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Short communication

Synthesis, characterization and application of zinc oxide nanoparticles (n-ZnO)

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Abstract

In present study, zinc oxide (n-ZnO) nanoparticles were synthesized by simple solution based approaches. Synthesized n-ZnO particles were characterized by XRD, TEM, SEM and FTIR. XRD and TEM confirmed the formation of nanosized zinc oxide particles in the size range of 18–31 nm. n-ZnO nanoparticles were used for the removal of Cd(II) from aqueous solutions. A high (92%) removal Cd(II) from its aqueous solutions with initial concentration of 200 mg/L by n-ZnO particles was achieved. Further, the nanoparticles were efficient at other concentrations also.

Keywords: A. Calcination; Characterization; Cd(II); Nanoparticles; Zinc oxide

1. Introduction

In recent years, application of nanoparticles within size range of 1–100 nm has received significant attention due to their novel properties and has come up as an area of extensive research [1–4]. Nanoparticles differ in characteristics from those of bulk materials [5]. Due to numerous applications, studies on the synthesis, characterization and properties of nanoparticles have received significant attention in the past several years. Among various of nanoparticles, ZnO nanoparticles (n-ZnO) have received more attention. ZnO is a wide band gap semiconductor having large excitation binding energy of 60 meV at room temperature and it has high transmittance and good electrical conductivity also [6]. ZnO's resistance to radiation damages make it useful in various space applications [7]. ZnO nanoparticles have widespread applications as biosensors, gas sensors, solar cells, ceramics, nanogenerators, photo detectors, catalysts, active fillers for rubber and plastic, UV absorbers in cosmetics and anti-virus agent in coating, pigments, optical materials, cosmetics, photocatalytic, electrical and optoelectronic processes and systems and additives in many industrial products [8–16] and in treatment of water and waste water [17] also. Various approaches have been employed to synthesize ZnO nanoparticles (n-ZnO). Sol–gel, spray pyrolysis, microemulsion techniques, thermal evaporation, laser ablation, chemical vapor deposition, mechanical milling, microwave method and hydrothermal synthesis are some of the methods which are employed for synthesis of naoparticles [18–28]. However, in most of these techniques, nanoparticles tend to agglomerate due to their high surface energy. Among the above techniques, solution-based approach is simplest. In this technique, morphology of nanoparticles can be controlled by optimizing various reaction conditions such as pH, concentration of precursors, temperature and reaction time [29]. Recently nanoparticles have been utilized for treatment of water and wastewater. The nanoparticles offer various advantages over usual adsorbents that the nanoparticles offer a 'high surface area to volume ratio'. Nanoparticles have larger active sites for the interaction of pollutant species.

In the present work, ZnO nanoparticles have been synthesized by solution-based approach and characterized by various techniques. Further, some of the preliminary experiments have been carried out to investigate the efficiency of synthesized nanoparticles (n-ZnO) for removal of highly toxic metal, Cd(II) from its aqueous solutions.

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2. Materials and method

2.1. Synthesis of zinc oxide nanoparticles

For synthesis of n-ZnO particles, 0.2 M solution of zinc chloride was prepared by dissolving zinc chloride ($ZnCl_2$ dry purified powder, Merck, 136.28 g/mol) in distilled water. After preparation of $ZnCl_2$ solution, ammonium hydroxide was drop wise added to it from burette. The reaction mixture was continuously stirred in a magnetic stirrer at room temperature till complete precipitation. The precipitate was washed with distilled water and then dried in a hot air oven at 100 °C for complete drying. Dried precipitate was crushed, milled and then sieved to get uniform sized particles. After sieving, the precipitate was calcined in a muffle furnace (Libratherm Instrument PID 300 Naskar & Co.) at 450 °C for 2 h by keeping the heating rate at 5 °C. The sample of ZnO was characterized by X-ray diffraction (RIGAKU, MINIFLEX II, Desktop X- Ray Diffractometer, Japan), Transmission Electron Microscopy (TECHNAI 200 kV, HR-TEM), Scanning Electron Microscopy (INSPECT S50, MAKE FEI) and Fourier Transform Infra Red Spectroscopy (Varian 1000 FT-IR, Scimitar Series).

