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Original Research Article

Removal of Pb (II) from aqueous solution by gel combustion derived nano Co3O4- ZnO

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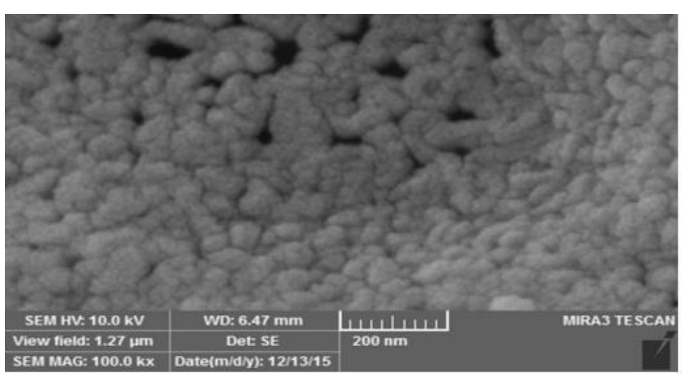
ABSTRACT

Nano Co_3O_4/ZnO have been successfully synthesized by a simple and green gel combustion method followed by calcination at 600 o C. Sugar was used as fuel for combustion in this work. The nano Co3O4–ZnO were characterized by X-ray diffraction (XRD), Energy Dispersive XRay analysis (EDAX) and Scanning electron microscopy (SEM). Co_3O_4–ZnO was applied as an adsorbent to remove lead from aqueous solution. EDAX strongly proved the adsorption of lead on the surface of Co_3O_4-ZnO adsorbent. By increasing the amount of ZnO on the structure of the Co_3O_4-ZnO samples, the adsorption of Pb^{2+} on the surface increased too. The SEM images also help the confirmation of lead adsorption on the surface of as synthesized samples. The concentrations of remained Pb^{2+} ions were also measured by atomic absorption spectroscopy (AAS) and reported in the terms of removal efficiency.

Graphical Abstract



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Introduction

By increasing heavy metals in the environment, heavy metals pollution has become a critical issue and attracted considerable attentions because of both acute and chronic toxicity [1]. Heavy metals have released to the environment by industrial manufacture such as pesticides, fertilizers, dyes, drugs, battery, tannery, fossil fuel, ceramic and glass industries printing [2, 3]. Lead (Pb^{2+}), as a heavymetal, exist as pollutant in soil and water.

Lead should be removed from water because of its high toxicity, nonbiodegradable nature and bioaccumulation in the food chain [4, 5]. Pb^{2+}causes serious nervous system problems, gastrointestinal diseases, blood and brain disorders, and cancer [6, 7]. To remove Pb^{2+} from wastewaters, several methods have been handled such as coagulation [8], floatation [9], precipitation [10], solvent extraction [11], adsorption [12] and ion exchange [13]. Adsorption, among the mentioned method, because of simplicity, and low cost is the most promising one [14, 15]. Many different adsorbent have been applied to remove lead from wastewaters including zeolites [12], activated carbons [16], fly ash [17], and metal oxides [18].

Co_3O_4, a p-type semiconductor, has many attractive properties including high catalytic activity [19], supercapacity [20], heavy metal removal [21], and gas sensing [22]. On the other hand, Zinc oxide (ZnO) is an n-type semiconductor with wide direct band gap (3.4 eV) [23] and various applications such as hydrogen storage [24], photocatalyst [25], piezoelectric sensor [26] and heavy metal removal [27]. Consequently, combination of these two significant metal oxides will expand their potential application area.

Different synthetic method have been reported to produce nano Co_3O_4- ZnO such as electro-spinning process [28], homogeneous precipitation method [29], plasma enhanced–chemical vapor deposition [30], and photochemical coating method [31]. Co_3O_4- ZnO were used as photocatalyst for degradation of rhodamine B dye [28], piezoelectric transducer [32], and gas sensor [30]. Herein, we have synthesized nano Co_3O_4-ZnO by simple and green gel combustion method. The fuel was used for combustion in this work is Sugar. This method has never been reported for the synthesis of such material previously. The nano Co_3O_4-ZnO were characterized and the adsorption of Pb^{2+} on its surface was investigated. To prove the adsorption of lead on the surface of as synthesized samples we used EDAX and SEM analysis. Moreover, the concentrations of remained Pb^{2+} ions were also measured by atomic absorption spectroscopy (AAS).

