

Synthesis, Characterization of Silica Nanoparticles and Adsorption Removal of Cu^{2+} Ions in Aqueous Solution

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Abstract A successive method has been used, to synthesize monodisperse and uniform-size silica nanoparticles using ultrasonication assisted sol-gel method. The amorphous nature of silicon oxide nanoparticles was analyzed by X-ray diffraction technique. The silica particles were obtained by hydrolysis of tetraethyl orthosilicate (TEOS) using ethanol as medium and the reagent ammonia in concentration of (2.8–28 mol L⁻¹), ethanol (1–8 mol L⁻¹), water (3–14 mol L⁻¹) and TEOS (0.012–0.12 mol L⁻¹) were used. The amorphous nature of nanoparticles analyzed by X-ray diffraction technique, the particles sizes in the range of 25-55 nm calculated by SEM image and also study for the preparation of nanosorbents and adsorption of Cu^{2+} ions on its surface analyzed by EDX. Adsorption isotherms were well described by Langmuir equations with maximum adsorption capacity (qm) of 2.68mole/gm. The effect of contact time, pH and adsorbent dose were studied and optimized. Finally, it was found that 92-98% copper was adsorbed under optimized conditions. The amount of metal ions adsorbed was calculated by plotting calibration graph using UV-VIS spectrophotometer. The adsorbent stability in acidic and basic medium, desorption study as well as its reusability and recyclability were also tested satisfactorily.

Keywords— Sol-gel, TEOS, SEM-EDX, Adsorption, Desorption.

I. INTRODUCTION

Water is one of the most essential commodities to sustain life process. Clean and safe drinking water is the key to protect public health. But environmental pollution due to rapid development in human civilization in the form of industrialization, urbanization as well as geological erosion and natural calamities are the major sources of water pollution [1-2]. Contamination of water with toxic heavy metals such as, copper, chromium, cadmium, arsenic, nickel, lead and mercury in ground water are of major concern for its hazardous effect on the environment [3]. Generally, heavy metal toxicity cause chronic degenerative diseases such as symptoms like muscles-joint pain, mental disorders, gastro-intestinal disorders, chronic fatigue, susceptibility to fungal infection etc [4].

Although small quantities of heavy metals are essential for healthy life as they play key role in important biological activities but large amount of them may cause acute or chronic toxicity [5]. For instance, copper has an essential element in human metabolism, play a critical roles in the development of bones, central nervous system and connective tissues. The acceptable limit of copper in drinking water is .05mg/l but normally its concentration vary from .01-.5mg/l which is tolerable and poses no serious health threat to human life, but when concentration of copper exceeds the 1.5mg/l in water due to natural sources and human activities it causes serious health effects. Some examples of natural sources are decaying vegetation, forest fires and sea spray, and other examples of human activities are mining, industrial settings, landfills, phosphate fertilizer production and waste disposals. Because copper is released both naturally and through human activity it is very widespread in the environment. Most copper compounds will settle and be bound to either water sediment or soil particles. Soluble copper compounds form the big threat to human health. Usually water-soluble copper compounds occur in the environment after release through application in agriculture. Hence it is necessary to remove copper from water by using cost-effective and environmental friendly techniques [6].

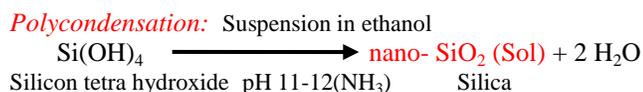
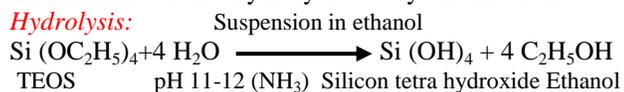
Till now numerous processes are available to remove dissolved toxic metals from water including biological and chemical methods such as chemical precipitation, solvent extraction, ultrafiltration, electro-dialysis, adsorption, ion-exchange process etc.[7-9]. Nowadays application of nanomaterials as a nanosorbents is attractive and efficient method for the removal of toxic metals from ground water [10-12]. The unique physico-chemical properties of nano materials such as size in nm range, larger surface area to volume ratio, high mechanical strength, easy surface functionalization with different chemical groups etc, makes them an efficient nanosorbents to be target selective for the pollutants in water purification [13-15].