2.2. Adsorption experiment

Stock solution of Cd was prepared by dissolving cadmium chloride (Merck, Mumbai, India) in double distilled water. The working cadmium solutions of different concentrations were prepared by diluting the stock solution. Experiments were carried out in batch mode to study the adsorption/removal efficiency of n-ZnO particles. For batch experiments, 0.10 g of nanoparticles were added in 50 mL of cadmium solution of different concentrations viz. 20, 50,100 and 200 mg/L in capped reagent bottles and the solutions were agitated on a thermostatic water bath shaker. After 1 h, the nanoparticles were separated from the solution by filtration. The residual concentration of Cd(II) in aliquot was determined by Atomic Absorption Spectrophotometer (AA 7000, Shimadzu, Japan). All the removal experiments were carried out in duplicate and average value of each result were used for accuracy of the results. The percentage removal of Cd(II) in aqueous solutions and the amount of Cd(II) ions adsorbed per unit mass of the adsorbent were calculated as follows:

$$\text{Removal of Cd(II) ions} = \left(\frac{C_i - C_e}{C_i}\right) \times 100 \tag{1}$$

$$q_e = \left(\frac{C_i - C_e}{W}\right) \times V \tag{2}$$

where, C_i and C_e are the initial and equilibrium concentrations (mg/L) of Cd(II) respectively and q_e is the amount of Cd(II) adsorbed per unit mass of nanoparticles.

3. Results and discussions

Following reaction is supposed to take place in the preparation of nanoparticles of zinc oxide:

$$ZnCl_2 + NH_4OH \rightarrow Zn(OH)_2 + 2NH_4Cl \qquad (\text{Step} - 1)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \qquad (\text{Step} - 2)$$

In step I, zinc chloride gives precipitate of zinc hydroxide with ammonium chloride in a ratio of 2:2. Further, after washing, drying and on calcination of dried precipitate of zinc hydroxide, the nanoparticles of zinc oxide are obtained in controlled atmosphere. Calcination of zinc hydroxide at 450 °C resulted in the formation of the n-ZnO in smaller range. During calcination, OH of hydroxide gets eliminated in form of H_2O while ammonium chloride is removed in form of ammonia gas. XRD of dried precipitate and n-ZnO are shown in Figs. 1 and 2. XRD of dried precipitate and n-ZnO was matched with the standard data using JCPDS files for qualitative phase analysis. Fig. 1 shows the formation of zinc hydroxide during precipitation of zinc chloride with ammonia solution. Some peaks of ammonium chloride were also observed in XRD of dried precipitate. Comparing this with standard data, it was observed that all the peaks were matched with the standard data of

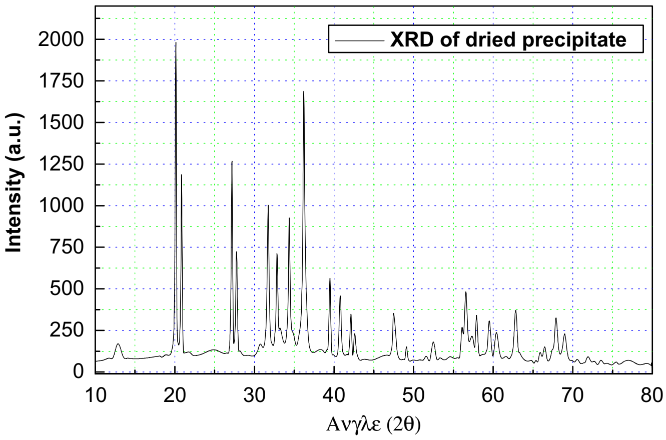

Fig. 1. XRD of dried precipitate.

