

# Cadmium Filter Cake of a Hydrometallurgical Zinc Smelter as a New Source for the Biological Synthesis of CdS Quantum Dots

Mehran Bakhshi, Mohammad Raouf Hosseini, Mohammadhosein Rahimi

**Abstract**—The cadmium sulfide nanoparticles were synthesized from the nickel-cadmium cake of a hydrometallurgical zinc producing plant and sodium sulfide as  $\text{Cd}^{2+}$  and  $\text{S}^{2-}$  sources, respectively. Also, the synthesis process was performed by using the secretions of *Bacillus licheniformis* as bio-surfactant. Initially, in order to obtain a cadmium rich solution, two following steps were carried out: 1) Alkaline leaching for the removal of zinc oxide from the cake, and 2) acidic leaching to dissolve cadmium from the remained solid residue. Afterward, the obtained  $\text{CdSO}_4$  solution was used for the nanoparticle biosynthesis. Nanoparticles were characterized by the energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) to confirm the formation of CdS crystals with cubic structure. Also, transmission electron microscopy (TEM) was applied to determine the particle sizes which were in 2-10 nm range. Moreover, the presence of the protein containing bio-surfactants was approved by using infrared analysis (FTIR). In addition, the absorbance below 400 nm confirms quantum particles' size. Finally, it was shown that valuable CdS quantum dots could be obtained from the industrial waste products via environment-friendly biological approaches.

**Keywords**—Biosynthesis, cadmium cake, cadmium sulfide, nanoparticle, zinc smelter.

## I. INTRODUCTION

NANOTECHNOLOGY has developed as a new thrilling aspect of material research [1], [2]. The optoelectronic and physicochemical properties of materials are size and shape dependent [3]. As the size of a semiconductor crystallite approaches the exciton Bohr diameter, its electronic and optical properties change [4], [5]. Quantum dots of II-VI semiconductors have attracted particular attention, as they are rather easy to synthesize in the size range essential for quantum confinement [6]-[8]. Generally, the smaller the crystal size, the greater the band gap, and consequently the wider the space between the energy of the highest valence band and the lowest conduction band. Hence, more energy is required for crystal excitation, and more energy is released when it returns to the resting state [5].

Nanomaterials are synthesized by implementing physical, chemical, and biological methods [2], [7]. The chemical

process includes the rapid injection of reagents into a hot solvent to start nucleation followed by crystal growth to obtain nanoparticles [9]. The use of some biological reagents such as carbohydrates, peptides, nucleotides, and fusion proteins, has also been proposed for nanocrystal production.

Microorganisms such as bacteria, yeast, and fungi which have widely exploited in the remediation of toxic metals through the reduction of metal ions, now are in the center of interest as nanofactories [10]. It is believed that nanoparticle synthesis through biological methods is simple, safe, and environmentally friendly [2], [6].

Cadmium sulfide (CdS) with a direct band gap of 2.43 eV at room temperature is an important semiconducting material due to its unique electronic, electrical, magnetic, and optical properties [2], [5], [11]. So, among the various quantum dots, the properties of CdS nanocrystals which differ from the bulk material and even single atom [5], [10], [11] have led to an increasing interest in energy, magnetics, and biomedical applications [10]. These properties are the result of high surface to volume ratio of CdS nanoparticles [5].

CdS nanoparticles have been biologically synthesized using a wide range of microbes, like *Fusarium oxysporum* [3], [12], *Schizosaccharomyces pombe* [13], *Rhodospseudomonas palustris* [3], *Coriolus versicolor* [14], and *Escherichia coli* [15]-[18].

However, all the previous research utilized commercial, reagent-grade chemicals as the cadmium source. Consequently, high costs of the raw chemicals could limit the production and utilization of the nanoparticles in full-scale engineering processes. Therefore, other low-cost resources should replace the pure commercial chemicals [19]. Filter cakes of hydrometallurgical zinc smelting companies which contain a large amount of zinc, cobalt, nickel, and cadmium can be considered as the secondary important source of cadmium.