Silica nano materials have special advantage in water purification technology due to its adsorptive property, least toxicity and biodegradable, environmental friendly, easy and facile synthesis [16-18]. Till now in various research studies on silica nanomaterials such as SiO₂ and SiO₂@Zno and its composites with variety of inorganic and organic compounds have been successfully applied in water purification as a nanosorbents [19-21]. UV-Vis spectrophotometer technique is also applied to the determination of equilibrium Cu²⁺ metals ions concentration in the solutions with the help of calibration graph. This will helpful in the calculation of percentage recovery of heavy metal ions.

The sol-gel technique is the most common method for synthesizing silica nano-particles. It involves the simultaneous hydrolysis and condensation reaction of the metal alkoxide [22]. Kolbe in 1956 observed the formation of silica particles by reacting TEOS in alkali solution with water in the presence of certain bases [23]. It is imperative to have silica particles of a narrow size distribution with high purity [24]. Depending on the synthesis, the structure of colloidal particles may vary from isolated spherical particles to agglomerates of complex structures [25]. Therefore, a major concern associated with obtaining colloidal silica particles is the control of structural features, such as average diameter and morphology of particles [26]. The purpose of the present study was to investigate different solvents and their effects in preparing monodispersed silica particles. Colloidal silica nanoparticles are based on the hydrolysis reaction of silicon alkoxide where the resulting particle size and morphology depend strongly on the hydrolysis kinetics. In the selected constituent concentrations, spherical, silica particles can be obtained. A typical sol-gel reaction is hydrolysis and condensation of TEOS as a precursor of silica. Both reactions are concurrent and reversible depending on the reaction conditions such as pH, temperature and so on [27-31]. The Sol-gel reaction can be written in two steps:

Process: Sol - Gel - Synthesis - Precipitation

Chemical reactions: Hydrolysis – Polycondensation



II. MATERIALS AND METHODS

2.1. REAGENTS

Tetraethyl orthosilicate (TEOS) (99.99%, Aldrich), ethanol (99.99%, Aldrich), and ammonium hydroxide (28%,Wako) was used without any further purification. Milli-Q water (18.2 mol L⁻¹) was used throughout the experiment.

2.2. Synthesis of silica nanoparticles

The monodisperse uniform-sized silica nanoparticles were prepared by hydrolysis of TEOS in ethanol medium in the presence of ammonium hydroxide. First, ethanol (1–8 mol L⁻¹), was taken to make suspension with Milli-Q water (3–14 mol L⁻¹) and kept in a sonication bath, after 10 min, known volume of TEOS (0.012–0.12 mol L⁻¹) was added while sonication, and after 20 min, 28% ammonia (2.8–28 mol L⁻¹), was added as a catalyst to promote the condensation reaction. Sonication was continued for a further 60 min to get a white turbid suspension. All the above experiments were conducted at room temperature.

2.3. Adsorption experiment

Adsorption experiment was carried by stirring fixed amount of a nanocomposite as a nano sorbent (0.1gm) with 10 ml of 0.1M solution of copper sulfate for 15 minutes at room temperature. Metal loaded adsorbent was separated magnetically. The concentration of unadsorbed metal ions was found out with the help of calibration graph of copper solution at a fixed wavelength with varying initial metal concentration. After the equilibration the pH of the reaction medium was changed prior to finding out the metal concentration of the filtrate, pH was stabilized to 6.5. The amount of adsorbed metal were found out by applying the formula-

$$C_a = C_i - C_f$$

Where C_i= initial concentration, C_f= final concentration. Percentage recovery factor (% R) was calculated by the following the equation-

$$\% R = C_a/C_o \times 100$$

Where C_a and C_o are adsorbed and initial concentration of metal ions.

2.3.1. Adsorption isotherm

Adsorption isotherm was determined by mixing 0.1gm adsorbent with 10ml of metal solution with varying initial metal concentration ranging from 0.01M-0.1M, followed by stirring for 15 minutes at room temperature to attain equilibrium [32].