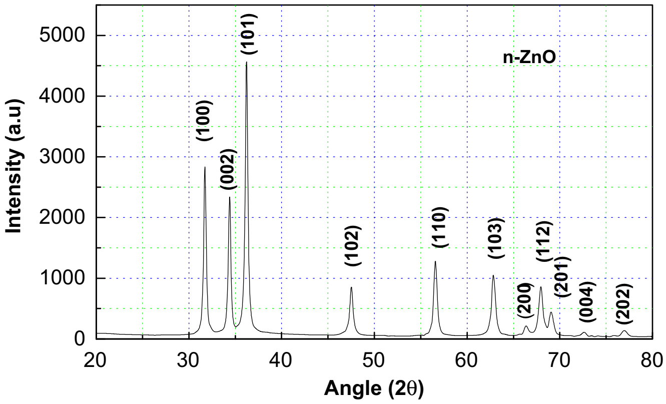

Fig. 2. XRD of zinc oxide nanoparticles.

hexagonal phase of zinc oxide (JCPDS card no. 36-1451) (Fig. 2). Various details regarding XRD of n-ZnO are given in Table 1. No peaks of any other phase were observed confirming synthesis of pure zinc oxide powder in the process.

Different particle sizes of n-ZnO particles (nm) determined by the XRD data are shown in Fig. 3. It is clear from Fig. 3 that particles are in the range of 18–31 nm. The width of XRD peaks is related to crystallite size. Scherrer equation [30] was used for calculating the average crystallite diameter

$$D = \frac{(k\lambda)}{(\beta \cos\ \theta)} \tag{3}$$

where D is mean crystallite size of the powder, θ is the Bragg diffraction angle, β is the full width at half-maximum, λ is the wavelength of Cukα and k is a constant.

Table 1
Different angles and their corresponding hkl values with FWHM and size.

Angle,2θ(deg)	hkl	FWHM(deg)	Size(nm)
31.724	100	0.3045	28.32
34.4051	002	0.3084	28.16
36.1505	101	0.2795	31.22
47.4705	102	0.34	26.65
56.5657	110	0.3633	25.93
62.7389	103	0.4267	22.77
66.3518	200	0.3607	27.48
67.8606	112	0.4799	20.84
69.0275	201	0.5587	18.02
76.8405	202	0.5585	18.96

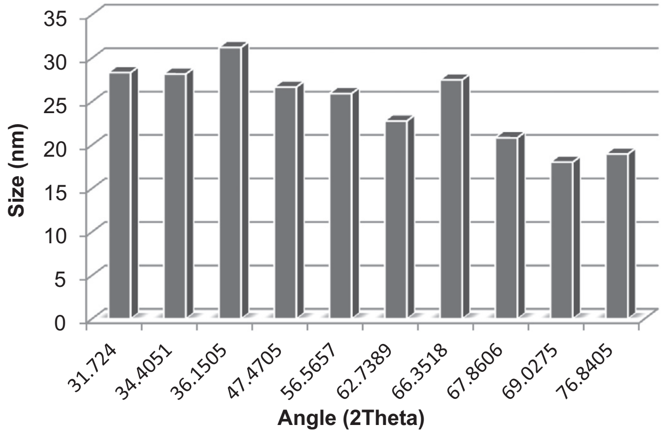

Fig. 3. Variation of particle size of zinc oxide nanoparticles.

TEM images of the nanoparticles confirm the formation of ZnO nanoparticles in the range of 17–50 nm (Fig. 4a and b). The difference between particle size variation in TEM and XRD data may be due to agglomeration of powder.

SEM of precipitate and n-ZnO powder is shown in Fig.5 and 6. It is clear from the SEM of precipitate that particles are in 95–450 nm range. Some rod shaped structures were also observed in the precipitate. Fig.5b indicates that the particles were found to be in less than 100 nm range. Due to high surface area and surface energy, n-ZnO particles were found to agglomerate resulting in bigger size particles. Similar results were also observed by other researchers [31].

The FT-IR spectroscopy is the powerful technique for the analysis of structure of compounds. The FTIR of precipitate and n-ZnO particles is shown in Fig. 7. A broad absorption peak in the range of 3000–3500 cm^{-1} is present in both the figures which can be attributed to the characteristic absorption of hydroxyl groups (O–H) [32,33]. Presence of absorption peak at 1385 cm^{-1} is attributed to ammonium ion angular deformation.

Peaks at 1635 cm^{-1} is due to bending of water molecules. The peak in the range of 450–500 cm^{-1} is due to the presence of Zn–O bond [34,35]. Some unresolved peaks in precipitate may be due to some impurities.

