SYNTHESIS OF ZnO NANO POWDERS USING POLYETHYLENE GLYCOL BY THE CONTROLLED MICROWAVE METHOD

A. S. Abdulhadi¹, Gamal A. Gouda¹,*, A. M. Hamed¹, M. A. Abu-Saied² and M.A. El-Mottaleb¹

¹Department of Chemistry, Faculty of Science, Al–Azhar University, Assiut Branch, Assiut, Egypt
²Advanced Technology and New Materials Research Institute, the City of Scientific Research and Technological Applications (SRTA-City), New Borg Al-Arab, Alexandria 21934, Egypt

Zinc oxide nanoparticles (ZnO NPs) was synthesized using some factors influencing such as the polyethylene glycol (PEG) as a stabilizing agent at different pH and temperatures. The best conditions for preparing ZnO NPs were at pH 11, 0.1 M (7.5 mL) of PEG with molecular weights of 20000 and 60 oC. Properties of synthesized ZnO NPs were confirmed using different techniques (FTIR, UV-Vis, XRD, SEM and TEM). Obviously, UV-Vis spectrum of ZnO NPs showed an adsorption peak at 268 and 362 nm with a direct bandgap of 3.39 eV. PL spectra of ZnO NPs showed an emission peak at 420 nm. The average sizes calculated of ZnO NPs powder using the XRD line broadening method were 19.71 nm. TEM observation showed that the prepared ZnO NPs is spherical with different diameters in the range 22.2–27.8 nm. Moreover, the ZnO NPs prepared have an excellent adsorption capacity for the removal of some cations from water. The adsorption capacities were 391.6 and 437.2 mg/g for Mn(II) and Cd(II) respectively. Langmuir, Freundlich and Temkin models would be well described the adsorption process. Thermodynamically, the adsorption processes of ZnO NPs were spontaneous, endothermic, and physical in nature. The good removal efficiency of Mn(II) and Cd(II) by ZnO NPs with their exceptional adsorption capability suggests that the ZnO NPs have great potential applications in environmental protection.

Keywords: ZnO nanoparticles, polyethylene glycol, synthesis, characterization, applications.

INTRODUCTION

Zinc oxide is a rare inorganic material in the natural environment. ZnO has been the bandgap from 3.27 eV for the single crystal to 3.55 eV for the deposited film¹², so it has semiconductor and piezoelectric properties. The variation in bandgap in deposited film and nanostructured of ZnO has been related to the structural morphology and defects present in the crystal³⁴. For clinical purposes, ZnO is used potentially, it is more competent for the synthesis of nanoparticles than that of another metals⁵⁶. ZnO nanoparticles can be synthesized through numerous physiochemical pathways, such as soil-gel, co-precipitation, laser vaporization, and microemulsion⁷⁸. ZnO nanoparticles are widely used additives in sunscreen and cosmetics that help block ultraviolet radiation. The smaller size of these nanoparticles provides the skin with greater protection against ultraviolet damage⁹. The variety of structures of ZnO nanoparticles means that ZnO can be classified among new materials with potential applications in different fields of nanotechnology, ZnO may occur in one- (1D), two- (2D), and three-dimensional (3D) structures. Dimensional structures are the largest group, including nanorods¹⁰¹¹, needles¹², -helixes, -springs and -rings¹³, -ribbons¹⁴, -tubes¹⁵, -belts¹⁶, and -wires¹⁷¹⁸. ZnO is available in 2D structures, such as nanoplates/nanosheets and nanobelts¹⁹²⁰.

