Zinc Oxide Nanoparticles Preparation for Pd²⁺ Ions Adsorption From Aqueous Wastewaters: A Green Technique

Reza Davarnejad (✉ reza_davarnejad@yahoo.com.ph)

Arak University

Kourosh Nikandam

Arak University

Research Article

Keywords: Centaurea cyanus, Green technology, Heavy metal removal

Posted Date: August 24th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-826667/v1>

License: This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

ZnO nanoparticles (NPs) were easily synthesized using zinc nitrate through centaurea cyanus extract (as a reducing agent) at ambient conditions. XRD results demonstrated that ZnO NPs have a high-crystalline hexagonal structure with an average size of 48 nm in diameter. FT-IR spectral analysis indicated an active contribution of centaurea cyanus-derived biomolecules in zinc ions bioreduction. According to SEM analysis, ZnO NPs were properly dispersed and had a hexagonal shape. Batch experiments were performed to investigate the impact of several process parameters such as initial pH of solution, adsorption dosage, Pd^{2+} ions initial concentration and contact time on the Pd^{2+} ions adsorption from the solution. The Freundlich isothermal model could excellently legitimize a multilayer adsorption. Furthermore, the adsorption process followed a pseudo-second-order reaction kinetic. The maximum adsorption (99.24%) was experimentally found at pH of 5.5, adsorption dosage of 1.63 g.L^{-1} , Pd^{2+} ions initial concentration of 77.5 mg.L^{-1} and contact time of 91.25 min.

1. Introduction

Palladium and its compounds are mostly used in the catalytic converters. They can convert around 90% of the harmful gases such as hydrocarbons, carbon monoxide, and nitrogen dioxide into the less noxious substances such as nitrogen, carbon dioxide and water vapor [1, 2]. Palladium is also used in electronics, dentistry, medicine, hydrogen purification, chemical applications, groundwater treatment, and jewelry. Palladium is a key component of fuel cells, which react hydrogen with oxygen to produce electricity, heat, and water [3–6].

A large number of carbon–carbon bonding reactions in organic chemistry are facilitated by palladium compound catalysts such as Lindlar's palladium [7]. Furthermore, palladium is an excellent electro-catalyst for oxidation of primary alcohols in alkaline media. Palladium can also be applied in the homogeneous catalysis, used in combination with a variety of ligands [8]. Palladium is used in small amounts (about 0.5%) in some alloys of dental amalgam to decrease corrosion and increase the metallic luster [9]. Palladium is also produced in nuclear fission reactors and can be extracted from spent nuclear fuel [10]. Several modern industries such as batteries, pesticides, fertilizers, paper and chemical ones produce wastewaters containing some heavy metals.

Many researches classified the nanosized metal oxides (NMOs) as powerful adsorbents for the heavy metals adsorption from aqueous solutions [11–12]. There are several researches on the iron oxides, manganese oxides, aluminum oxides, CuO, NiO, ZnO and TiO_2 nanoparticles on treating the wastewaters [13–19]. ZnO nanoparticles are nontoxic and stable ones which can be used as additives into numerous products such as plastics, glass, cement, rubber, ceramics, paints, lubricants, adhesives, foods (source of zinc nutrients), batteries, and space craft protective coatings, fire retardants, as a catalyst, photocatalyst, semiconductor devices, and the other applications [20].

Various methods such as controlled precipitation [21], microemulsion [22], solvothermal [23] and sol-gel method [24] were reported in the literature for the ZnO nanoparticles production.

Wang et al. prepared the plate-like nanostructured ZnO nanoparticles by solvothermal method. The prepared nanoparticles had a particle size of 5–20 nm and surface area 147 m²/g. The nanoparticles of ZnO tested for the removal of Cu(II) and the results showed high adsorption capacity up to 1600 mg/g [25]. Ma et al. prepared zinc oxide nanosheets with square sides of about 1 μm and thickness in nano scale by hydrothermal method [26].