The hazardous high-cadmium content of filter cake that is around 8-12% wt. poses an inevitable risk to public health and the environment. So, the recovery of metals from nickel-cadmium cake, and controlling its threat is a great concern among researchers not only for the environmental concerns but also for the economic reasons [20].

In this study, biosynthesis of CdS nanoparticles from the leaching solution of a cadmium filter cake using *Bacillus licheniformis* is reported. Also the obtained nanoparticles were characterized by XRD, TEM, EDS, FTIR, and UV-vis analyses.

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## II. MATERIALS AND METHODS

### A. Materials

The Ni-Cd filter cake was obtained from the Isfahan Zinc Smelting Company (IZSC), Isfahan, Iran. Also, the bacterium *Bacillus licheniformis* PTCC1320 was purchased from the Iranian Research Organization for Science and Technology (IROST). In addition, all chemicals were purchased from Titrachem®, Iran.

### B. Cadmium Recovery

Cadmium was recovered from Ni-Cd cake by using a two-step leaching process. Firstly, the zinc content of the cake was separated by using an alkaline leaching process. Then, nickel and cadmium metals were extracted by an acidic leaching.

Leaching processes were carried out for one hour in a beaker placed in a thermostatically controlled water bath (75 °C), and using an agitator (500 rpm). In the first alkaline leaching test, 50 g solid residue was dissolved in 500 ml of 8 M sodium hydroxide to remove the zinc contents. Afterward, the residue was undergone the second alkaline leaching step using the same settings. The final residue was washed, dried, and transferred to 80 g/L (pH 1-1.5) sulfuric acid solution (liquid/solid: 10/1) and agitated for 1.5h [21]. Finally, the obtained green filtrate was analyzed by using ICP-MS (Varian 735, Australia). Also, in order to minimize the amount of dissolved elements other than cadmium, pH of the solution was adjusted to 7.5, and the precipitates separated by filtration. The final cadmium rich solution (Fig. 1 (a)) was kept for the biosynthesis process.

### C. Synthesis of CdS Nanoparticles

*B. licheniformis*, previously grown on a PDA (potato, dextrose, agar) medium, was inoculated into 100 ml autoclaved (121 °C for 15 min) liquid culture medium in 500 ml flasks containing peptone, 5 g/L; meat extract, 3 g/L;  $MnCl_2$ , 10 mg/L;  $CaCl_2$ , 100 mg/L;  $MgSO_4$ , 500 mg/L, and then placed in a shaker-incubator (Jaltajhiz, Iran) for 36h at 35 °C and rotational speed of 150 rpm. Finally, the bacterial cells were isolated from the medium by centrifugation using Hettich (Universal, 320R) at 5000 rpm for 20 min and then washed with distilled water thrice. The obtained bacterial cells were transferred to a 500 ml flask including 100 ml distilled water, and incubated for 96h for the bio-surfactant production. Afterward, cells were isolated by centrifuging at 5000 rpm for 20 min, and the remaining liquid was kept for the biosynthesis

of nanoparticles.

In the biosynthesis step, 300 µl of the cadmium-containing leach solution was transferred to the biologically produced surfactants, and then, an aqueous solution of sodium sulfide was added dropwise at the rate of 0.5 ml/min under mixing condition (1500 rpm) until its concentration reached 1 mM. Again, the solution was placed in the shaker-incubator (35 °C, 150 rpm) for another 48h to complete the reaction. Finally, a yellow colloid dispersion (Fig. 1 (b)) was obtained and centrifuged at 12000 rpm for 30 min. Despite the persistent yellow color of the dispersion which was an indication of the presence of ultra-fine colloidal CdS particles, the settled powder was dried and subjected to further studies.