Materials

Zinc nitrate hexahydrate, cobalt nitrate hexahydrate were used as precursors. Commercial sugar purchased from the local market was used as a fuel for combustion. lead nitrate solution was used for adsorption, which was prepared by dissolving lead nitrate (Merck; >99%, LR grade).

Synthesis of Co_3O_4

Co_3O_4 was synthesized by the gel combustion method, which is used to synthesize ZnO nano structures, before [2]. Cobalt nitrate hexahydrate was applied as the cobalt precursor. 0.01 mol (2.91 g) of cobalt nitrate hexahydrate and 5 g of sugar were dissolved in 30 mL distilled water. The reaction mixture was placed on a hot plate at 250 ˚C. During the heating process, water vapor and nitric gases were released and the gel is formed. The gel was then calcinated at 600 °C for 2 hours and characterized for further use.

Synthesis of Co_3O_4- ZnO

To prepare ZnO-Co_3O_4 samples, different aqueous metal nitrate solutions were prepared by dissolving each cobalt nitrate and zinc nitrate in water at different ratio (5:5, 8:2, 7:3, and 9:1). After mixing the desired solution, 5 g of sugar was addes to the mixture. The reaction mixture was then placed on a hot plate at 250 ˚C. During the heating process, water vapor and nitric gases were released and the gel is formed. The prepared gel was then calcinated at 600 °C for 2 hours and characterized for further use.

Adsorption Studies of Pb on the Surface

0.125 gram of synthesized Co_3O_4 and each ZnO-Co_3O_4 samples were separately added to the 15 mL of 0.5 M lead nitrate solution taken in a 50 mL conical flask and the solution was shaken by mechanical shaker for three hours. Co_3O_4 and each ZnO-Co_3O_4 adsorbents were then filtered and filtrates was dried at 200 ˚C. The dried powders were characterized SEM and EDAX analysis. The concentrations of remained Pb^{2+} ions in supernatant were also measured by atomic absorption spectroscopy (AAS) and the sample absorbance was measured. The adsorption efficiency (R%) were measured using the following equation:

$$R\% = \frac{C_0 - C_f}{C_f} \times 100$$

Where C_0 is the initial metal ions concentration (mg l^{-1}) and C_f the final Pb^{2+} concentration (mg l^{-1}).

Results and Discussions

X-ray diffraction (XRD) analysis

XRD of Co_3O_4 is represented in Figure 1a. The sample in Figure 1a having crystalline morphology with broad peaks match well with the Co_3O_4 JCPDS card 43-1003. The apparent peaks at 2θ values of 19.01, 31.22, 37.12, 38.95, 44.18, 55.87, 59.50, 65.48 and 77.23 correspond to the crystal planes of (111), (220), (311), (222), (400), (422), (511), (440) and (533) respectively, which confirms the formation of pure Co_3O_4 [28]. The crystal size of the sample was calculated by Scherrer equation. The average particle size of the cobalt oxide was found to be 43.685 nm. XRD patterns of as synthesized Co_3O_4-ZnO nanoparticles are shown in Figure 1b-e. It is observable that ZnO peaks is presented on the patterns. The average particle size of Co_3O_4-ZnO 9:1, 8:2, 7:3, and 5:5 are 35.023, 40.915, 46.600, and 52.950 respectively.