*Corresponding author: Gamal A. Gouda, E-mail: ggouda73@azhar.edu.eg
Recently, significant efforts are ongoing to improve and investigate the uses of NPs in applications such as membrane isolation, sensing, catalysis, adsorption, and processing with a view to improved environmental safety. ZnO was approved by the United States Food and Drug Administration (FDA) as a GRAS compound (generally known to be safe). In numerous studies, ZnO nanoparticles showed high absorption in the UV region as well as strong yellow-orange emission. Moreover, the ZnO nanoparticles demonstrated good antibacterial activity against some organisms and a fair photocatalytic degradation of methylene blue dye pollutants. Also, the synthesized ZnO nanoparticles reveal interesting features for various potential future applications. A major application of nanomaterials is the removal of heavy metals in water. A heavy metal can be defined as any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Their concentrations in aquatic environments have increased due to mining and industrial activities and geochemical processes. Due to heavy metals such as Mn, Cu, Hg, Pb, Cd, etc. could pose a serious threat to human health because they can be stored biologically in the food chain. For example, heavy metals can cause damage to the kidneys, mental and central nervous functions, lungs, and another organs. Therefore, it was necessary to look for cheap nanomaterials able to remove those elements that pollute the water. Recently, several studies were carried out on low-cost natural and chemical adsorbents for the removal of some metal ions from natural resources. Zinc compounds based on nanomaterials are good adsorbents of some heavy metal ions from wastewater.

In the current work, ZnO NPs was prepared and characterized. The obtained nanoparticles of ZnO were used as a tool for the removal of selected metal ions.

### Chemicals and reagents

The main chemicals and reagents used are of high grade, they are used without further purification. In all experiments, water deionized water was used to wash all glassware. Various chemicals and reagents were used in this study, as follows: Zinc (II) sulfate heptahydrate (ZnSO$_4$·7H$_2$O) with a purity of 98 % was obtained from Sigma-Aldrich; Cadmium (II) chloride 2.5-hydrate (CdCl$_2$·2.5H$_2$O) with a purity of 99.9 % was obtained from Wako. Manganese (II) sulfate monohydrate (MnSO$_4$·H$_2$O) with a purity of 99.9 %, was obtained from Morgan Chemical IND, Egypt; Polyethylene glycol (PEG) with M.wt is 1000, 6000, 8000, and 20000 was obtained from Panreac, Spain; Sodium hydroxide (NaOH) pellets (Extra pure) was obtained from Oxford.

### Synthetic parameters that effect of ZnO NPs formation

Several experiments were conducted to determine the ideal conditions for the formation of ZnO NPs. The main studied factors that affected ZnO NPs morphology were: (i) The effect of pH on the reaction medium was tested at pH 7, 9, 11, and 13. (ii) Effect of added amount (at 5, 7.5, 10, and 12.5 ml) of the stabilizing agent (PEG with M.wt 20000). (iii) Effect of temperature (at 30, 40, 50 and 70 °C).

In the current study, ZnO NPs powder was prepared by microwave method heating of a mixture that contains ZnSO$_4$·7H$_2$O (0.1 M) with stabilizing agent as the polyethylene glycol (PEG) and sodium hydroxide solution (NaOH) as precursors which slowly added dropwise to solutions under vigorous stirring at different temperatures of the mixture. In microwave oven the mixture was heated for 3 minutes then the precipitates were washed by distilled water and filtered. The precipitate was dried in an oven for three hours at 75 °C. The best factors effecting the synthesized of ZnO NPs such as the amount of stabilizing agent, pH, and temperature can be summarized in the following Table 1.

<table>
<thead>
<tr>
<th>Type of factor</th>
<th>ZnO NPs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stabilizing agent</td>
<td>Polyethylene glycol with M.wt is 20000</td>
</tr>
<tr>
<td>Amount of stabilizing agent</td>
<td>0.1 M (7.5 ml)</td>
</tr>
<tr>
<td>pH</td>
<td>11</td>
</tr>
<tr>
<td>Temperature</td>
<td>60 °C</td>
</tr>
</tbody>
</table>

### Characterization of synthesized ZnO NPs

All samples and chemicals for solutions preparation were weighed using an Analytical...
Balance Model-220 of (Denver Instrument Co., U.S.A.) with a sensitivity of 4-10 g. The adsorption was measured using a Labomed double-beam UV-visible spectrophotometer equipped with 1 cm quartz cells controlled by a PC performing the spectrophotometric. The synthesized ZnO NPs was dispersed in DMF and optical characterizations were performed. PL spectroscopy has been recorded with JASCO spectrofluorometer FP-6300. The prepared ZnO NPs was confirmed by FT-IR spectroscopy using the Thermo Fisher-model: Nicolet iS10 FT-IR spectrophotometer. The size of ZnO NPs was determined by a Philips X-ray diffractometer, PW 1710. The size and form of prepared nanomaterials were studied using scanning electron microscopy [(SEM; JEOL (JSM 5400LV)] and transmission electron microscopy [(TEM; JEOL (JEM-100 CXII)].