Sheela et al. investigated the ZnO nanoparticles with particle size of 26 nm, prepared by precipitation method for the removal of Zn(II), Cd(II) and Hg(II) [27].

Kumar et al. synthesized ZnO nanorods in a hexagonal shape with 24.5 nm dimension by hydrothermal method and used them in the removal of Pb(II) and Cd(II) [28].

Angelin et al. used zinc oxide nanoparticles impregnated polymer hybrids as an adsorbent for the removal of Pb(II), Hg(II) and Cd(II) ions from the aqueous solutions. The Langmuir isotherm and pseudo-second order kinetics models could properly legitimize the adsorption process [29]. Pandey et al. prepared nanosized zinc oxide encapsulated in urea-formaldehyde (UF) resin during acid catalyzed polymerization process. The results showed that the synthetic nanocomposite could eliminate 80% of Cu(II) from an aqueous solution during 15 min [30]. Mosayebi et al. studied the adsorption of copper ions from an aqueous solution by zinc oxides and zinc hydroxide loaded on the activated carbon cloth [31].

Centaurea cyanus as a wildling plant in North America, Australia and Asia (Iran) was successfully applied as a reducing agent during the nanoparticles preparation [32].

According to the literature, there were no previous researches on the *Centaurea cyanus* extract as an inexpensive and biocompatible reducing agent for the Zinc oxide nanoparticles preparation. Therefore, Zinc oxide nanoparticles (ZnO NPs) were synthesized through *Centaurea cyanus* extract. Then, they were applied in the Pd²⁺ ions adsorption from a wastewater. The impact of several variables such as the initial concentration of Pd²⁺ in the solution, pH, adsorbent dosage, and time on Pd²⁺ ions adsorption was statistically and experimentally studied and optimized. Finally, the kinetic and equilibrium of Pd²⁺ ions adsorption on the synthesized nanoparticles were investigated.

2. Materials And Methods

2.1. Materials and chemicals

Palladium chloride (PdCl₂), Zinc nitrate [Zn(NO₃)₂.6H₂O], sodium hydroxide (NaOH) and chloride acid (HCl) were purchased from Merck Co. (Germany). The dried *Centaurea cyanus* plant was purchased from a local herbal market. The extract of *Centaurea cyanus* plant was provided according to a technique mentioned in the literature [32].

2.2. Synthesis and preparation of ZnO NPs

14.9 g of the zinc nitrate salt was dissolved in 500 ml of distilled water. It was then added to 500 ml of the *Centaurea cyanus* extract. The solution was mixed at the ambient temperature [33]. Rapid formation of a white sediment in the solution indicates the ZnO NPs synthesis. The synthesized nanoparticles were then separated from the solution at 4500 rpm. The sediment was purified by several re-dispersions in deionized water and centrifuged. It was finally dried at 80°C through an oven.

2.3. Characterization of zinc oxide nanoparticles

The ZnO NPs were characterized by X-ray diffraction (XRD) through a X'pert PROMPD X-ray diffractometer (Philips, Netherland). The functional groups of ZnO NPs were analyzed through a FT-IR (ALPHA BRUKER, US). Fourier Transform Scanning Electron microscopy (FT-SEM) was used to study the surface morphology of the ZnO NPs (MIRAIII TESCAN, Czech Republic). Energy dispersive X-ray analysis (EDAX) was used to reveal the phase of Zn and O presented in the samples. This confirms the elemental composition of ZnO.