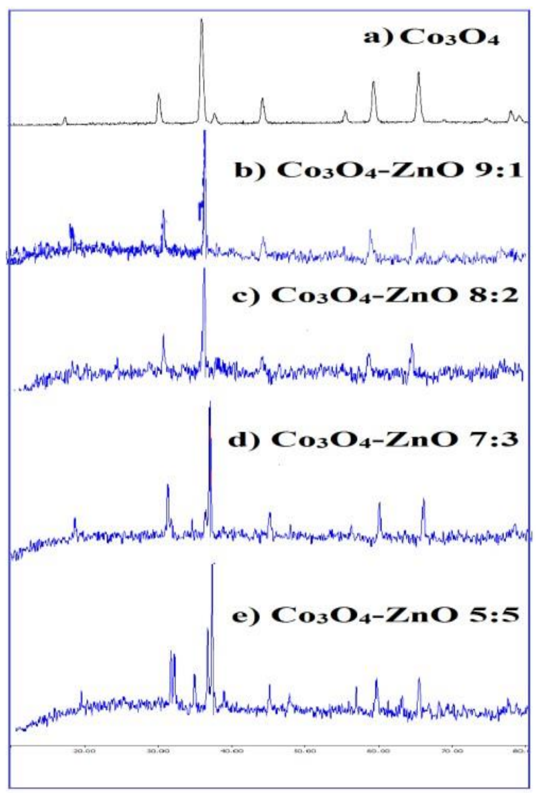

Figure 1. XRD patterns of a) pure Co_3O_4, b) Co_3O_4-ZnO 9:1, c) Co_3O_4-ZnO 8:2, d) Co_3O_4-ZnO 7:3, and e) Co_3O_4-ZnO 5:5

Energy dispersive X-Ray analysis (EDAX) analysis

The EDX analyses results depict the presence of only cobalt and oxygen elements in the as-synthesized Co_3O_4 sample (Figure 2a). The EDAX analysis data of the Co_3O_4-ZnO indicate the presence of Zn atoms besides Co and O atoms, which prove the samples, are properly synthesized (Figure 2b-e). Moreover, it is clear that no other peak related to any other impurity has been detected in the EDAX, which confirms the synthetic process was carried out appropriately. Mass and atomic percentages of different elements is presented in Table 1 (the rest are impurities).

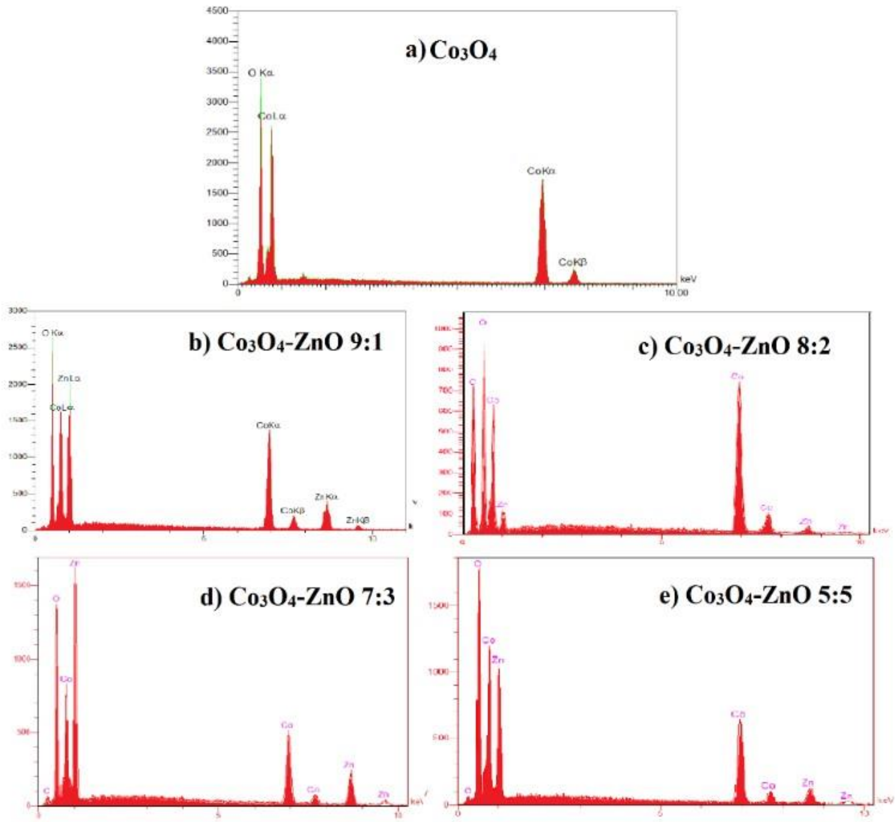

Figure 2. EDAX spectra of a) pure Co_3O_4, b) Co_3O_4-ZnO 9:1, c) Co_3O_4-ZnO 8:2, d) Co_3O_4-ZnO 7:3, and e) Co_3O_4-ZnO 5:5

Table 1. EDAX results of the as-synthetized samples

Sample	Element content weight%			Element content atomic%		
	Co K	Zn K	O K	Co K	Zn K	O K
Co_3O_4	77.91	0	27.62	39.78	0	56.22
Co_3O_4-ZnO 9:1	65.35	4.77	21.06	42.58	1.60	49.87
Co_3O_4-ZnO 8:2	48.20	10.32	27.12	26.12	5.38	45.14
Co_3O_4-ZnO 7:3	46.17	21.28	29.64	24.54	10.16	57.83
Co_3O_4-ZnO 5:5	35.17	39.49	23.97	21.22	21.48	53.26

