

## High Efficient Nanocomposite for Removal of Heavy Metals ( $\text{Hg}^{2+}$ and $\text{Pb}^{2+}$ ) from Aqueous Solution

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### ABSTRACT

In current work, CdS/black carbon nanocomposites were successfully synthesized with the aid of chestnut and cadmium nitrate as the starting reagents. Besides, the effects of preparation parameters such as reaction time, and precursor concentration on the morphology of products and removal of heavy metals ( $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ) were studied by scanning electron microscopy images and batch adsorption mode. CdS/black carbon nanocomposite introduced as new and high efficient system for removal of heavy metal ions. The as-synthesized products were characterized by powder X-ray diffraction, scanning electron microscopy, and spectra energy dispersive analysis of X-ray.

### INTRODUCTION

II–VI binary compound semiconductors have drawn considerable attention due to their interesting optical and electronic properties. They play important roles in both basic science and application fields. It has been well accepted that size and morphology of nanomaterials are crucial issues for their application and great efforts have been devoted to achieve size and morphological controllable synthesis of semiconductor nanocrystals [1]. Cadmium sulphide (CdS), a direct band gap material with  $E_g$  of 3.5 eV at room temperature, has important applications in the optoelectronic devices [2-4]. And it receives a wide range of research interest because of their unique properties and their wide variety of potential applications. For instance, potential applications for laser light emitting diodes, solar cells, non-linear optical, optoelectronic and electronic devices are in discussion [5-9]. During the past decades, various methods have been applied to fabricate cadmium sulfide nanocrystallines, such as electrochemically induced

deposition [10, 11], thermal decomposition [12], laser assisted catalytic growth method [13], ultrasound irradiation [13], solvothermal method [14-17], and hydrothermal method [18, 19]. Most of the products have different morphologies such as dendrites [20], flakes [21], spheres [22], nanorods [23, 24], nanowires [25, 26], triangular and hexagonal plates [27], flower-like shape [28] and sea-urchin-like shape [29]. Activated carbon, also called activated charcoal, activated coal, carbo activatus or an “AC filter”, is a form of carbon processed to have small, low-volume pores that increase the surface area available for adsorption or chemical reactions.[30] Due to its high degree of microporosity, just one gram of activated carbon has a surface area in excess of 500 m<sup>2</sup> (5,400 sq ft), as determined by gas adsorption.[31] An activation level sufficient for useful application may be attained solely from high surface area; however, further chemical treatment often enhances adsorption properties. Activated carbon is usually derived from charcoal and, increasingly, high-porosity biochar. lead, mercury and chromium are often detected in industrial wastewaters, which originate from metal plating, mining activities,

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smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries, etc., [32]. The concentration of these metals in wastewater may therefore rise to a level that can be hazardous to human health, livestock and the aquatic environment. Lead is of particular interest because of its toxicity and its widespread presence in the environment [33]. All Pb compounds are considered cumulative poisons. Acute Pb poisoning can affect the gastrointestinal track and nervous system [34]. To eliminate such environmental hazards associated with heavy metals, wastewater streams should be treated using robust techniques. Various treatment methods such as chemical precipitation, reverse osmosis, ion exchange, solvent extraction, coagulation and adsorption are utilized to remove metal ions from aqueous solutions. The efficiency of adsorption depends on many factors, including the surface area, pore size distribution, polarity, and functional groups of the adsorbent [35]. Adsorption technique though robust in nature, suffers from massive mass transport resistance due to the size of the adsorbents. To overcome this limitation, advance techniques in material design are required. This can be achieved through nanotechnology. Characteristics such as large surface area, potential for self assembly, high specificity, high reactivity, and catalytic potential make nanoparticles excellent candidates for water treatment applications. Nano adsorbents are quite efficient for the fast adsorption of heavy-metal ions and organic molecules from aqueous solutions because of their high specific surface areas and the absence of internal diffusion resistance [36]. Materials with high adsorption capacities are very attractive from an economical point of view. Different solids such as zeolites, clay minerals, metal oxides, organic polymers, etc., have been tested as insoluble adsorbents [37]. In this paper, we report the black carbon/CdS composite as high efficient system for removal of heavy metal ions for the first time. The present study aimed to investigate Pb(II) and Hg(II) absorption characteristics carbon/CdS composite using a batch sorption mode. Furthermore, the effects of reaction time, and precursor concentration on the sorption rate of carbon /CdS composite were studied.

## MATERIALS AND METHODS

### *Characterization*

X-ray diffraction (XRD) patterns were recorded by

a Philips-X'PertPro, X-ray diffractometer using Ni-filtered Cu K $\alpha$  radiation at scan range of  $10 < 2\theta < 80$ . Scanning electron microscopy (SEM) images were obtained on LEO-1455VP equipped with an energy dispersive X-ray spectroscopy. The energy dispersive spectrometry (EDS) analysis was studied by XL30, Philips microscope.

