

Removal of Cu (II) from Water Using Hydrothermally Synthesized Strontium Doped Zirconium Oxide Nano Adsorbents

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Abstract

Strontium doped zirconium oxide (SZO) nano particles were synthesized by a hydrothermal particle growth technique and were employed for removal of Cu (II) from water. The synthesized nano adsorbents were characterized by Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS) and UV-visible spectral studies. The adsorption experiments were affected in batch to establish the influence of pH, contact duration/time, temperature and initial metal ion concentration on adsorption efficiency. This work demonstrates the success of employing SZO nano adsorbents towards efficient removal of Cu (II) from water.

Keywords: Hydrothermally; Strontium; Nano adsorbents; Hydrothermal; Microscopy

Introduction

The substantial increase of toxic heavy metal ion discharge has imposed the scientific community to design novel eco-friendly strategies of heavy metal ion treatment through various physico-chemical methods, owing to its hazardous effects on environmental biota. Some of the major causative metals of heavy metal ion pollutants include copper (Cu), chromium (Cr), lead (Pb) and so forth.

The burgeoning sources of heavier metallic ions in potential water bodies encompass metal ions from fertilizers, chemical fungicides and metallic residues from paint pigment industries [1]. These heavy metal ions are known to effect the survival, when followed inappropriate disposal techniques. However, the rapidly increasing heavy metal content has also led to an exponential increase in the number of strategies (physical/chemical) employed towards affecting efficient heavy metal amputation including ion exchange methodologies, precipitation and flocculation techniques in addition to various membrane processes [2-6]. Among, the available strategies, heavy metal removal through physisorption (physical adsorption) is considered as a synergistic technique that aids cost cutting in addition to high removal efficiencies. The rate of physisorption is however dependent on the porosity of the adsorbent in addition to larger available surface areas and a relatively smaller diffusion resistance [7,8]. Thus, nano sized metal oxide fillers with high surface areas and higher affinity to heavy metallic ions are considered potential heavy metal adsorbents. Wherein, the electron rich oxygen centres affect efficient removal of heavy metal ions from their solutions through surface adsorption of heavy metal ions on nano ceramic adsorbents [9-15]. Thus, in this investigation, an attempt is made to establish the heavy metal ion Cu(II) adsorbing efficacies of hydrothermally developed SZO nano particles through physical adsorption [16]. However, the partial solubilities of metal oxide nano ceramic during adsorption studies may also lead to toxic effects, Cu (II) solutions are made to encounter a dual filtration technique wherein, the nano particle treated Cu(II) solutions are passed through charcoal which owing to its high porosity affects Cu(II) coated SZO nano particle entrapment leading to enhanced heavy metal ion amputation. The effects of hydronium ion content (pH), contact time and temperature on adsorption kinetics have also been established.

Experimental and Materials

Materials and methods

The strontium doped zirconium oxide nano particles were synthesized by hydrothermal route [17-19] using strontium nitrate [Sr(NO₃)₂], Zirconyl nitrate [ZrO(NO₃)₂] and Hexa methylene Tetra ammine (HMTA)[(CH₂)₆N₄], obtained from Sigma-Adrich. The Copper sulphate [CuSO₄.6H₂O] used in the metal sorption experiments were procured from Merck. Double distilled water used for solution preparation. All the reagents employed were of analytical grade and were used as such, without any further purification. The as synthesized nano sized adsorbents were characterized by X-ray powder diffraction measurements affected by Bruker X-ray diffractometer with CuKα as the radiation source, while optical properties of strontium doped Zirconium oxide nano particles were established by electronic (UV-visible)spectral studies using Shimadzu UV-1800 spectrophotometer. The quantification of Cu(II) content before and after adsorption were achieved using Shimadzu AA-680/G atomic absorption spectrophotometer, while ELICO (Model-LI 617) was used for pH measurements.

Synthesis of strontium doped zirconium oxide (SZO) nano particles

SZO nano particles were developed through hydrothermal technique involving high temperature/elevated pressure route. The synthesis involved homogenisation of 1:1 molar concentrations of Sr(NO₃)₂ : ZrO(NO₃)₂ in 100 ml of distilled water by mechanical shearing for 2h. Stoichiometric amount of HMTA was then added to the homogenised mixture so as to maintain Sr(NO₃)₂ : ZrO(NO₃)₂ : (CH₂)₆N₄ in the molar ratios of 1:1:1.5. The solution was then autoclaved

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for at 95°C for 2h and the resultant powder was then subjected to high temperature (~600°C) annealing in oxygen atmosphere to obtain the desired nano particles.