The EDAX spectrum of the synthesized lead adsorbed samples were shown in Figure 3a-e. EDAX spectrums show just the presence of cobalt, zinc, lead and oxygen elements indicating the purity of both the adsorbent and adsorbate. By comparing Figure 2a and Figure 3a, it is observable that two spectrum are approximately the same, showing that Co_3O_4 sample did not adsorb any lead. This similarity are also observable in Figure 2b and 2c, indicating the sample Co_3O_4-ZnO 9:1 did not adsorb lead on the surface. The peaks found in between 2.5 to 3 Kev in Figure 3c-e indicate the presence of lead on the surface of Co_3O_4-ZnO 8:2, Co_3O_4ZnO 7:3, and Co_3O_4-ZnO 5:5. EDAX strongly proved the adsorption of Pb on the surface of Co_3O_4-ZnO adsorbent. As can be seen in Figure 3, by increasing the amount of ZnO on the structure of the samples, the adsorption of Pb on the surface increased too. Mass and atomic percentages of different elements is presented in Table 2 (the rest are impurities).

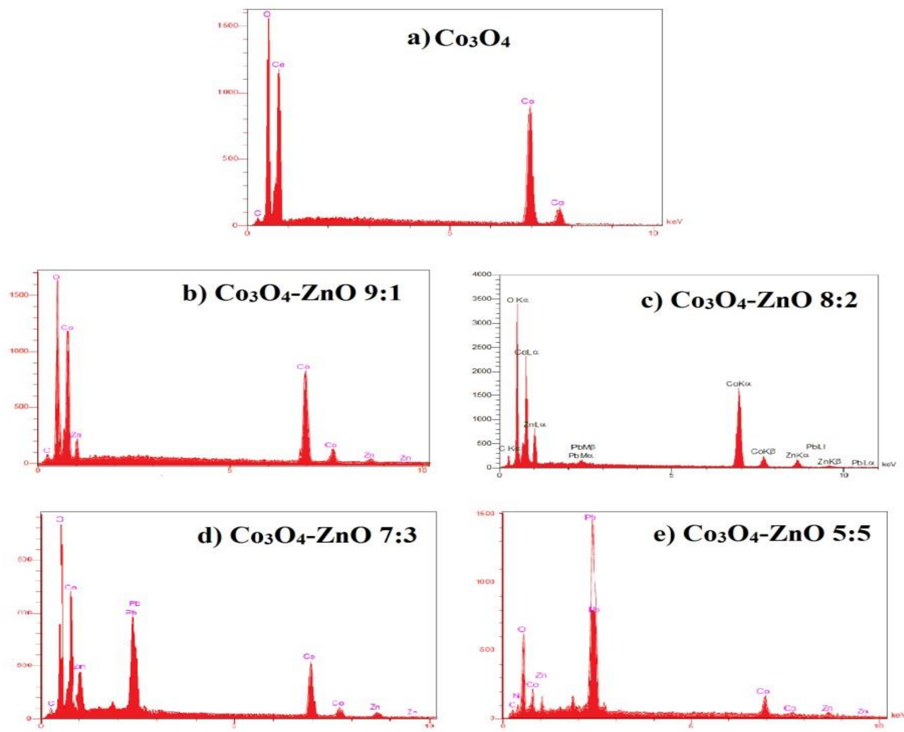

Figure 3. EDAX spectra of Pb^{2+} adsorbed a) pure Co_3O_4, b) Co_3O_4-ZnO 9:1, c) Co_3O_4-ZnO 8:2, d) Co_3O_4-ZnO 7:3, and e) Co_3O_4-ZnO 5:5

Table 2. EDAX results of the as-synthetized samples after Pb^{2+} adsorption

Sample	Element content							
	weight%				atomic%			
	Co K	Zn K	O K	Pb K	Co K	Zn K	O K	Pb K
Co_3O_4	68.82	0	25.22	0	32.68	0	51.24	0
Co_3O_4-ZnO 9:1	63.45	5.47	25.68	0	40.28	2.90	55.67	0
Co_3O_4-ZnO 8:2	44.51	4.81	32.12	16.17	24.13	2.41	46.18	2.35
Co_3O_4-ZnO 7:3	39.19	6.76	34.18	24.57	15.87	3.20	66.17	3.67
Co_3O_4-ZnO 5:5	10.45	3.01	23.88	52.56	6.48	1.68	54.58	9.27