### D. Characterization of Nanoparticles

The formation of CdS nanoparticles was checked by the XRD technique using an X-ray diffractometer (Asenware AW/XDM 300, China) with Cu K $\alpha$  radiation  $k=1.5405 \text{ \AA}$  over a wide range of Bragg angles ( $10 < 2\theta < 80$ ). Also, FTIR spectra were recorded by using Bruker Tensor 27 (USA). The elemental composition of the prepared particles was studied by using Energy Dispersive X-ray analysis (EDS), (Seron AIS 2300, Korea). Furthermore, TEM images were obtained by Philips CM200 (Netherlands) microscope with an accelerating voltage of 200 kV. Finally, UV-Vis adsorption of the product was performed by Unico 2100 (USA) spectrophotometer.

## III. RESULTS AND DISCUSSION

In the leaching process, an alkaline dissolution step was carried out for the zinc elimination, because the applied filter cake contains a great amount of zinc oxide. In addition, second alkaline leaching was performed to maximize the zinc removal efficiency. As the solubility of cadmium and nickel are low in the alkaline pH, this process does not affect the cadmium and nickel dissolution, and they remain in the leaching residue. The acidic leaching step was conducted in order to extract nickel and cadmium from the residue in the form of metal sulfate solution. After obtaining the cadmium and nickel sulfate solution, the pH was increased to 7.5 to precipitate most of the contaminating elements including nickel. Table I indicates that after pH adjustment, cadmium has the highest concentration in the solution. The increase in the amount of sodium is due to the addition of sodium hydroxide.

TABLE I  
ELEMENTAL ANALYSIS OF THE LEACH SOLUTION (A) BEFORE, AND (B) AFTER pH ADJUSTMENT

Solutions	Elements (g/L)							
	Ni	Fe	Mn	Cd	S	P	Na	Zn
A	3.45	1.01	2.22	19.24	11.99	0.0068	4.98	2.196
B	1.31	<0.0001	1.95	17.32	11.40	0.002	14.33	0.054

Prior to the biosynthesis step, the cadmium-rich solution was diluted 330 times to reduce the cadmium concentration to 260 mg/l. Consequently, the concentration of other contaminating ions reached a very low level that could not interfere with the CdS synthesis process as their standard

reduction potential became much lower than  $Cd^{2+}$ .

In the biosynthesis process, sodium sulfide was added as  $S^{2-}$  source to electrochemically reduce the  $Cd^{2+}$  ions to CdS nuclei. After this step, the solution color turned to yellow (Fig. 1 (b)), which is a preliminary sign of CdS formation. As the

produced dispersion did not settle after months, it was speculated that the dispersion was colloidal, and the size of the particles was in the nanometer range. Moreover, even after centrifugation at 12000 rpm, the remaining liquid was still yellow, and illuminated green light under UV irradiation. This emission proves that the band gap of the particles is probably in the range of their Bohr radius. This means that they may be CdS quantum dots with semiconducting properties.

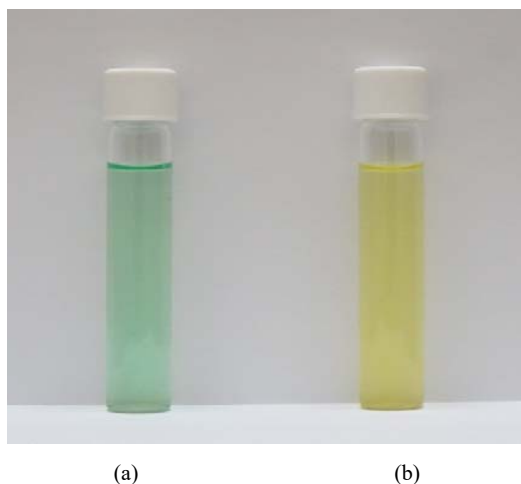


Fig. 1 The solution of (a) after leaching, (b) after NP<sub>s</sub> formation

The crystal structure of the produced nanoparticles was determined using XRD analysis. According to the results illustrated in Fig. 2, the presence of two wide peaks proves that the particles have very small crystal size. These two peaks which are located at  $2\theta$  values of  $26.784^\circ$  and  $45.364^\circ$  could be indexed to the (1 1 1) and (2 2 0) facets of the cubic phase CdS nanoparticles. The observed pattern is in good agreement with the reference code of JCPDS 01-075-0581. Also, the corresponding lattice constants are  $a = b = c = 5.811$ .