2.4. Adsorption process

The Pd²⁺ ions were adsorbed by ZnO nanoparticles in the batch systems. The experiments were designed using Design Expert software (version 11). The applied pH range was at 1–7 (because a red sediment is rapidly formed at the bottom of beaker at pH of 7 while a good results are usually obtained through the acidic conditions. The other conditions ranges are extracted from the literature for heavy metals adsorption [32]) at ambient temperature with a shaking of 200 rpm (without any vortex observation). The samples were withdrawn from the shaker at each contact time and the consumed adsorbents were extracted from the solutions by centrifugation at 4500 rpm (Sigma, Osterode am Harz, Germany) with whatman filter paper. The absorbance of solution was measured by monitoring the absorbance through an Atomic Adsorption apparatus (Shimadzu-AA-6800). Effect of pH was carefully studied by adjusting the pH of palladium solutions by 0.1 N HCl and NaOH solutions.

The amount of Pd²⁺ ions adsorbed by the adsorbent was calculated using the following equation:

$$\% \text{ Removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where, C_0 and C_e (mg.L⁻¹) are initial and final concentrations of palladium before and after adsorption process. The equilibrium adsorption of palladium can be calculated by:

$$q_e = \frac{C_0 - C_e}{w} \times V \quad (2)$$

where, q_e (mg.g⁻¹) is the equilibrium amount of palladium adsorbed on the nanoparticles, v (L) is the volume of solution and w (g) is the mass of adsorbent.

2.5. Response surface methodology (RSM)

Central composite design (CCD) is applied under RSM technique through the DoE software. Four independent variables such as pH, contact time, adsorbent dosage and initial concentration of solution (based on Pd²⁺ ions) are carefully studied on the Pd²⁺ ions removal as a dependent variable (response). These vary at five different levels (-2, -1, 0, +1, +2) as shown in Table 1.

Table 1
Variables and surfaces for various parameters for Pd²⁺ ions adsorption

Independent	Surfaces				
Variable	- α	-1	0	+1	+ α
pH	1	2.5	4.0	5.5	7
Time (min)	5	33.75	62.5	91.25	120
Dosage (g/40mL)	0.02	0.065	0.11	0.155	0.2
Initial Concentration (mg/L)	10	32.5	55	77.5	100

Analysis of variance (ANOVA), regression analysis and optimization of the process are considered through the software. The coefficient of regression (R²) and p-value of the ANOVA are used to determine the model acceptability.

3. Results And Discussion

3.1. X- ray diffraction analysis

XRD analysis can be used to provide some information about the crystalline structure and crystallite size of particles. The diffraction pattern will be investigated using High Score Expert software. According to JCPDS card No. 00-048-1066, the ZnO nanoparticles will be formed at 2 θ =36.29°. The average size of ZnO nanoparticles can be determined by the Scherrer's equation:

$$D = \frac{K\lambda C_u}{\beta \cos \theta} \quad (3)$$

where, D is the crystallite size of the particle, K represents the Scherrer constant (K is a dimensionless shape factor with a value close to unity), which is equal to 0.9, λ is the wavelength of light used for diffraction ($\lambda = 1.54 \text{ \AA}$) and β is the FWHM (full width at half maximum) of the diffraction peak and θ is

the angle of reflection [34]. Therefore, the average size of ZnO nanoparticles was found at 48 nm. Figure 1 shows XRD pattern of the synthesized ZnO nanoparticles through the centaurea cyanus extract.

3.2. SEM analysis

SEM image is used to observe the surface morphology and structure. Figure 2(a) shows the SEM image of ZnO nanoparticles. It shows a hexagonal uniform morphology of nanoparticles. Furthermore, a compact structure is seen after the adsorption process [Figures 2(b) and 2(c) show ZnO nanoparticles morphology before and after adsorption, respectively]. The observed agglomeration is due to polarity and electrostatic attraction of ZnO nanoparticles [35].