Scanning electron microscopy (SEM)

SEM was used to study the surface morphology of the synthesized samples. Figure 4 shows the SEM pictures of Co_3O_4 and Co_3O_4-ZnO nanoparticles prepared by the gel combustion method. As shown in Figure 4, the synthesized particles are relatively spherical. Besides, the synthesized nanoparticles are approximately homogeneous in nature. In the samples Co_3O_4 and Co_3O_4-ZnO 9:1 aggregation were occurred however, the other samples are distributed properly.

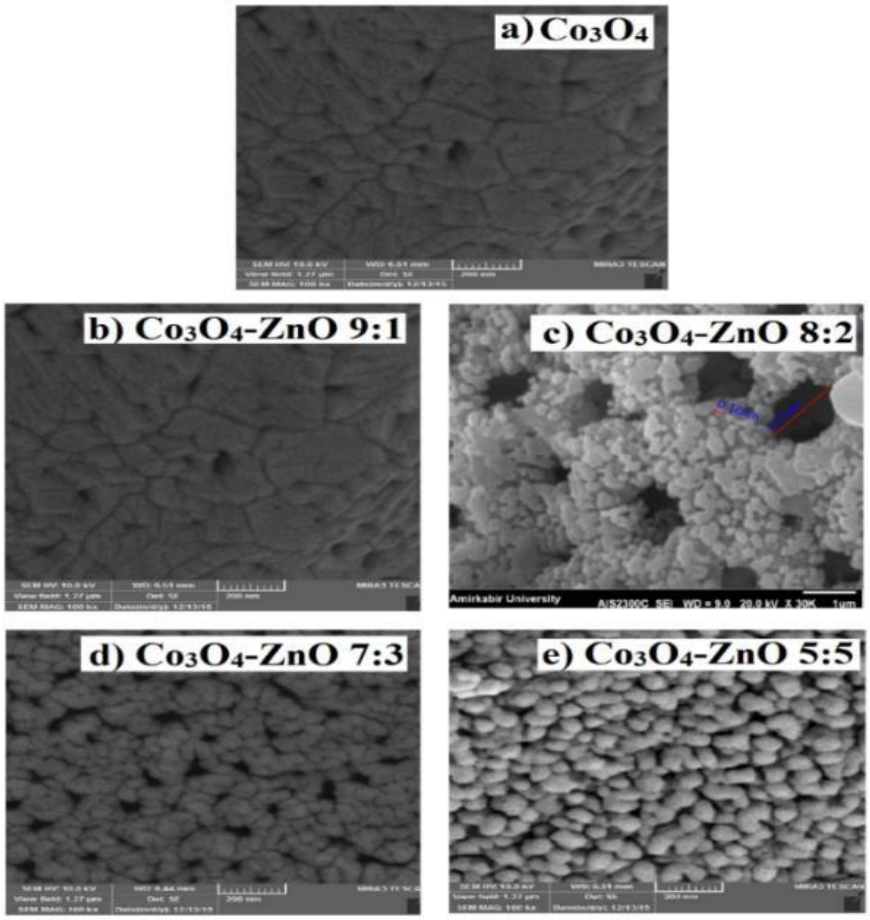

Figure 4. SEM images of a) pure Co_3O_4, b) Co_3O_4-ZnO 9:1, c) Co_3O_4-ZnO 8:2, d) Co_3O_4-ZnO 7:3, and e) Co_3O_4-ZnO 5:5

Figure 5 depicts the SEM image of lead adsorbed Co_3O_4 and Co_3O_4-ZnO nanoparticles. SEM images of Co_3O_4 and Co_3O_4-ZnO 9:1 before and after adsorption are not different because the pores between particles are not reachable by lead (comparing Figure 4 and 5a and b). However, for the other Co_3O_4-ZnO samples, it is obvious that the distances between nanoparticles are covered after adsorption, which indicates the nucleating growth of lead on the surface of the adsorbent. These images help the confirmation of lead adsorption on the surface of as synthesized samples.