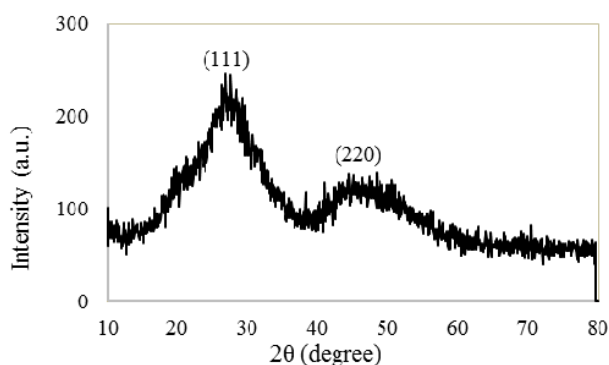


Fig. 2 The XRD pattern of biosynthesized CdS nanoparticles

Elemental spectra of the produced nanoparticles obtained by the Energy Dispersive X-ray Spectroscopy (EDS) are presented in Fig. 3. The most intense peaks in the diagram are associated with cadmium and sulfur elements. In addition, the existence of carbon, oxygen, and phosphor peaks are possibly

due to the presence of extracellular polymeric substances (EPS) which accompany the synthesized nanoparticles.

Considering that these nanoparticles are prepared from an impure leach solution, the presence of other elements such as manganese, iron, sodium, nickel, etc. seems natural. It is speculated that the biological covers of the synthesized particles have absorbed these ions from the initial solution.

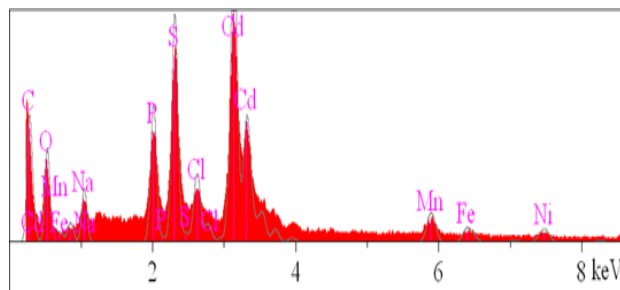


Fig. 3 EDS analysis on the nanoparticles produced from the Ni- Cd cake

Fig. 4 illustrates the FTIR spectra derived from the biosynthesized QDs. A number of absorption peaks were detected in the graph that can be associated with several functional groups which present in the bacterial EPS. The Cd-S stretching is observed at  $715\text{ cm}^{-1}$  [22]. Also, the bands at  $1045\text{ cm}^{-1}$  can be attributed to the C-N stretching vibrations of the aliphatic amines [10]. Moreover, the C-O stretching vibration gives an intense peak at  $1120\text{ cm}^{-1}$  that indicates the existence of ether or ester molecules [5]. The weak peak due to C-C stretching is observed at about  $1162\text{ cm}^{-1}$  [6]. In addition, the band at  $1439\text{ cm}^{-1}$  is assigned to the methylene scissoring vibrations from the proteins in the solution [14]. The strong peak at  $1638\text{ cm}^{-1}$  is due to the presence of C=O bonds in amide I [14]. Also, the amide II band due to the N-H stretching vibration showed up at  $1545\text{ cm}^{-1}$  [23]. Furthermore, the peaks observed at  $2927\text{ cm}^{-1}$  are assigned to the vibrations of the -CH groups of the hydrocarbons like phenols and alcohols which present in bacterial secretions [10]. Also, the absorbance band of the peak occurred at  $3444\text{ cm}^{-1}$  corresponds to the -OH stretching of carboxyl groups of amines which proves the presence of proteins and enzymes in the sample [23]. Therefore, probably the nanoparticles were rapidly covered and stabilized by bio-surfactants secreted by the bacterial cells after their generation, and this proteinaceous shells prevented the nanocrystals from further growth and increase in particle size.