3.3. FTIR analysis

Fourier transform infrared (FTIR) spectroscopy is a characterization technique for the detection of functional groups in compounds. The phase formation of the ZnO powders is further characterized by the FTIR spectroscopy. Figure 3 shows the FTIR spectrum of ZnO NPs in the wavelength range of 400–4000 cm^{-1} . The peak at 3414 cm^{-1} corresponds to the symmetric O-H stretching vibration group [36] while the peak at 2921 cm^{-1} corresponds to cholesterol, phospholipids and creatine. The band at 2852 cm^{-1} in the extract confirms C-H stretching [37] while the peak at 1740 cm^{-1} is attributed to C = O stretching which corresponds to lipids [38]. A major peak around 1633 cm^{-1} is primarily due to C = O stretching vibrations of the protein amide-I bonds [39] although the peaks at 1544 cm^{-1} and 1383 cm^{-1} respectively are related to the tensile group C = C, N-H and C-H. The peaks at 1143 cm^{-1} and 1100 cm^{-1} can be drawn to the stretch of C-O-H, ethers and C-O (near the recent band).

Carbohydrate C-O-C ether bond of polysaccharides illustrates vibration almost at 1021 cm^{-1} . The peaks of 829 cm^{-1} and 797 cm^{-1} were assigned asymmetric pulling of PO and bending C = O group. The peaks at 630 cm^{-1} , 589 cm^{-1} , 534 cm^{-1} and 470 cm^{-1} correspond to the aromatic compounds of alkanes in the extract and ZnO group. The bands at 400–500 cm^{-1} are attributed to the stretching vibrations of Zn-O [40]. This confirms the formation of ZnO numeral [41–45].

3.4. Energy-dispersive X-ray spectroscopy (EDX)

Figure 4 shows the elemental composition analysis of the ZnO NPs by the EDX. The EDX spectra confirms Zn and O elements presence with high purities (69.2% and 30.8%) in the synthesized ZnO NPs.

3.5. Experiments design

The experiments design was used to determine the individual and interactive effects of the process variables. The result of the experiments design was illustrated in Table 2.

Table 2
The Experiments design based on the independent variables and response

	A: pH	B: Time (min)	C: Adsorbent dosage (g/40 mL)	D: Initial concentration of Pd²⁺ ions in the solution (mg/L)	Removal %
1	2.5	33.75	0.065	32.5	91.69
2	5.5	33.75	0.065	32.5	93.42
3	2.5	91.25	0.065	32.5	88.71
4	5.5	91.25	0.065	32.5	98.00
5	2.5	33.75	0.155	32.5	91.85
6	5.5	33.75	0.155	32.5	94.00
7	2.5	91.25	0.155	32.5	83.69
8	5.5	91.25	0.155	32.5	98.71
9	2.5	33.75	0.065	77.5	97.03
10	5.5	33.75	0.065	77.5	97.50
11	2.5	91.25	0.065	77.5	96.97
12	5.5	91.25	0.065	77.5	98.20
13	2.5	33.75	0.155	77.5	92.90
14	5.5	33.75	0.155	77.5	97.64
15	2.5	91.25	0.155	77.5	96.45
16	5.5	91.25	0.155	77.5	97.83
17	1	62.5	0.11	55	20.90
18	7	62.5	0.11	55	97.10
19	4	5	0.11	55	72.20
20	4	120	0.11	55	41.82
21	4	62.5	0.02	55	29.10
22	4	62.5	0.2	55	81.20
23	4	62.5	0.11	10	83.30
24	4	62.5	0.11	100	93.96
25	4	62.5	0.11	55	80.71

	A: pH	B: Time (min)	C: Adsorbent dosage (g/40 mL)	D: Initial concentration of Pd ²⁺ ions in the solution (mg/L)	Removal %
26	4	62.5	0.11	55	79.98
27	4	62.5	0.11	55	75.13
28	4	62.5	0.11	55	80.93
29	4	62.5	0.11	55	80.33
30	4	62.5	0.11	55	80.00

All experiments were carefully carried out based on the operating conditions as illustrated in Table 2. The samples were analyzed in terms of Pd²⁺ ions by the Atomic Adsorption apparatus. The highest percentage removal (98.71%) was observed at contact time of 91.25 min, adsorbent dosage of 3.87 g/L, pH of 5.5 and solution concentration of 32.5 mg/L.