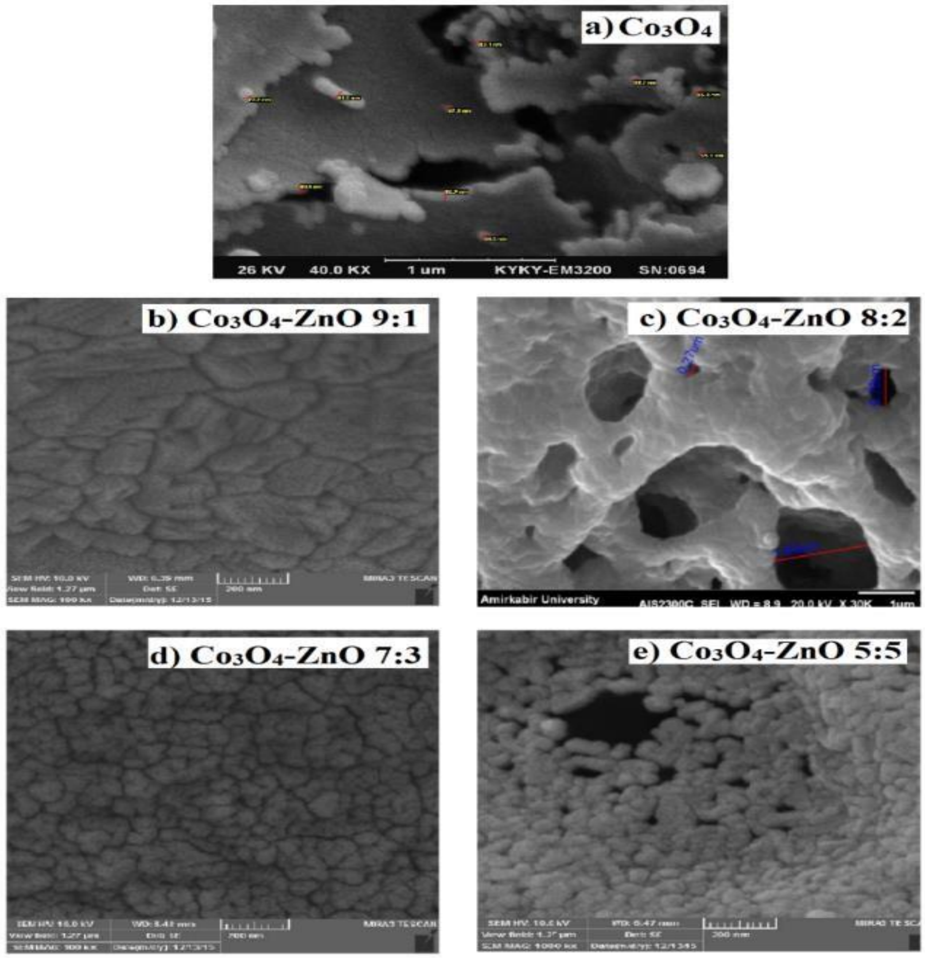

Figure 5. SEM images of a) pure Co_3O_4, b) Co_3O_4-ZnO 9:1, c) Co_3O_4-ZnO 8:2, d) Co_3O_4-ZnO 7:3, and e) Co_3O_4-ZnO 5:5 after Pb^{2+} adsorption

To study Pb^{2+} adsorption on the surface of Co_3O_4-ZnO samples, the concentrations of remained Pb^{2+} ions in supernatant were also measured by atomic absorption spectroscopy (AAS) and the sample absorbance was measured. The results of these experiments were shown in Table 3. It seems that pure Co_3O_4 is not able to act as dependent to remove lead from solution. As can be seen, adsorption efficiency increase with increase in ZnO in the Co_3O_4-ZnO structures, for pure Co_3O_4 the adsorption efficiency was 0% and further increase in the ZnO the efficiency increase to 77.17% for Co_3O_4-ZnO 5:5. Consequently, Co_3O_4ZnO 5:5 is the best adsorbent of Pb^{2+} compared to other adsorbents studied in this research.