The pH of the reaction medium was set at 6.5 as an optimized value. After adsorption, the metal loaded sorbent was magnetically separated and final metal concentration in supernatant was determined by the calibration graph as shown in figure 4, plotted by diluting concentration of standard solution in a fixed ratio and Corresponding absorption is measured with the help of UV-Vis spectrophotometer at a fixed Wavelength (λ_{max}). The concentration of adsorbed metal ions was calculated as a difference between the initial concentration in the solution and the final concentration after the equilibration. A number of metal ions adsorbed at time t, q_t in mg/gm were calculated as a mass balance equation

$$q_t = \{C_0 - C_t\} v/m$$

Where C_0 , C_t , V, m are initial concentration of metal ions, the concentration of metal ions after time t, the volume of the solution and the mass of the adsorbent. Langmuir adsorption equation is described as below

$$1/q_e = 1/q_m b C_e + 1/q$$

where q_e is the equilibrium adsorption capacity of adsorbent toward Cu(II) (mg/g), C_e is the equilibrium Cu(II) concentration in solution (mg/L), q_m is the maximum capacity of adsorbent (mg/g), and b is the the Langmuir adsorption constant pertaining to the energy of adsorption (L/mg).

2.3.2. Effect of adsorbent dose

To observe the effect of adsorbent dosage on the adsorption capacity, 10ml of 0.1M metal solutions were taken and pH of the solutions were adjusted at 6.5. Then various amount of adsorbents were added to the solutions on ultrasonic stirrer at room temperature for 15 minutes. After the reaction and separation the residual metal concentrations was determined with the help of UV-Vis spectrophotometer.

2.3.3. Effect of pH

The effect of pH on adsorption capacity was tested by taking 0.1 gm of the adsorbent with 10 ml of 0.1M metal solutions with varying pH values ranging from 2- 6.5, at room temperature, followed by stirring for 15 minutes. After adsorption and separation, residual metal concentrations were determined.

2.3.4. Effect of time

To study the effect of time on adsorption capacity, 0.1 gram of adsorbent was mixed with 10 ml of 0.1M metal solutions, followed by stirring at room temperature for various time intervals ranging from 5-20 minutes.

2.4. Desorption and reusability

Desorption study was carried out by using 0.1M HCl solution as an eluent for eluting the adsorbed metal ions from the adsorbent. For this fixed amount of metal loaded adsorbent was mixed with 10 ml of HCl, followed by ultrasonic stirring at room temperature for 15 minutes for desorption of metal ions. After complete elution, the unloaded adsorbent was separated magnetically and metal concentration in the supernatant was determined. Recovered adsorbent was reused till five recycling process successfully.

III. RESULTS AND DISCUSSION

The characterization of the prepared silica nanoparticles was carried out by XRD, SEM-EDX, Adsorption and desorption studies have been discussed with reference to these techniques.

3.1 XRD Analysis

It indicates that a high percentage of particles were amorphous but a few of them were crystalline. The major phase of SiO_2 was quartz and the minor phase of SiO_2 cristobalite. Figure1 shows the XRD of silica nanoparticles. Using related data and Scherer equation, average size of silica nanoparticles was predicted. From our results, it was found that the various nano-sized nanoparticles were the maximum diameter of 55nm, spherical in structure. [35-38].

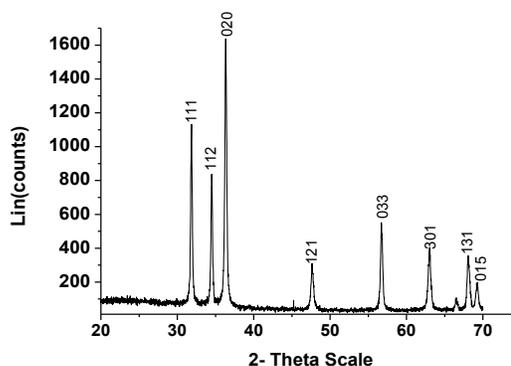


Figure 1: XRD spectra of synthesized silica nanoparticles

3.2 Surface Morphology and Elemental Analysis

It is evident from figure 2 the SEM images of the nanosorbents reveal the surface morphology and size. SEM images shows that the size of the nanosorbents was spherical in shape with the diameter of about 25-55nm.