**Adsorption process**

The principal application of this study is the removal of Mn(II) and Cd(II) ions from wastewater using ZnO NPs as adsorbent by the adsorption method. The metal ions solutions were prepared by dissolving MnSO₄·H₂O or CdCl₂·2H₂O in deionized water to prepare different concentrations: the initial metal concentration of Mn(II) is 500 mg/L and Cd(II) is 550 mg/L. All adsorption tests were conducted in batches using 100 ml tapered flasks at room temperature. Different parameters affecting the adsorption process were examined, including: (i) Effect of contact time; experiments are performed using 10 mL of Mn(II) and Cd(II) solution with 25 mg of prepared adsorbent ZnO NPs at pH 4.81. This system was left at various predetermined intervals at a temperature of 30 °C. The residual concentration of Mn(II) and Cd(II) was determined for different contact times (from 3 to 300 min). (ii) Effect of adsorbent dosage; adsorption of Mn(II) and Cd(II) ions on ZnO NPs was investigated by changing the amount of adsorbent from 0.015 to 0.25 g/L in the test solution with keeping the initial Mn(II) and Cd(II) concentrations at 500 and 550 mg/L respectively, the temperature at 30 °C, pH 4.82 and equilibrium time 24h. (iii) Effect of pH; the experiments performed in the pH range 1.57-7.02 keeping all other parameters constant. The solution pH was adjusted to the required value using 0.1M HNO₃ or 0.1M NaOH. pH values of the waste solutions were adjusted using a pH meter (Denver Instrument Co., U.S.A.). (iv) The effect of the temperature; the adsorption of Mn(II) and Cd(II) ions by ZnO NPs was performed by using 0.025 g of the substrate in contact with an aqueous solution of Mn(II) and Cd(II) at 500 and 550 mg/L, respectively, at 25, 30, 35 and 40 °C. Constant temperature shaker bath (901N0073 Fisher Scientific, U.S.A.) is used for studying the effect of wastewater temperature on the treatment process using ZnO NPs. For all experiments, the reaction mixtures were left for 24h until equilibrium followed by centrifuging at 5,000 rpm for 20 min. Then the supernatants were analyzed to measure the concentrations of Mn(II) and Cd(II) by ICP-OES (Thermo Co., model ICAP6500 Duo S.N. ICP-20101916, England) in triplicate and the mean value was reported in the analysis study. The measured repeatability in the same experiment was less than 1.0 %. The amount of Mn(II) and Cd(II) metal ions at equilibrium qₑ was calculated from the mass balance equation given as below equation (1):

\[
q_e = \frac{V(C_o - C_e)}{m} \times 100
\]  

where qₑ (mg/g) is the amount of Mn(II) or Cd(II) per mass unit of adsorbents at a certain time t. C₀ and Cₑ (mg/L) are concentrations of Mn(II) or Cd(II) at the initial time and at time t, respectively. V is the volume of the solution (mL), and m is the mass of adsorbent (mg). The percent of metal ions removal (Adsorption %) by ZnO NPs was determined for each equilibrium by the expression presented as equation (2):

\[
\text{Adsorption} \% = \frac{(C_o - C_e)}{C_o} \times 100
\]  

**Isotherm models**

The isotherm models used to describe the adsorption process in water treatment were developed by Langmuir, Freundlich and Temkin, and their constants were calculated. The Langmuir isotherm is generally used for monolayer adsorption at specific homogenous sites on adsorbents surface”. The Langmuir isotherm is described mathematically by equation (3):  

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}
\]
where: $q_m$ is monolayer sorption capacity (mg/g) and $K_L$ is Langmuir equilibrium constant (L/mg). The fundamental features of the Langmuir isotherm can be described in terms of separation factor or equilibrium parameter $R_L$, which is defined by the following expression equation (4):

$$R_L = \frac{1}{1 + bC_o}$$

The value of $R_L$ indicates the isotherm shape to be unfavorable ($R_L > 1$), favorable ($0 < R_L < 1$) and irreversible ($R_L = 1$).