Fig. 5 shows a TEM micrograph of the produced CdS nanoparticles. Looking at this picture, biologically stabilized quantum dots with the approximate size of 5 nm are obviously dispersed in the bacterially produced polymeric pattern. As stated before, these proteins and peptides molecules stabilized the generated CdS nuclei and prevented their agglomeration [18].

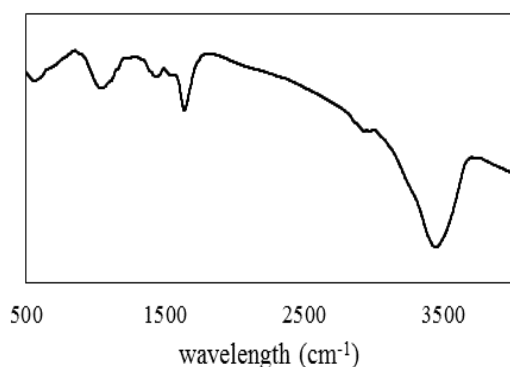


Fig. 4 FTIR spectra of the biosynthesized CdS nanoparticles

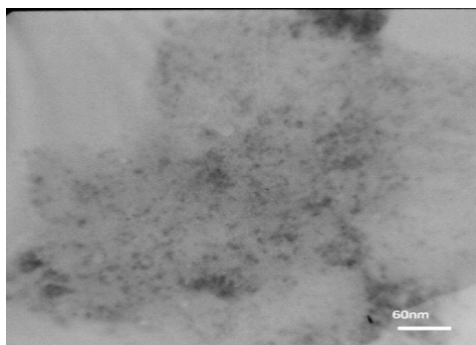


Fig. 5 TEM image of the biosynthesized CdS nanoparticles

Fig. 6 shows a UV-Vis graph of biosynthesized CdS nanoparticles. The sharp peak at the wavelength of 290 nm shows the presence of the bio-surfactants in solution, which is previously confirmed by FTIR analysis. The absorbance of wavelength between 300 and 400 nm is due to the formation of CdS nanoparticles. In addition, the particle size was determined by TEM analysis.

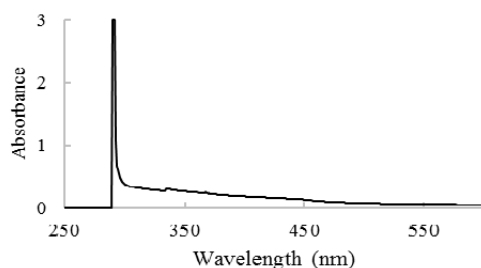


Fig. 6 UV-Vis spectra of biosynthesized CdS nanoparticles

#### IV. CONCLUSION

This research indicates that mineral processing tailings and by-products like filter cakes have the potential for being reused for the recovery of metals in the form of valuable nanoparticles. The impure CdS solution obtained by two-step alkaline and acidic leaching, was used as a precursor for synthesizing CdS quantum dots. CdS nanoparticles were biologically prepared by using the secretions of *bacillus*

*licheniformis* as a stabilizer. The composition and cubic structure of the nanoparticles were revealed by XRD analysis. Also, TEM micrographs showed that the particle size was in the range of 2-10 nm. Also, IR spectra confirmed the existence of bio-surfactants on the produced particles. In addition, UV-Vis absorption spectra indicated that the product was able to absorb wavelengths below 400 nm that is another specification of CdS quantum dots.

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