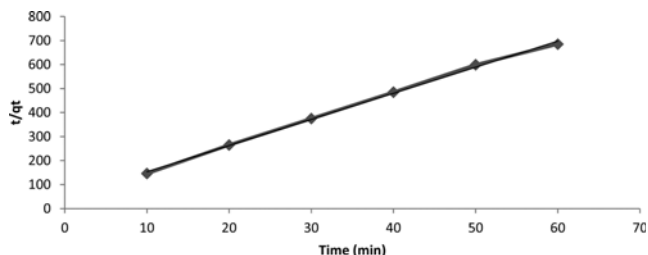


Fig. 5. Plot for second order kinetic model for the adsorption of As (III) on Y.A-3.

ε^2 (Fig. 4), (Table 2). Mean sorption energy can be calculated by the following equation:

$$E = \frac{1}{\sqrt{2}} K_{DR} \quad (6)$$

The calculated value of energy (E) (Table 2) is less than 8 kJ/mol. Hence, it can be concluded that physical adsorption phenomenon takes place on the surface of the newly synthesized adsorbent.

6. Kinetics of Adsorption

Pseudo first- and pseudo second-order rate equations (Eq. (7) and (8)) have been tested to evaluate the kinetics of the reaction as well as to find the order of the reaction.

$$\ln(q_e - qt) = \ln q_e - k_1 t \quad (7)$$

$$\frac{t}{qt} = \frac{1}{k_2 q_e} + \frac{t}{q_e} \quad (8)$$

Table 2. Adsorption isotherms for adsorption of As (III) on the surface of Y.A-3

| Freundlich parameters | | | | Langmuir parameters, | | | | Dubinin Rudshkevich, parameters | | | | | |
|-----------------------|-------|----------------|-------|----------------------|--------------|----------------|----------------|---------------------------------|-----------|------------|--------------|------------|-------|
| Adsorbent | n^a | K_f^a (mg/g) | R^2 | Adsorbent | q_m (mg/g) | K_L^b (L/mg) | a_L^b (L/mg) | R^2 | Adsorbent | K_{DR}^c | X_m (mg/g) | E (kJ/mol) | R^2 |
| Y.A-3 | 29.41 | 1.968 | 0.983 | Y.A-3 | -0.158 | -1000 | 6321 | 0.999 | Y.A-3 | 0.000065 | 4.56 | 0.087706 | 0.942 |

^aFreundlich constants

^bLangmuir constants

^cDubinin Rudshkevich constant

Table 3. Kinetic Measurements for adsorption of As (III) on the surface of Y.A-3 at 298 K

| Adsorbent | q_e^a (exp) mg/g 1 st | q_e^a (exp) mg/g 2 nd | q_e^a (cal) mg/g 1 st | q_e^a (cal) mg/g 2 nd | k_1 1 st | k_1 2 nd | R^2 1 st | R^2 2 nd |
|-----------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| Y.A-3 | 0.19 | 0.19 | 0.11 | 0.13 | 0.017 | 0.937 | 0.034 | 0.978 |

^aConcentration of As (III) adsorbed at equilibrium

Adsorption rate constants k_1 and k_2 are calculated from experimental data by plotting $\ln(q_e - qt)$ versus t and t/qt versus t for first- and second-order equations, respectively (Table 3). Better correlation coefficient proves that the adsorption follows second-order kinetics (Fig. 5).

CONCLUSIONS

It can be concluded that 40 minutes and 0.6 g are optimum conditions for synthesized adsorbent's efficiency. These conditions are fruitful for optimum removal of As (III) and nitrate ions from drinking water by mechanism of adsorption in between voids and into pores. Adsorption results are well more likely fit to the Langmuir model, which indicates that As (III) species are adsorbed on the adsorbent's surface in monolayer form. Value of n in the Freundlich isotherm indicates that the adsorption process is favorable. Physical adsorption is suggested from lower values of the mean sorption energy, calculated from the D-R model. External and internal mass transfer are occurring at the same time in the present adsorption work of As (III) on YA-3. This mass transfer is concluded from a pseudo second-order rate equation.

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