Monodispersity of the nano particles was also confirmed by narrow size distribution of the particles in SEM image [39-44].

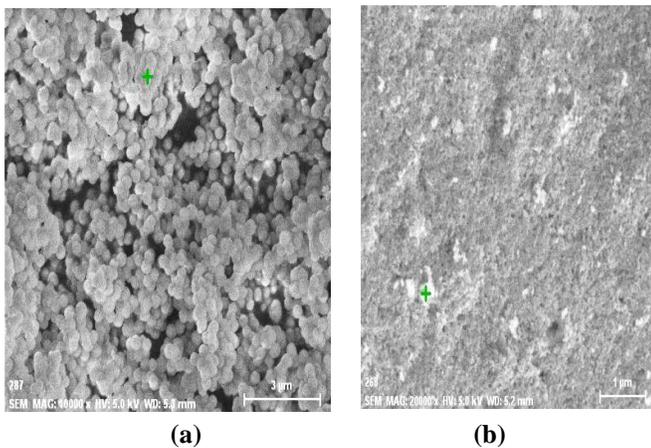


Figure 2: (a) SEM image of synthesized SiO₂ nanoparticles and (b) adsorbed Cu²⁺ ions on the surface of SiO₂ nanoparticles

Qualitative elemental analysis and element localization on samples was analyzed by EDX as shown in figure 3. The EDX spectra of nanosorbents before and after Cu (II) metal loaded on the nanosorbents are shown in Figure 3(a) and 3(b). Results showed that the observable peak of Cu (II) clearly (Fig. 3b) and nanosorbents laden with Cu (II) ions [34].

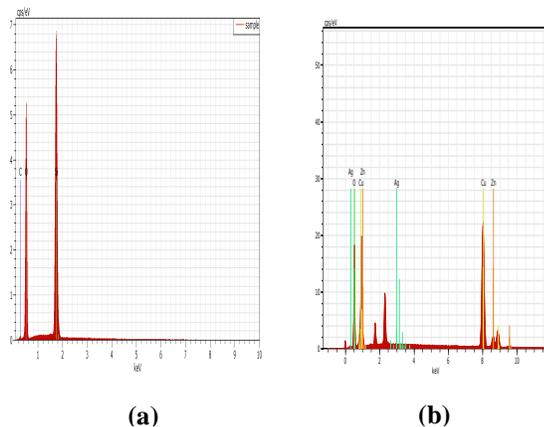


Figure 3: (a) EDX Spectra of SiO₂ nanoparticles and (b) Adsorbed Cu²⁺ ions on the surface of SiO₂@Zno nanoparticles

3.3 Adsorption isotherm

To determine the sorption capacity of the nanosorbents, sorption studies were carried out with varying initial concentration of metal solutions ranging from 0.02-0.1 mol/l at constant temperature as shown in figure 4.

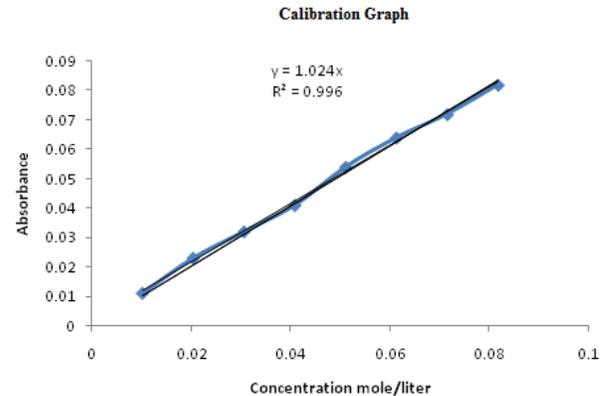


Figure 4: Calibration graph for Cu(II) at 615 nm wavelength

The equilibrium adsorption isotherms for Cu²⁺ on the nanosorbents and this adsorption behaviour are described by Langmuir model. Langmuir adsorption isotherm assumes that the monolayer adsorption occurs on a homogenous surface of the adsorbent with no lateral interaction between adsorbate molecules as shown in figure 5.