Batch studies to quantify Cu (II) adsorption measurements

The adsorption measurements were affected in 250 ml beakers containing 50 mgL⁻¹ acidified (pH = 4) Cu (II) solutions added with 0.3 g of SZO nano particle. The effect of pH on adsorption kinetics were monitored by suitably altering the hydronium ion concentration in the solutions using NaOH/HNO₃. The suspension were then subjected to mechanical shearing at various contact times at ambient temperatures.

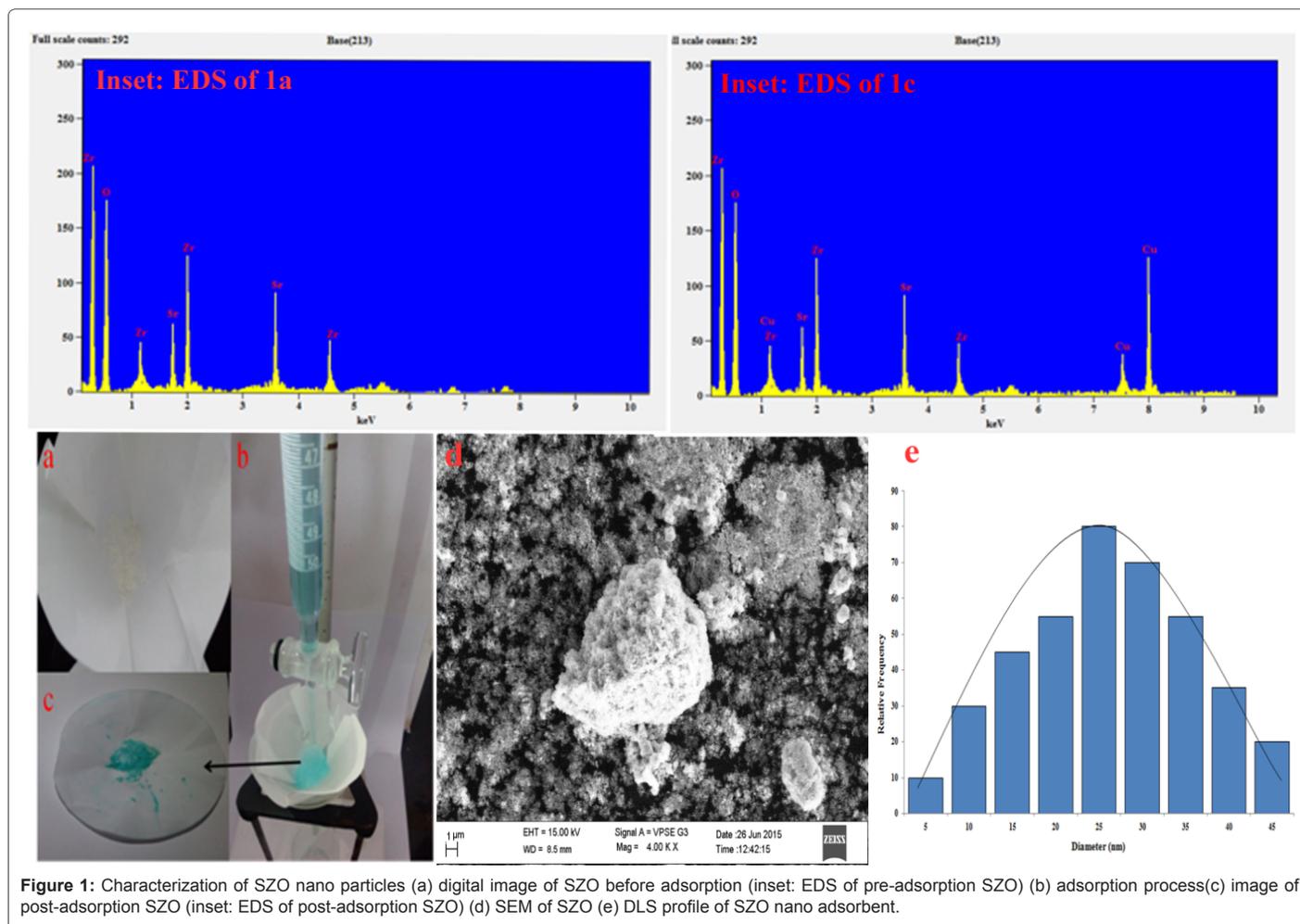
Results and Discussions

Characterization of SZO nano particles

The success of SZO nanoparticle synthesis was assessed by energy dispersive x-ray (EDX) spectral studies (Figure 1a), which shows EDX characteristic peaks at binding energies corresponding to Sr, Zr and While, Scanning electron microscopic (SEM) images (Figure 1d) support the porous nature of SZO particles that aid enhanced metal ion adsorption abilities. Furthermore, the photographic images (Figure 1c) validates the Cu(II) adsorption abilities of SZO nano particles, with otherwise whitish powders appearing bluish green after Cu(II), which is also established by EDX profiles (Figure 1c) of post adsorption SZO particles.

Effect of pH: The effect of hydronium ion concentration on the rate of Cu(II) adsorption was established by carrying out adsorption studies at varied pH conditions by adding appropriate quantities of NaOH and HNO₃. As can be seen from Figure 2, the Cu(II) adsorption was relatively low under strongly acidic conditions (pH < 2). However, an increase in pH brought about significant enhancement in metal ion adsorptions, showing an adsorption maximum of 77% at pH 4. A further increase in pH, however decreases the adsorption rate. The observed trend may be attributed to the possible changes in the surface charges of SZO nano particles on increasing the solution basicity. The adsorption studies are usually affected using lower pH solutions, since at higher pH there exists a possibility of precipitation of metallic ions as their respective hydroxides [20]. With increasing pH favouring the deprotonation