Freundlich isotherm is usually used for heterogeneous surface energy systems (non-uniform distribution of sorption heat), (Eq. 5).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where: $K_F$ and $n$ are Freundlich constants, the $K_F$ is adsorption capacity while $n$ is adsorption intensity; while $1/n$ is a function of the strength of the adsorption process.

The Temkin isotherm is usually used for heterogeneous surface energy systems (non-uniform distribution of sorption heat), (Eqs. 6&7).

$$q_e = B \ln A + B \ln C_e$$

$$B = \frac{R_T}{b_T}$$

where $A$ is the binding constant (L/mg) and it was related to the maximum binding energy while $B$ is Temkin adsorption constant that is related to the sorption heat. $B$ constant is related to sorption heat (J/mol) obtained From the Temkin plot ($q_e$ versus $\ln C_e$). $R$ is the universal gas constant (8.314 J/mol K), $T$ is the absolute temperature, 303 K.

**Thermodynamic study**

The changes in Gibb's free energy change, $\Delta G^o$ (kJ/mol), standard enthalpy change, $\Delta H^o$ (kJ/mol), standard entropy change, $\Delta S^o$ (kJ /mol K) of the adsorption process were calculated by using the (Eqs. 8-10) respectively.

$$\Delta G^o = -RT \ln K_d$$

$$K_d = \frac{C_s}{C_e}$$

$$\ln K_d = \Delta S^o / R - \Delta H^o / RT$$

**RESULTS AND DISCUSSION**

**IR spectra**

The IR of ZnO NPs showed strong peaks at 608 cm$^{-1}$ (Zn-O vibrational stretching) and the broadband at 3405 cm$^{-1}$ for ZnO NPs corresponding to O-H has absorbed water. The wavenumber at 1632, 1117, and 708 cm$^{-1}$ correspond to the vibration of O-Zn-O group (Fig. 1).

**Optical study**

UV–vis spectrum of the synthesized ZnO NPs was recorded in the range of 200-800 nm (Fig. 2). The spectrum of ZnO NPs is characterized by a weak absorption peak in the UV band at 268 nm that is attributed to the interband transition, whereas a broad peak around 362 nm reflects the quantum confinement of these structures.

**Fig. 1:** FTIR spectrum of synthesized ZnO NPs

**Fig. 2:** UV-vis absorption spectroscopy of ZnO NPs.
peak is mainly depending on the particle size. The energy band interval is usually calculated from the relationship Tauc equation (11) relating the wavelength with the absorption coefficient.

\[ \alpha h\nu = A (h\nu - E_g)^n \]  

(11)

where \( \alpha \) is the optical absorption coefficient and \( h\nu \) the photon energy (\( h \) is Planck's constant, \( \nu \) is the frequency of light), \( A \) is a transition parameter, and \( E_g \) is the bandgap energy, \( n= 2 \) (direct) and \( n= \frac{1}{2} \) (indirect) transitions. The direct and indirect band gaps (Fig. 3) were obtained by extrapolating the linear region up to the energy axis by plotting \((\alpha h\nu)^2\) and \((\alpha h\nu)^{1/2}\) vs the photon energy \((h\nu)\). The as-prepared ZnO NPs has \( E_g \) wider range than the ordinary band gap which reported around 2.2-4.5 eV. However, it is observed that the direct bandgap energy of synthesized ZnO NPs is 3.39 eV due to the quantum size effect. Similarly, the indirect bandgap energy of ZnO NPs is 1.932 eV.

PL spectroscopy was recorded for investigating the optical emission characteristic of ZnO NPs. The PL spectra of ZnO NPs excited by 325 nm excitation wavelengths are shown in (Fig. 4). Generally, there are two reasons to explain the luminescence of ZnO NPs: the structural defects in the crystals and the quantum size effect. The emission band at \( \sim 420 \) nm may be attributed to the surface state emission or deep trap emission which is in good agreement with a PL spectrum of nanoparticle ZnO NPs. The emission peak at about 420 nm can be related to the combination of conduction band electrons and valence band holes. In Figure 4(B) the bandgap recorded 3.39 eV and this band gap value is an agreement with the recorded value of UV analysis (Fig. 3).