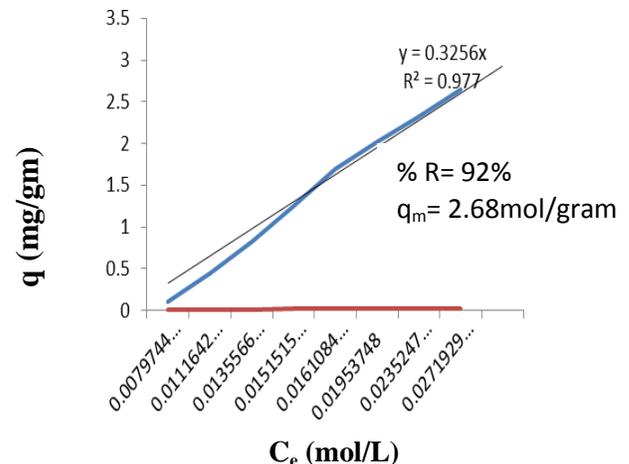


Figure 5: Langmuir adsorption isotherm for Copper

The maximum adsorption co-efficient (q_m) was calculated as 2.68mol/gm for the Langmuir adsorption isotherm model. The value of %R calculated was 92% for 0.19gm adsorbent.

3.4. Effect of adsorbent and its optimized condition

The adsorption process is dependent upon the amount of adsorbent as shown in figure 6.

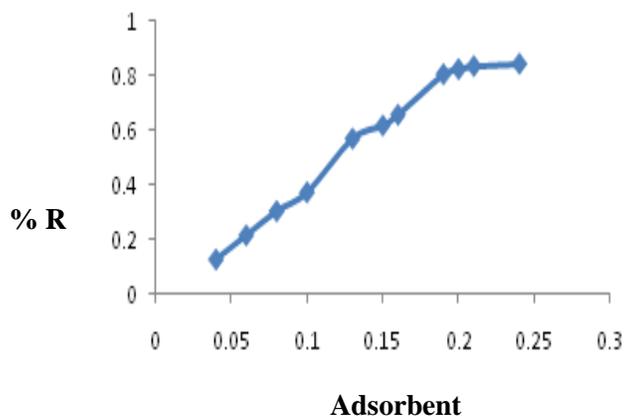


Figure 6: Effect of adsorbent on the adsorption of copper metal ions

The adsorption is negligible in the beginning as the adsorbent is very low (0.03gm to 0.05gm) in quantity, as soon as amount of adsorbent is increased (0.04gm to 0.19gm) the more metals are happened to be adsorbed hence adsorption capacity is increased very fast. It also showed that there is no further increase in recovery of metal ions when the amount of nanosorbents was above 0.19 gm. The reason for the decrease in adsorption capacity beyond the optimize quantity is the fully occupied reaction sites and no more sites are available for further chelation or complexation. Hence 0.19 grams are taken as an optimized amount for the maximum adsorption.

3.5. Effect of pH and its optimization in adsorption of Cu (II)

The effect of pH on ion exchange (surface adsorption phenomenon) of Cu^{2+} was studied at room temperature by varying the pH of reaction medium ranges from 2 to 10 while keeping constant other parameters. It was observed that adsorption was highly pH dependent in the beginning when pH was 2-4 in range; adsorption was found to be negligible. As soon as pH was increased from 4-6, adsorption also increased, it continued to increase till pH reached 6.5 as shown in figure 7.

Adsorption was maximum at pH 6.5 and started decreasing beyond this value. This suggests that at lower pH, the concentration of H^+ ions is higher and it competes for chelation or complexation with metal ions on the reaction sites. At higher pH, OH^- would dominate in reaction medium and metal ions would have a tendency to get precipitated in the form of metal hydroxides. Hence, fewer metal ions would escape binding with reaction sites [33]. For this reason pH, 6.5 had been taken as an optimized value for further adsorption process. Therefore optimization of pH is necessary for quantitative recovery of metals.