Fig. 8a and b depict the % removal of Cd(II) from aqueous solutions and amount of Cd(II) adsorbed per unit mass of adsorbent(mg/g) respectively. It is clear from this figure that ZnO nanoparticles showed high removal efficiency for Cd(II). For the 20 mg/L of adsorbent dose, the removal was ~55%

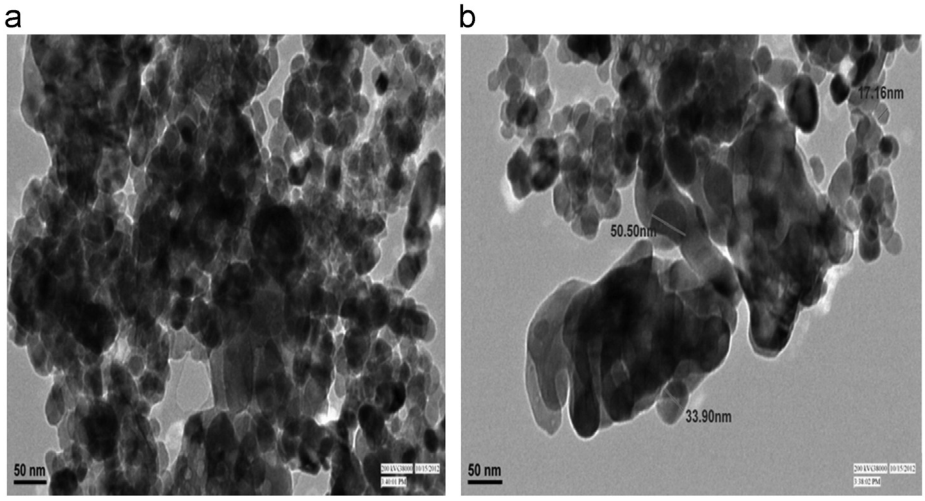

Fig. 4. a,b TEM figures of zinc oxide nanoparticles.