3.6. Three dimensional plots for the regression model

Figures 5(a-d) show the combined effects of the independent variables on the Pd²⁺ removal percentage.

Figure 5(a) shows the interactive effects of pH and adsorbent dosage on the Pd²⁺ removal percentage. The influence of solution pH is one of the important parameters on the Pd²⁺ adsorption. In fact, pH affects both degree of ionizations of some adsorbates and surface charge of adsorbents [46, 47]. The removal percentage increased at high a pH (acidic condition) and a high adsorbent dosage [47].

Figure 5(b) shows the interactive effects of pH and contact time on the Pd²⁺ removal percentage. An initial rapid rate of adsorption (first 33 min) was observed while it gradually increased up to the equilibrium conditions. The initial rapid trend is due existing high numbers of unfilled sites in the adsorbent [48]. The result showed that increase in pH led to an increase in adsorption efficiency.

Figure 5(c) shows the combined relationship between pH and concentration of Pd²⁺ ions. The plot indicates that pH and concentration had significant effect on the Pd²⁺ ions adsorption.

The interactive effects of contact time and adsorbent dosage are shown in Fig. 5(d). The highest percentage of adsorption is observed at the lowest contact time when the highest adsorbent dosage is used. The results show that an increase in the adsorbent dosage led to increase in the Pd²⁺ ions removal. Its reason is due to increasing adsorbate molecules diffusion across the external boundary layers. According to the analysis by software (confirmed by the experiments), the operating parameters effect follows the following trend as:

pH > adsorbent dosage > contact time > solution concentration

3.7. Response surface modeling

Central composite design (CCD) as a module of the Design-Expert software under response surface methodology (RSM) was applied to model this process. High correlation coefficient (R^2) and low standard as the best model. The relationship between the response and independent variables is shown through a polynomial equation (Eq. 4) obtained by the software:

$$R\% = 79.51 + 19.05A - 7.60B + 13.02C + 2.66D + 569.44AB - 567.66AC + 567.05AD - 568.44BC + 568.71BD - 568.40CD - 5.13A^2 - 5.63B^2 - 6.09C^2 + 2.28D^2 \quad (4)$$

where, A, B, C and D are pH, time (min), adsorbent dosage (g/40mL) and Pd^{2+} ions initial concentration in the solution ($mg.L^{-1}$), respectively. The above coded equation is used to predict the Pd^{2+} ions removal from the solution. High and low levels of the factors are coded as + 1 and – 1, respectively.

The deviations were together studied to select the most appropriate model for this process. The quadratic model with a standard deviation of 2.18 and correlation coefficient (R^2) of 1.00 was suggested.

3.8. Analysis of variance (ANOVA)

The analysis of variance data are given in Table 3. This is used to evaluate the significance of the quadratic model parameters. They would be significant if the p-value ≤ 0.05 [49]. Moreover, a higher F-value indicates greater significance of each term on the response [50].

Table 3
ANOVA for the adsorption process

Source	Sum of Squares	DF	Mean Square	F-value	p-value	
Model	8.009×10^7	24	3.337×10^6	7.018×10^5	< 0.0001	Significant
A	2903.22	1	2903.22	610.58	< 0.0001	
B	461.47	1	461.47	97.05	0.0002	
C	1357.20	1	1357.20	285.44	< 0.0001	
D	56.82	1	56.82	11.95	0.0181	
AB	5.188×10^6	1	5.188×10^6	1.091×10^6	< 0.0001	
AC	5.156×10^6	1	5.156×10^6	1.084×10^6	< 0.0001	
AD	5.145×10^6	1	5.145×10^6	1.082×10^6	< 0.0001	
BC	5.170×10^6	1	5.170×10^6	1.087×10^6	< 0.0001	
BD	5.175×10^6	1	5.175×10^6	1.088×10^6	< 0.0001	
CD	5.169×10^6	1	5.169×10^6	1.087×10^6	< 0.0001	
A ²	631.20	1	631.20	132.75	< 0.0001	
B ²	759.60	1	759.60	159.75	< 0.0001	
C ²	890.36	1	890.36	187.25	< 0.0001	
D ²	124.67	1	124.67	26.22	0.0037	
Pure Error	23.77	5	4.75			
Cor Total	8.009×10^7	29				