**Fig. 3:** Plots of \((\alpha h\nu)^2\) and \((\alpha h\nu)^{1/2}\) vs \( h\nu \) (eV) for the direct and indirect bandgap ZnO NPs (A, B). The calculated direct and indirect bandgap of ZnO NPs (3.39, 1.932 eV).

**Fig. 4:** Excitation and emission spectra (A), and Bandgap energy of ZnO NPs by PL spectrum (B).
SEM and TEM analysis

The morphology of the prepared adsorbent was recorded using SEM and TEM micrographs (Fig. 5). The SEM micrograph of ZnO NPs is shown in (Fig. 5(A)). The result showed that the synthesized ZnO NPs were spherical with a diameter of approximately 22.50 nm. TEM easily observed the shape and size of ZnO NPs (Fig. 5(B)). TEM image (Fig. 5(B)) show that by heating the sample, the purity of the ZnO NPs can be increased, and it is more clear. The ZnO NPs obtained showed spherical morphology with various particle diameters from 22.2 to 27.8 nm and were aggregated with numerous nanoparticles. Zang et al. derived ZnO NP as hollow spheres and spheres by a solvothermal reaction in the presence of an ionic liquid (imidazolium tetrafluoroborate). The particle size distribution obtained from computed SEM and TEM images per 100 particles is presented in (Fig. 5(C&D)).

![SEM and TEM images of the synthesized ZnO NPs with 7.5 mL (0.1 M) of stabilizing agent, pH 11 and 60 °C; (A) SEM of ZnO NPs, (B) TEM of ZnO NPs, (C) and (D) particle size distribution for ZnO NPs.](image)

**Fig. 5**: SEM and TEM images of the synthesized ZnO NPs with 7.5 mL (0.1 M) of stabilizing agent, pH 11 and 60 °C; (A) SEM of ZnO NPs, (B) TEM of ZnO NPs, (C) and (D) particle size distribution for ZnO NPs.

![XRD patterns for ZnO NPs](image)

**Fig. 6**: XRD patterns for ZnO NPs
X-ray diffraction

The XRD models for ZnO NPs have been shown in (Fig. 6). The detected lattice peaks confirmed the presence of the ZnO NPs hexagonal phase as depicted in JCPDS #36-1451. The sharp intense diffraction peaks appearing at 2θ values; 32.56, 35.44, 36.58, 49.84, 57.04, 64.66, 68.26, 69.22, and 70.48 corresponding to (100), (002), (101), (102), (110), (103), (200), (112) and (201) planes of ZnO NPs with high crystallinity. The instrumental broadening and the sample impact are the sources of peak breadth in Bragg’s effect. The full widths at half maxima “FWHM” of the measured peaks were estimated and corrected according to the Pseudo-Voigt function of the line profile relation and it can be derived as the following equation (12):

\[ \beta_{hkl} = [\beta_{mes.}^2 - \beta_{inst.}^2]^{1/2} \]  

(12)

where \( \beta_{hkl} \) is the corrected FWHM, \( \beta_{mes.} \) is the measured FWHM, and \( \beta_{inst.} \) is the instrumental FWHM. The average crystallite size can be estimated using the Scherrer equation as the following equation (13):

\[ D_{sch} = 0.9 \lambda / \beta_{hkl} \cos(\theta_{hkl}) \]  

(13)