of nano sorbent surface [21,22], the higher pH values affect greater deprotonation leading to a substantial increase in the negatively charged sites enhancing the attractive forces between the sorbent surface and electropositive Cu(II) ions thereby enabling increased adsorption. In contrast, the low pH regions are dominated by positively charged sites that augments the repulsive forces between the sorbent surface metal ion leading to decreased adsorption.

Effect of contact time: The time required to equilibrate the adsorption of Cu(II) ions on SZO nano particle surface were optimized by probing the adsorption kinetics at varying contact times. As can be seen from Figure 3, contact time is a detrimental factor in the adsorption process and a maximum of 91% removal efficiency was achieved after



two hours of adsorbate/adsorbent contact, however, a further increase in contact duration brought about a decreased adsorption, owing to the decrease in the adsorption sites at contact times greater than the optimum levels. Therefore, two hours is the optimum contact time which was upheld throughout the studies.

Effect of temperature: The adsorption studies was also carried out at five different temperatures 290, 295, 300, 305 and 310 K, so as to establish the effect of varying temperature on adsorption efficacy of SZO nano particles. As can be seen from Figure 4, the maximum adsorption occurred at 295K and further increase in temperature decreases the adsorption efficacies, thereby indicating the process is exothermic.

Effect of initial metal ion concentration: The effect of metal ion content on the adsorption of Cu(II) was studied for concentration of (0.2-1.4 g/L). From Figure 5, the dosage of 1.4 g/L brings about maximum adsorption. However, there was no appreciating change in percentage adsorption of heavy metals after a dosage of (1.4 g/L). Hence 1.4 g/L is considered as optimum dosage for maximum removal of Cu(II) by SZO nano particles.

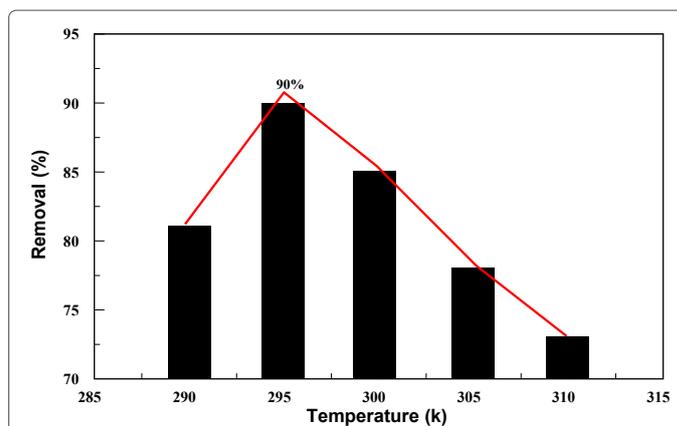


Figure 4: Effect of temperature on adsorption efficacy of Cu(II) ions by SZO nano particle.