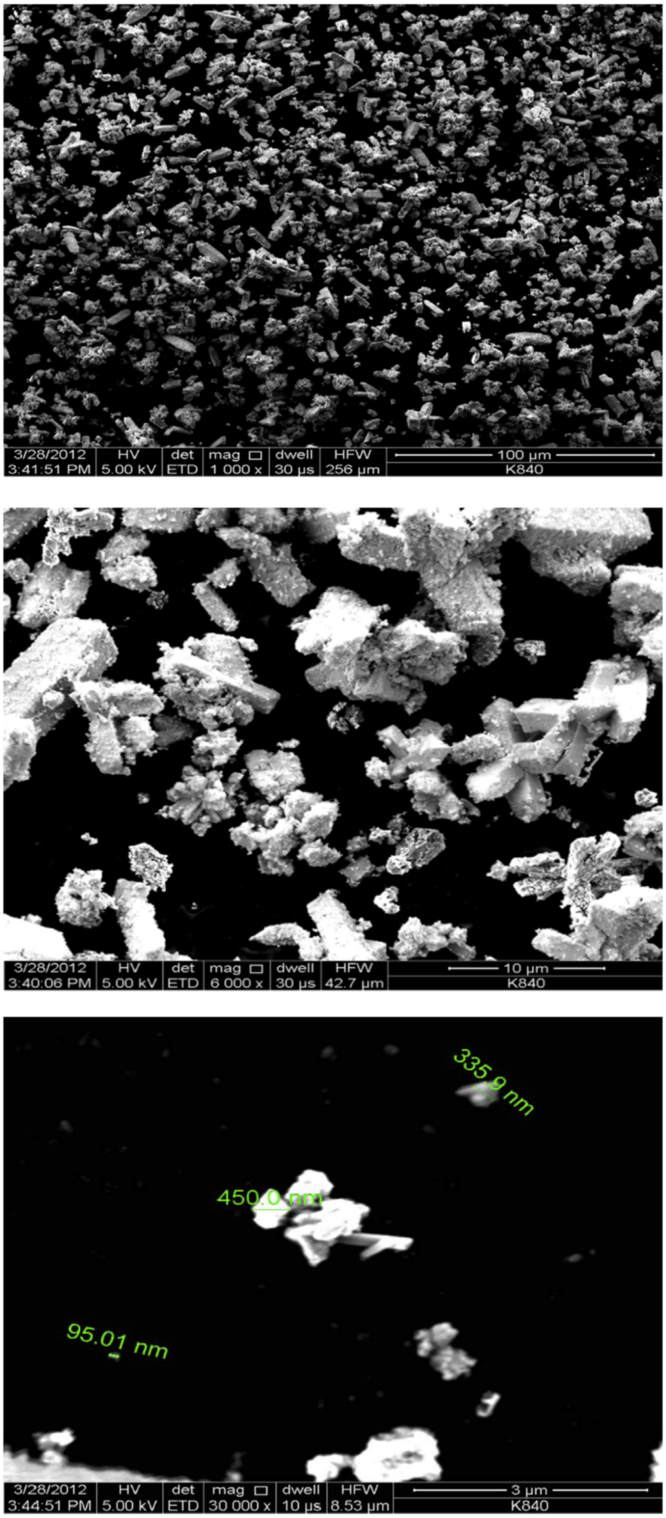

Fig. 5. a, b,c. SEM of dried precipitate at different magnifications.

and on increasing the dose to 200 mg/L, a 92% removal of Cd (II) within the 1 h of contact time was achieved. Thus, the n-ZnO could be successfully used for the removal of Cd from effluents. Further study on the optimization of removal process and kinetic and isotherm study are in progress.

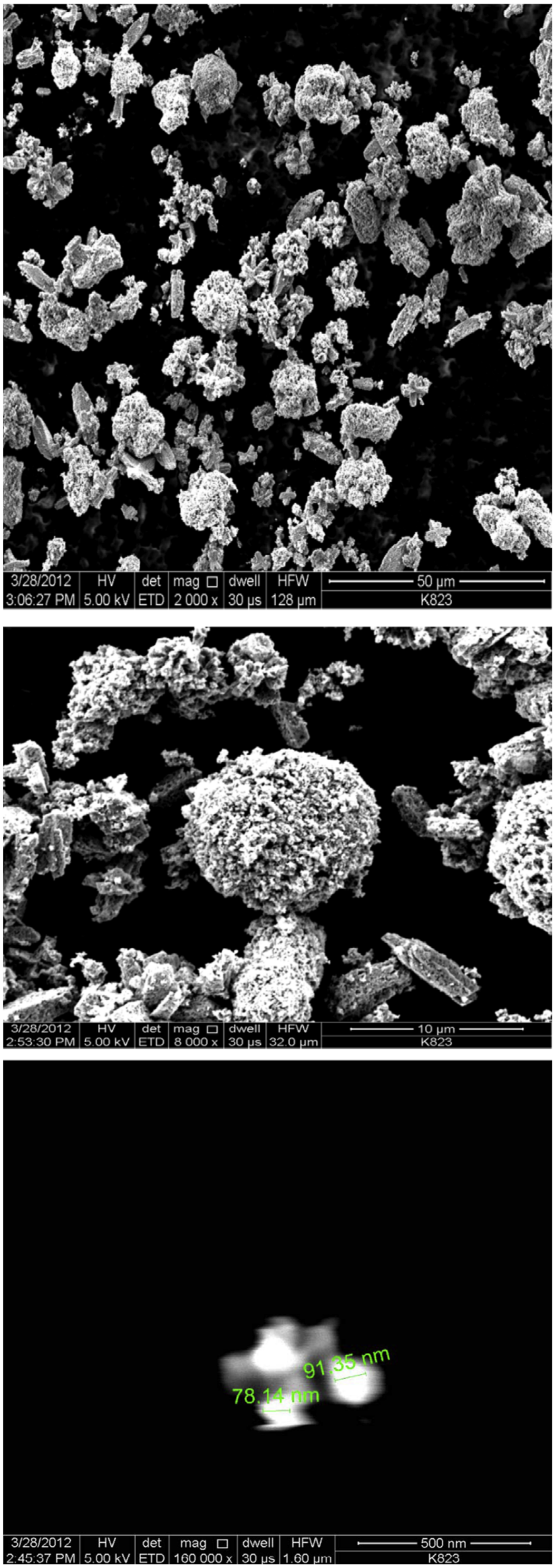

Fig. 6. a,b,c. SEM of zinc oxide nanoparticles at different magnification.