3.9. Optimization procedure

Various parameters were utilized for the adsorption process optimization. The optimum value of Pd²⁺ ions removal (98.2%) was statistically found at time of 91.25 min, adsorbent dosage of 0.065 g/40mL, Pd²⁺ ions initial concentration of 77.5 mg.L⁻¹ and pH of 5.5. The optimized conditions were experimentally provided and 99.24% of Pd²⁺ ions were removed. It was confirmed that the model is properly able to predict the Pd²⁺ ions removal from an aqueous solution.

3.10. Adsorbent reusability

The stability and durability of ZnO NPs was examined in five sequential cycles at the optimum conditions. After each cycle, the ZnO NPs were separated from the solution by centrifugation. They were then washed twice by HNO₃ and dried at room temperature [51]. According to Fig. 6, the adsorbent activity was conserved more than 99% by 5 cycles.

3.11. Adsorption isotherm

The isotherms equations and their parameters were extracted from the literature [32]. As shown in Table 4, each equation data were calculated. R² for Langmuir, Freundlich and Temkin isotherm models were at 0.4345, 1.0 and 0.9805, respectively. Therefore, the Freundlich model (as a non-ideal and multilayer adsorption) was the best one compared with the others.

Table 4
Isotherm models data for the adsorption of
Pd²⁺ ions adsorption

Isotherm	Parameter	Calculated data
Langmuir	q _{max}	83.33
	K _L	0.0137
	R ²	0.4345
Freundlich	K _F	5.89
	n	0.498
	R ²	1
Temkin	B _T	18785
	A _T	53.925
	R ²	0.98

3.12. Adsorption kinetics

The kinetic parameters were extracted from the literature [32]. The fitting data for the pseudo-first-order and pseudo-second-order models are shown in Table 5. R^2 data for the pseudo-first-order and pseudo-second-order models were around 0.9319 and 1.0, respectively. Therefore, the adsorption of Pd^{2+} ions onto the synthesized ZnO NPs was properly fitted with the pseudo-second-order model. This shows that Pd^{2+} ions adsorption onto the ZnO NPs should be a chemisorption process. The pseudo-second order model is based on the adsorption capacity of the solid phases.

Table 5
Pseudo-first-order and pseudo-second-order models data
for the adsorption of Pd^{2+} ions adsorption

Model	Parameters	Calculated data
Pseudo-first-order	K_1	0.000233
	q_e	2.66
	R^2	0.9319
Pseudo-second-order	K_2	0.576
	q_e	11.696
	R^2	1

4. Conclusions

In the present study, ZnO nanoparticles were synthesized by centaurea cyanus aqueous extract as a reducing and stabilizing agent. A white color sediment in the solution was observed and several tests such as FTIR, XRD, SEM and EDX were carried out. It was confirmed that ZnO NPs were properly produced. They were then applied to remove Pd^{2+} ions (as a symbol of heavy metals) from an aqueous solution (as symbol of wastewater). The optimum conditions were statistically obtained and validated by an experiment. The Pd^{2+} ions percentage removal increased with increasing adsorbent dosage, reducing pH and contact time. The film diffusion as the most probable rate-controlling step of the adsorption mechanism was investigated. The Freundlich isotherm model and pseudo-second order kinetic model could respectively legitimize the phase equilibria and chemisorption of Pd^{2+} ions adsorption.