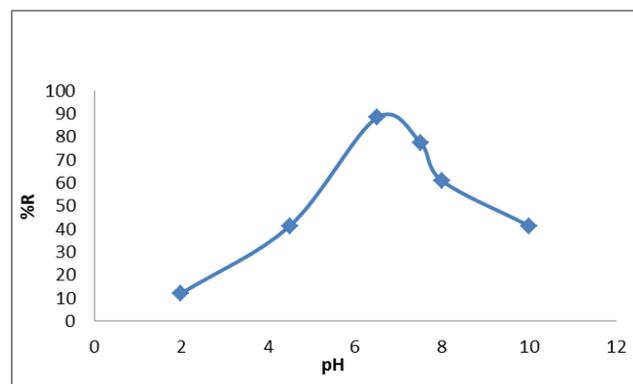


Figure 7: Effect of pH on the adsorption of copper metal ions

3.6. Effect of time on the adsorption capacity and its optimized condition

The adsorption process is time dependent as shown in figure 8. In this regard effect of time on adsorption was tested through a range of 5 minutes to 20 minutes. In the beginning adsorption of metal ions is almost negligible between time intervals 5-8 minutes. After that when time is increased for 10-15 minutes adsorption process increases and at 15 minutes maximum adsorption is reported. After 15 minutes further increased in time for a fixed amount of adsorbent (0.19 gram), adsorption starts decreasing. The reason behind this is no available reaction sites for further complexation with metal ions. Hence 15 minutes have to be considered as an optimized time for the adsorption. The percentage uptake of metal ions is highly dependent upon the initial concentration of metal ions and the nanosorbents. The maximum recoveries of Cu^{2+} were found (98 %) at pH=6.5.

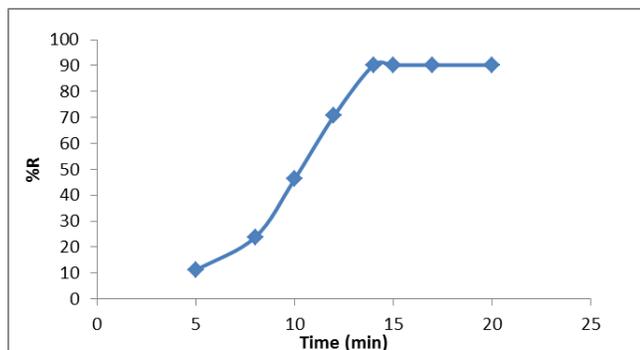


Figure 8: Effect of time on the adsorption of copper metal ion

3.7. Desorption and regeneration study

Desorption study is carried out by mixing 10 ml of 0.1M HCl with 0.19 gram adsorbent in a beaker followed by stirring on an ultrasonic stirrer for 15 minutes at room temperature. After that magnetic nanosorbent were separated by applying external magnetic field and the concentration of the eluted metal ions in the filtrate were measured with the help of calibration graph of Cu^{2+} by measuring the absorbance using UV-Visible Spectrophotometer. It was observed that desorption of Cu^{2+} in the beginning were 90-95%. Elution of metal ions is quite satisfactory till more cycles.

IV. CONCLUSION AND OUTLOOK

A new synthetic method for the preparation of nonporous silica based on the sol-gel process was investigated. Amorphous silica nanoparticles with regular spherical structure were obtained successfully using TEOS as a precursor. In order to achieve the best conditions for performing silica nanoparticles, the optimal parameters should be considered. It was found that the inner diameter of nanopore was about 25-55 nm. SEM study provided the conclusive evidence of their successful synthesis. It was found that the uptake of Cu^{2+} from aqueous solution by the nanosorbents by EDX analysis. The effects of PH, initial concentration of Cu^{2+} , amount of adsorbent and contact time on the adsorption capacity were studied. Adsorption isotherms were described by Langmuir equations with maximum adsorption capacity of 2.68mol/gm. It was observed that the adsorption was pH dependent and adsorption mechanism was noted as ion exchange. Reaction parameters were optimized for the maximum adsorption and found that 0.19 gram adsorbent was enough to extract 92% Cu (II) at pH 6.5 within 15 minutes.

Hence silica nanocomposite as an adsorbent would be a better option in remediation technology of waste water especially polluted with heavy metals due to its high adsorption capacity and easy separation ability.

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