### *preparing carbon black*

Herein carbon black was prepared from waste fruit and callouses compounds like nut and chestnut. In typical synthesis method, 50 ml H<sub>2</sub>SO<sub>4</sub> was added to 20 g of callouses compounds and was stayed for 1 day. Then solid compound was putted in furnaces in 550 °C for 2 h. The black powder was washed several time with ethanol and water.

### *preparing black carbon / CdS composite*

First, 0.1 mol of CdNO<sub>3</sub>·H<sub>2</sub>O was dissolved in 40 mL of distilled water and 0.1 mol of thiourea was dissolved in the above solution. Then 0.5g black carbon powder was added and stirred for 5 hours at 100 °C . Next, the solution was filtered using a Millipore filter and washed three times with 5 mL of distilled water and dried for 24 hours at 100 °C .

Through heat treatment at 100 in the electric furnace, then CdS-black carbon were synthesized. The effect of ratio between carbon and CdS, reaction time, and stirrer speed were investigated.

### *Remove of heavy metals*

The experiment was carried out in a 200 ml batch reactor with the initial Pb(II) and Hg(II) concentration of 30 ppm. At preordained time intermissions, 10 mL of the sample was taken from the reactor and filtered. Afterwards, residual Pb(II) and Hg(II) concentration were measured by an atomic absorption spectrophotometer (AAS). By performing appropriate material balance, the quantities of Pb(II) and Hg(II) adsorbed at the selected time intervals were determined. The effects of magnetic stirring time and its rpm on the absorption of Hg(II) and Pb(II) by CdS nanoparticles prepared by using reverse microemulsion method have been investigated.

### *Water treatment*

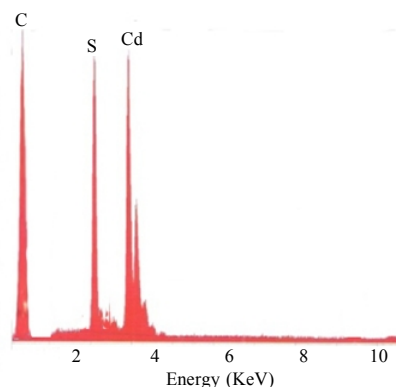
The experiment was carried out in a 1L batch reactor with the initial Pb(II) and Hg(II) concentration of 20 mg/L. The adsorbent mass was fixed at 0.1 g under stirring at room temperature. At preordained time

intervals, 15 mL of the sample was taken from the reactor and filtered. Afterwards, residual Pb(II) and Hg(II) concentration were measured by an atomic absorption spectrophotometer (AAS). By performing appropriate material balance, the quantities of Pb(II) and Hg(II) adsorbed at the selected time intervals were determined. The effects of the reaction time and CdS/carbon ratio on the sorption of Pb(II) and Hg(II) by CdS/black carbon composite have been investigated. It is believed that due to the presence of the sulfide sites on the surface of CdS nanoparticles they can act as a trapping site for metal ions and there is no necessity for further modification of the final particle. The presence of the electron pair on the sulfide groups of the products can interact with the metal ions and traps them on the surface of the particles.

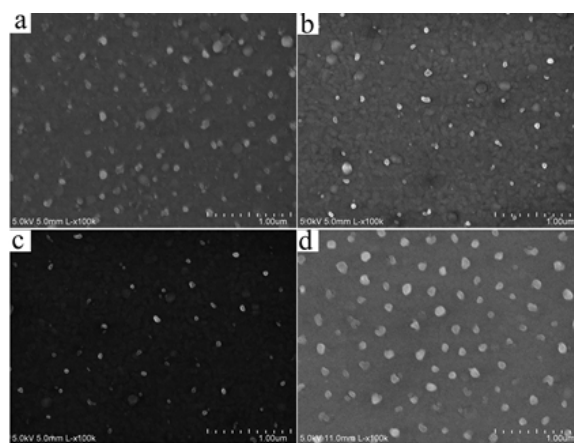
### RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the Black carbon/ CdS composite. The diffraction peaks corresponding to CdS is marked as Cd. The XRD patterns of the composites showed that the black carbon/ cadmium sulfide composite contained a mixture of cubic phase of CdS and carbon. In this the pattern, the diffraction peaks at  $26.3^\circ$ ,  $28.8^\circ$ ,  $48.5^\circ$ , and  $56.8^\circ$   $2\theta$  were assigned to 0.1 CdS-carbon. In the pattern of 0.2 CdS-carbon, additional peaks at  $26.5^\circ$ ,  $28.1^\circ$  and  $48.1^\circ$  were also observed, which were assigned to the CdS cubic phase. A typical EDS spectrum of CdS nanoparticles, as shown in Fig. 2, indicates the presence of C, S and Cd in the product. Therefore, both XRD and EDS analyses show that pure CdS nanoparticles are successfully produced via microemulsion method.