Declarations

Acknowledgment

The authors thank Oil Company Research and Technology (Arak Center) for analyzing the samples.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. J. Kielhorn, Ch Melber, D. Keller, I. Mangelsdorf, *Int. J. Hygiene and Environ. Health.* **205**, 417 (2002)
2. M. Miller, B. Askevold, H. Mikula, R. Kohler, D. Pirovich, R. Weissleder, *Nat. Commun.* **8**, 15906 (2017)
3. R. Rushforth, *Platinum Metals Review.* **48**, 30 (2004)
4. M. Hindsen, A. Spiren, M. Bruze, *Contact Dermatitis* **53**, 2 (2005)
5. N. Toff, *The flute book, a complete guide for students and performers* (Oxford University Publishing, 1996), p. 20
6. T. Weithers, *Foreign exchange: a practical guide to the FX markets* (Wiley, Publishing, 2013), p. 34
7. W.H. Brown, C. Foote, B. Iverson, *Organic chemistry*, fifth ed., (Cengage Learning, 2009), pp. 270
8. J. Tsuji, *Palladium reagents and catalysts: new perspectives for the 21st century* (John Wiley and Sons, 2004), p. 90
9. P. Colon, N. Pradelle-Plasse, J. Galland, *J. Dental Materials* **19**, 232 (2003)
10. Z. Kolarik, E. Renard, *Platin. Met. Rev.* **47**, 74 (2003)
11. H.K. Moghaddam, M. Pakizeh, *J. Ind. Eng. Chem.* **21**, 221 (2015)
12. M.R. Awual, M.M. Hasan, H. Znad, *Chem. Eng. J.* **259**, 611 (2015)
13. Z. Cheng, A.L. Kuantan, Y. Tao, D. Shan, K.E. Ting, X.J. Yin, *Int. J. Photoenergy*, 2012, 1 (2012)
14. A.K. Darban, Y. Kianinia, E. Taheri-Nassaj, *J. Environ. Health Sci. Eng.* **11**, 1 (2013)
15. I. Ghiloufi, Effect of indium concentration in zinc oxide nanoparticles on heavy metals adsorption from aqueous solution, 5th WSEAS International conference on Nanotechnology, (Cambridge, UK, 2013), pp. 329–335
16. J. Du, C. Jing, *J. Colloid and Interface Sci.* **358**, 54 (2011)
17. S. Singh, K.C. Barick, D. Bahadur, *J. Hazard. Materials* **192**, 1539 (2011)
18. G. Ghanizadeh, M. Ehrampoush, M. Ghaneian, *Iran. J. Environ. Health Sci. Eng.* **7**, 145 (2010)
19. C.M. Chou, H.L. Lien, *J. Nanoparticle Research* **13**, 2099 (2011)
20. A.K. Radzimska, T. Jesionowski, *Materials* **4**, 2833 (2014)
21. A.S. Lanje, S.J. Sharma, R.S. Ningthoujam, J.S. Ahn, R.B. Pode, *Adv. Powder Technol.* **24**, 331 (2013)
22. ÖA. Yildirim, C. Durucan, *J. Alloy. Compd.* **505**, 944 (2010)
23. J. Zhang, J. Wang, S. Zhou, K. Duan, B. Feng, J. Weng, H. Tang, P. Wu, *J. Mater. Chem.* **20**, 9798 (2010)
24. S. Yue, Z. Yan, Y. Shi, G. Ran, *Mater. Lett.* **98**, 246 (2013)