Table 3. Adsorption efficiency of as synthesized samples for lead removal

Adsorbent	Adsorption efficiency
Co_3O_4	0
Co_3O_4-ZnO 9:1	0
Co_3O_4-ZnO 8:2	70.95
Co_3O_4-ZnO 7:3	74.41
Co_3O_4-ZnO 5:5	77.17

Table 4 compares the characteristic data of the current method with other methods for adsorption of Pb in different samples [2, 32–34]. As can be seen, the result is better or in adsorbents. It can be inferred from this comparison that Co_3O_4–ZnO have a high lead adsorption capacity.

Table 4. Adsorption capacity of Co_3O_4–ZnO and other recently reported adsorbents.

Order	Adsorbent	Adsorption capacity (mg/g)	Route Followed	Reference
1	ZnO NPs	19.65	Gel combustion	[2]
2	CuO NPs	188.7	Sol-gel	[33]
3	ZnO/MMT nanocomposite	34.84	Heat method	[34]
4	Pretreated clinoptilolite	122.4	-	[35]
5	Co_3O_4–ZnO	185.2	Gel combustion	This work

Conclusion

In this research, nano Co_3O_4–ZnO have been successfully synthesized by a simple and green gel combustion method followed by calcination at 600 °C. Sugar was used as fuel for combustion in this work. This study clearly establishes that Co_3O_4-ZnO is an efficient adsorbent for Pb (II) removal from aqueous solution. EDAX strongly proved the adsorption of lead on the surface of Co_3O_4-ZnO adsorbent. The SEM images also help the confirmation of lead adsorption on the surface of as synthesized samples. The obtained results of AAS show the adsorption efficiency increase with incensement of ZnO in the Co_3O_4-ZnO structures. Co_3O_4-ZnO 5:5 is the best adsorbent of Pb^{2+} compared to the other adsorbents studied in this research. In comparison with recent studies, in this work the adsorbent was synthesized by method that is more convenient with better or in some cases comparable results for lead removal.

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Disclosure Statement

No potential conflict of interest was reported by the authors.

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References

[1]. Islam A., Ahmad H., Zaidi N., Kumar S. *ACS Appl. Mater. Interfaces*, 2014, **6**:13257 [Crossref], [Google Scholar], [Publisher]

[2]. Venkatesham V., Madhu G, Satyanarayana S, Preetham H. *Procedia Eng.*, 2013, **51**:308 [Crossref], [Google Scholar], [Publisher]

[3]. Kılıc M., Kırbıyık C., Çepelioğullar Ö., Pütün A.E. *Appl. Surf. Sci.*, 2013, **283**:856 [Crossref], [Google Scholar], [Publisher]

[4]. Pardo R., Herguedas M., Barrado E., Vega M. *Anal. Bioanal. Chem.*, 2003, **376**:26 [Crossref], [Google Scholar], [Publisher]

[5]. Needleman H. *Annu Rev Med.*, 2004, **55**:209 [Crossref], [Google Scholar], [Publisher]

[6]. Savio M., Parodi B., Martinez L.D., Smichowski P., Gil R.A. *Talanta*, 2011, **85**:245 [Crossref], [Google Scholar], [Publisher]

[7]. Fayazi M., Taher M.A., Afzali D., Mostafavi A., Ghanei-Motlagh M. *Mater. Sci. Eng.: C*, 2016, **60**:365 [Crossref], [Google Scholar], [Publisher]

[8]. Pang F.M., Kumar P., Teng T.T., Omar A.M., Wasewar K.L. *J. Taiwan Inst. Chem. Eng.*, 2011,