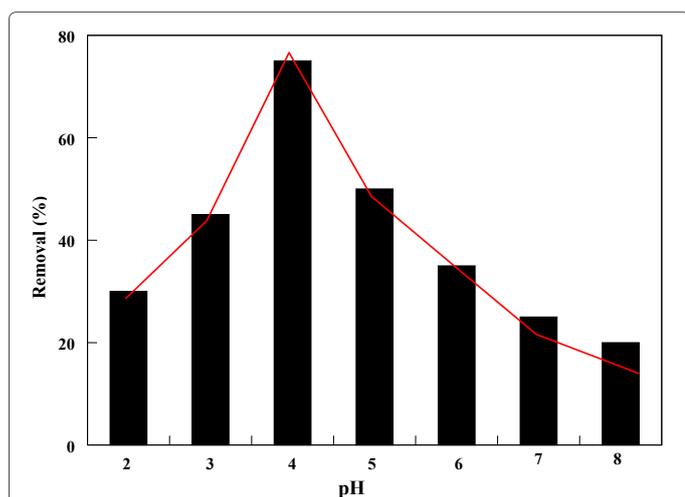


Figure 2: Effect of pH on adsorption efficacy of Cu(II) ions by SZO nano particle.

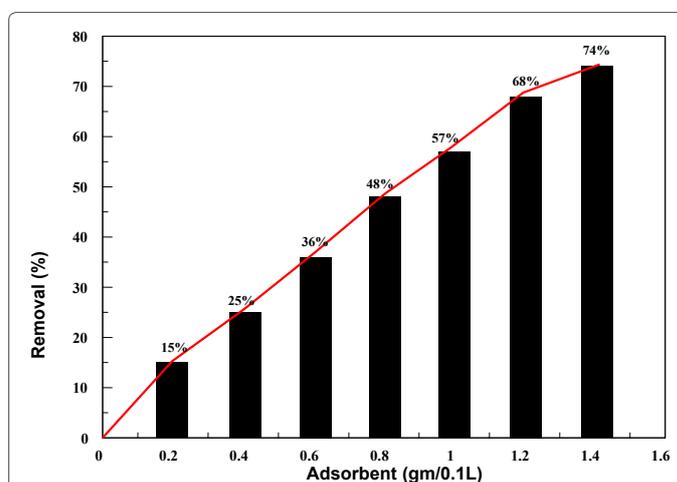


Figure 5: Effect of initial metal ion concentration on adsorption efficacy of Cu(II) ions by SZO nano particle.

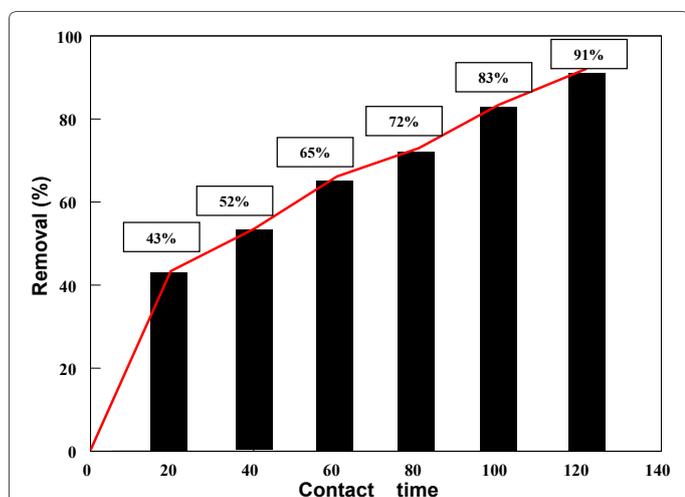


Figure 3: Effect of contact time on adsorption efficacy of Cu(II) ions by SZO nano particle.

Conclusion

Nano sized strontium doped Zirconium Oxide (SZO) was developed through hydrothermal synthetic route. The adsorption studies revealed that SZO particles with its high surface areas bring about efficient adsorption of Cu(II) in water, with post adsorption SZO nano particles showing EDS peaks for Cu in addition to Sr, Zn and O supporting the possible application of adsorption methodology towards developing Cu coated nano metal oxides. The adsorption efficiency was also established by UV-visible studies, with Cu deposited SZO nano particles showing a red shift in adsorption edge substantiating the presence of Cu(II) in SZO surface. The adsorption efficacy was found to maximum at optimum pH and temperature of 4 and 298K respectively. Furthermore, the observed results substantiate the possible applications of SZO nano particles for adsorption of heavy metals in waste water treatment.

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