25. X. Wang, W. Cai, Y. Lin, G. Wang, C. Liang, J. Mater. Chem. **20**, 8582 (2010)
26. X.F. Ma, Y.Q. Wang, M.J. Gao, H.Z. Xu, G.A. Li, Catal. Today **158**, 459 (2010)
27. T. Sheela, Y.A. Nayaka, R. Viswanatha, S. Basavanna, T.G. Venkatesha, Powder Technol. **217**, 163 (2012)
28. K.Y. Kumar, H.B. Muralidhara, Y.A. Nayaka, J. Balasubramanyam, H. Hanumanthappa, Powder Technol. **239**, 208 (2013)
29. K.B. Angelin, S. Siva, R.S. Kannan, Asian J. Sci. and Technol. **6**, 2139 (2015)
30. N. Pandey, S.K. Shukla, N.B. Singh, Adv. Mater. Lett. **6**, 172 (2015)
31. E. Mosayebi, S. Azizian, J. Molecular Liquids **214**, 384 (2016)
32. R. Davarnejad, A. Azizi, M. Mohammadi, S. Mansoori, Int. J. Environ. Anal. Chem. **4** (2020)
33. S. Vasantharaj, S. Sathiyavimal, P. Senthilkumar, F.L. Oscar, A. Pugazhendhi, J. Photochem. Photobiol. B Biol. **192**, 74 (2019)
34. R. Jacob, J. Isac, Int. J. Chem. Stud. **2**, 12 (2015)
35. Y. He, Powder Technol. **147**, 59 (2004)
36. G.I. Dovbeshko, N.Y. Gridina, E.B. Kruglova, O.P. Pashchuk, National Library of Medicine **53**, 233 (2000)
37. R.K. Sahu, S. Argov, A. Salman, M. Huleihel, N. Grossman, Z. Hammody, J. Kapelushnik, S. Mordechai, Technol. Cancer Res. Treat. **3**, 629 (2004)
38. H. Fabian, M. Jackson, L. Murphy, P.H. Watson, I. Fichtner, H.H. Biospectroscopy, **1**, 37 (1995)
39. A. Jabs, *Determination of secondary structure in proteins by fourier transform infrared spectroscopy (FTIR)* (Jena Library of Biological Macromolecules, 2005)
40. X.C. Li, G.H. He, G.K. Xiao, H.J. Liu, M.J. Wang, Colloid Interface Sci. **333**, 465 (2009)
41. M. Francavilla, Green Chem. **16**, 2876 (2014)
42. S. Nagarajan, K.A. Kuppusamy, Indian J. Nanobiotechnology **11**, 39 (2013)
43. G. Zhang, X. Shen, Y. Yang, J. Physical Chem. **115**, 7145 (2011)
44. J. Singh, S. Kaur, G. Kaur, S. Basu, M. Rawat, Green Processing and Synthesis **8**, 272 (2018)
45. S. Fakhari, M. Jamzad, & H. Kabiri Fard **12**, 19 (2019)
46. E. Bazrafshan, P. Amirian, A.H. Mahvi, A. Ansari-Moghaddam, Global Nest J. **18**, 146 (2016)
47. M. Bhowmik, M. Kanmani, D. Animesh, S. Biswajit, Powder Technol. **354**, 496 (2019)
48. Z. Ghader, K. Mahsa, O.K. Yusef, N. Heshmatollah, E. Shirin, J.M. Mohammad, R. Rajab, Toxin Rev. **38**, 307 (2018)
49. B. Preetha, T. Viruthagiri, J. Hazard. Materials. **143**, 506 ((2007),)
50. S. Gholamhossein, A.S. Seyed, S.A. Nedasadat, J. Taiwan Instit. Chem. Eng. **60**, 165 (2016)
51. L.P. Josh, P. Chris, L.G. Rachel, Ind. Crops Prod. **58**, 15 (2014)

Figures

Figure 1

XRD pattern of the synthesized ZnO nanoparticles through the centaurea cyanus extract

(a)

(b)

(c)

Figure 2

a) FESEM image of ZnO NPs synthesized through *Centaurea cyanus* extract. b) and c) ZnO nanoparticles morphology before and after Pd^{2+} ions adsorption, respectively

Figure 3

FT-IR spectra of ZnO NPs before adsorption

Figure 4

EDX analyses of ZnO nanoparticles

Figure 5

Various parameters effect on the removal percentage

Figure 6

Pd²⁺ ions adsorption by ZnO NPs by five adsorption-desorption cycles at the optimum conditions