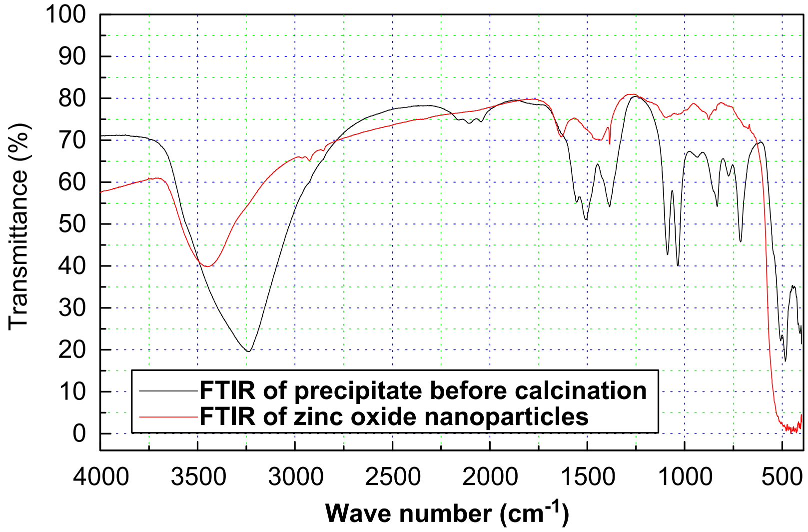

Fig. 7. FTIR of precipitate and zinc oxide nanoparticles.

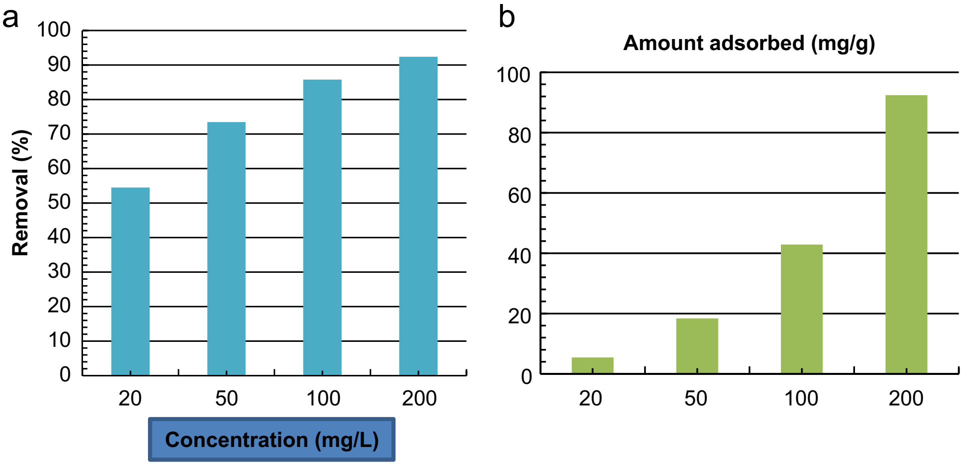

Fig. 8. a Removal(%) of Cd(II) from aqueous solutions and b amount of Cd(II) adsorbed per unit mass of adsorbent(mg/g).

4. Conclusions

On the basis of this study following conclusions may be drawn:

Nanoparticle of zinc oxide (n-ZnO) have been synthesized by the sol–gel method, a simple solution based approach.
Characterization of the nanoparticles was carried out by XRD,TEM and SEM. On comparison with standard data, it was observed that mostly peaks were matched with hexagonal ZnO.
Further, the nanosize of synthesized zinc oxide particles was confirmed by XRD and TEM. SEM of synthesized particles indicates the agglomerated particles. Some n-ZnO was also found as nanorods.
FTIR of nanoparticles confirmed presence of specific absorption peak of Zn–O bond.
The n-ZnO particles displayed significant efficiency of removal (~92%) of Cd(II) from aqueous solutions.
It seems that the n-ZnO particles can serve as an excellent material for the removal of Cd(II) from effluents.

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