The SEM images of the CdS-graphene composite are shown in Fig. 3. According to Fig. 3, we can observe that

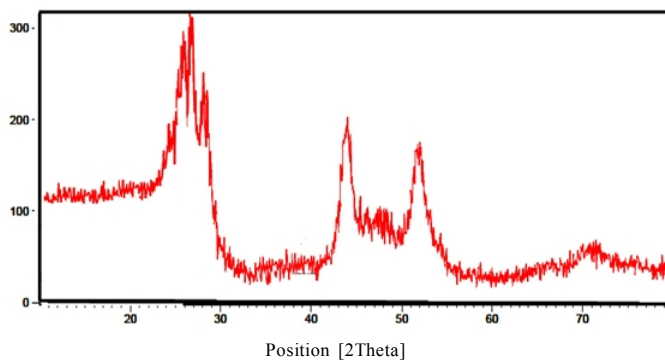


**Fig. 2.** EDS of as-synthesized CdS-carbon composite.



**Fig. 3.** SEM image of a) sample 1, b) sample 2, c) sample 3, and d) sample 4.

the CdS particles are fine and agglomerated on the surface of active carbon but are not uniform. The development of the pores on the carbon surface can be observed. Generally, it is considered that good particle dispersions can produce high efficient water treatment system.



**Fig. 1.** XRD pattern of as-synthesized CdS-carbon composite.

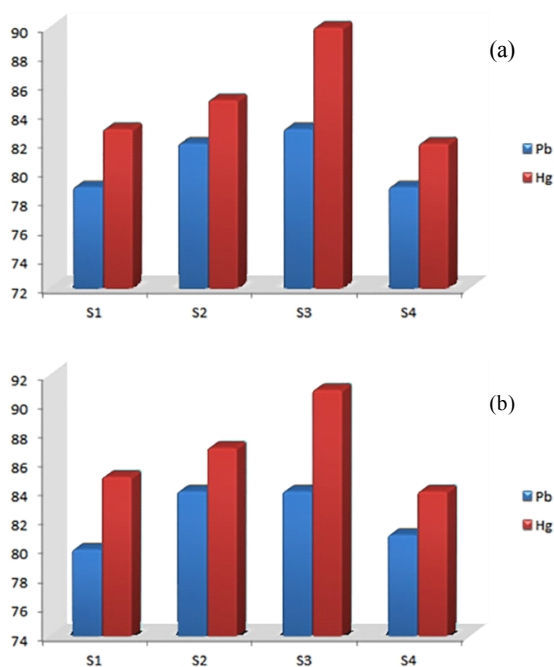


Fig. 4. a) the adsorption kinetics of Pb(II) and b) Hg(II) ions onto CdS/black carbon nano composite

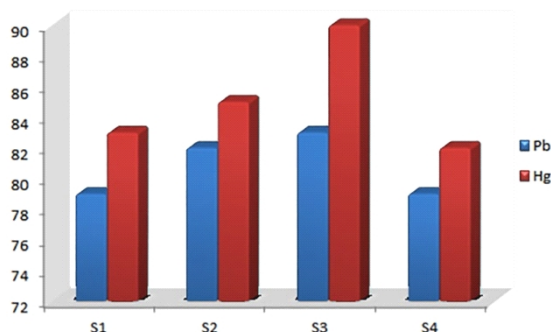


Fig. 5. The adsorption kinetics of 25 mg/L solution of Pb ion onto sample S1-S4

Fig. 4a and b show the adsorption kinetics of Pb(II) and Hg(II) ions onto carbon black and CdS/black carbon nano composite, respectively. It seems that the increase in reaction time and black carbon/CdS ratio result in an increase in adsorption of Pb(II) and Hg(II) ions. Also CdS/carbon composite show higher efficiency than carbon black.

Furthermore, increase in concentration of  $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  results in a decrease in adsorption of Pb(II) and Hg(II) ions due to agglomeration of nanoparticles. It seems Hg(II) ions, due to their atomic

radius, are absorbed more than Pb(II). To investigate the concentration of Pb ion on the remove percent, we used 25 mg/L solution of Pb ion. By increased concentration of ion, remove percent of Pb had been increased (Fig. 5).

## CONCLUSION

In summary, CdS/black carbon nanocomposite were successfully synthesized as high efficient catalyst for removal of heavy metal ions. Chestnut and  $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were used as starting. In this paper, we investigated the effect of preparation parameters such as reaction time, and precursor concentration on the morphology of CdS/black carbon nanocomposite. Finally, this optimized nanocomposite was introduced as high efficient system for water treatment. products were characterized by XRD, EDX, and SEM.

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## CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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