42:809815 [Crossref], [Google Scholar], [Publisher]
[9]. Thackston E.L., Wilson D.J., Hanson J.S., Miller Jr D.L. *J. Water Pollut. Control Fed.*, 1980, 317 [Google Scholar], [Publisher]
[10]. Macchi G., Marani D., Pagano M., Bagnuolo G. *Water Res.*, 1996, **30**:3032 [Crossref], [Google Scholar], [Publisher]
[11]. Shah D., Phadke A., Kocher W. *J. Air Waste Manag. Assoc.*, 1995, **45**:150 [Crossref], [Google Scholar], [Publisher]
[12]. Günay A., Arslankaya E., Tosun I. *J. Hazard. Mater.*, 2007, **146**:362371 [Crossref], [Google Scholar], [Publisher]
[13]. Ahmed S., Chughtai S., Keane M.A. *Sep. Purif. Technol.*, 1998, **13**:57 [Crossref], [Google Scholar], [Publisher]
[14]. Zamboulis D., Peleka E.N., Lazaridis N.K., Matis K.A. *J. Chem. Technol. Biotechnol.*, 2011, **86**:335 [Crossref], [Google Scholar], [Publisher]
[15]. Halimi M., Nasrabadi M., Soleamani N., Rouhani N. *Asian J. Nanosci. Mater.*, 2018, **1**:19 [Crossref], [Google Scholar], [Publisher]
[16]. Goel J., Kadirvelu K., Rajagopal C., Garg V.K. *J. Hazard. Mater.*, 2005, **125**:211 [Crossref], [Google Scholar], [Publisher]
[17]. Gupta V.K., Ali I. *J. Colloid Interface Sci..*, 2004, **271**:321 [Crossref], [Google Scholar], [Publisher]
[18]. Han R., Zou W., Zhang Z., Shi J., Yang J. *J. Hazard. Mater.*, 2006, **137**:384 [Crossref], [Google Scholar], [Publisher]
[19]. Yang P., Cui Q., Zu Y., Liu X., Lu G., Wang Y. *Catal. Commun.*, 2015, **66**:55 [Crossref], [Google Scholar], [Publisher]
[20]. Liao Q., Li N., Jin S., Yang G., Wang C. *Acs Nano*, 2015, **9**:5310 [Crossref], [Google Scholar], [Publisher]
[21]. Hu J.S., Zhong L.S., Song W.G., Wan L.J. *Adv. Mater..*, 2008, **20**:2977 [Crossref], [Google Scholar], [Publisher]
[22]. Vetter S., Haffer S., Wagner T., Tiemann M. *Sens. Actuators B Chem.*, 2015, **206**:133 [Crossref], [Google Scholar], [Publisher]
[23]. Klingshirn C. *Chem. Phys. Chem.*, 2007, **8**:782 [Crossref], [Google Scholar], [Publisher]
[24]. Wan Q., Lin C., Yu X., Wang T. *Appl. Phys. Lett.*, 2004, **84**:124 [Crossref], [Google Scholar], [Publisher]
[25]. He L., Tong Z., Wang Z., Chen M., Huang N., Zhang W. *J. Colloid Interface Sci..*, 2018, **509**:448 [Crossref], [Google Scholar], [Publisher]
[26]. Bhatia D., Sharma H., Meena R., Palkar V. *Sens. Bio-Sens. Res.*, 2016, **9**:45 [Crossref], [Google Scholar], [Publisher]
[27]. Kumar K.Y., Muralidhara H., Nayaka Y.A., Balasubramanyam J., Hanumanthappa H. *Powder Technol..*, 2013, **239**:208 [Crossref], [Google Scholar], [Publisher]
[28]. Kanjwal M.A., Sheikh F.A., Barakat N.A., Li X, Kim H.Y., Chronakis I.S. *J. Nanoeng. Nanomanufacturing*, 2011, **1**:196 [Crossref], [Google Scholar], [Publisher]
[29]. Sharma R.K., Ghose R. *J. Alloys Compd.*, 2016, **686**:64 [Crossref], [Google Scholar], [Publisher]
[30]. Bekermann D., Gasparotto A., Barreca D., Maccato C., Comini E., Sada C., Sberveglieri G., Devi A., Fischer R. *ACS Appl. Mater. Interfaces*, 2012, **4**:928 [Crossref], [Google Scholar], [Publisher]
[31]. Tak Y., Yong K. *J. Phys. Chem. C*, 2008., **112**:74 [Crossref], [Google Scholar], [Publisher]
[32]. Hu Y.C., Lee T.H., Chang P.Z., Su P.C. *Thin Solid Films*, 2015, **584**:112 [Crossref], [Google Scholar], [Publisher]
[33]. Bhanjana G., Dilbaghi N., Kim K.H., Kumar S. *J. Mol. Liq.*, 2017, **244**:506 [Crossref], [Google Scholar], [Publisher]
[34]. Sani H.A., Ahmad M.B., Hussein M.Z., Ibrahim N.A., Musa A., Saleh T.A. *Process Saf. Environ. Prot.*, 2017, **109**:97 [Crossref], [Google Scholar], [Publisher]

[35]. Günay A., Arslankaya E., Tosun I. *J. Hazard. Mater*., 2007, **146**:362371 [Crossref], [Google Scholar], [Publisher]

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