Table 2: XRD characteristics and the estimated structural parameters of ZnO NPs (\( \lambda = 0.1541838 \) nm)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Miller indices</td>
<td>(100)</td>
</tr>
<tr>
<td>h² + k² + l²</td>
<td>1</td>
</tr>
<tr>
<td>( \theta_{mes.} ) in degree</td>
<td>32.56</td>
</tr>
<tr>
<td>( \theta_{mes.} ) in radian</td>
<td>0.284</td>
</tr>
<tr>
<td>Gaussian FWHM from origin ( \beta_{mes.} )</td>
<td>0.36</td>
</tr>
<tr>
<td>Gaussian FWHM from origin ( \beta_{mes.} ) in radian</td>
<td>0.005</td>
</tr>
<tr>
<td>FWHM ( \beta_{inst.} ) in degree</td>
<td>0.16</td>
</tr>
<tr>
<td>FWHM ( \beta_{inst.} ) in radian</td>
<td>0.003</td>
</tr>
<tr>
<td>Gaussian ( \beta_d = \sqrt{\beta_{mes.}^2 - \beta_{inst.}^2} ) in radian</td>
<td>0.006</td>
</tr>
<tr>
<td>Gaussian ( (1/\beta_d) )</td>
<td>177.7</td>
</tr>
<tr>
<td>Sin( \theta_{mes.} )</td>
<td>0.280</td>
</tr>
<tr>
<td>Sin( \theta_{mes.} )</td>
<td>0.078</td>
</tr>
<tr>
<td>Placing distance ( d = \lambda / 2 \sin \theta )</td>
<td>0.047</td>
</tr>
<tr>
<td>Cos ( \theta_{mes.} )</td>
<td>0.956</td>
</tr>
<tr>
<td>Gaussian ( \beta_h ) ( \cos \theta_{mes.} )</td>
<td>0.346</td>
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<tr>
<td>Cos ( \theta_{mes.} )</td>
<td>0.921</td>
</tr>
<tr>
<td>Tan ( \theta_{mes.} )</td>
<td>0.292</td>
</tr>
<tr>
<td>Gaussian ( D_{sch} = 0.9 \lambda / \beta_d ) ( \cos \theta_{mes.} ) in nm</td>
<td>35.68</td>
</tr>
<tr>
<td>Lattice constants ( a = d \sqrt{h^2+k^2+l^2} ) in Å</td>
<td>0.047</td>
</tr>
<tr>
<td>Gaussian average ( D_{sch} ) in nm</td>
<td>19.71</td>
</tr>
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</table>
Table 3. The calculated average crystallite size of ZnO NPs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>The average crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>XRD method</td>
</tr>
<tr>
<td>ZnO NPs</td>
<td>19.71</td>
</tr>
</tbody>
</table>

Adsorption process

All desorption tests of Mn(II) and Cd(II) ions removal by nano-adsorbent, ZnO NPs from aqueous solutions, were carried out using a batch method. The process of removing Mn(II) and Cd(II) ions from wastewater such as contact time, the concentration of hydrogen ion concentrations (pH), amount of adsorbent, and the temperature of solutions, all these factors are studied.

Effect of contact time

The effect of contact time on Mn(II) and Cd(II) ions sorption was studied in different time intervals ranging from 0 min to 180 min with the initial metal concentration of Mn(II) is 500 mg/L and Cd(II) is 550 mg/L and at pH= 7 and 0.25 g (ZnO NPs) and 350 rpm agitation. (Fig. 7) illustrates the sorption of Mn(II) and Cd(II) ions by ZnO NPs with respect to contact time. At 0-90 min, absorption of Mn(II) and Cd(II) ions was increased sharply. Afterward, the percent removal was remained steady and, in some cases, decreased at higher times. This can be attributed to the desorption of Mn(II) and Cd(II) ions from the surface of the nanoadsorbent for a long time of contact with the aqueous medium. This shows that ZnO NP material is more selective. The best uptake rate of ZnO NP can be attributed to its high specific surface area. Since there is no significant increase in sorption Mn(II) and Cd(II) when the time is 100 min., the equilibration time could be considered to be 180 minutes, to ensure complete sorption. The slight increase in the percentage removal of heavy metal ions from the aqueous solution was observed by ZnO NPs, 91 % and 93 % for Mn(II) and Cd(II), respectively. The percentage removal of Mn(II) and Cd(II) increases with increasing time.

Effect of Dosage

For studying the effect of dosage we take a different amount of ZnO NPs adsorbent (from 0 to 2 gm) at pH= 7 and 350 rpm agitation for 2hrs. after that we measured Mn(II) and Cd(II) concentrations. Initially, the rate of adsorption was very rapid up to 0.25 g/L for ZnO NPs. This is because, at a higher dose of adsorbent, more adsorption sites are available, leading to greater elimination of Mn(II) and Cd(II) ions. Above 0.50 g/L removal of metal ions becomes very slow, as the surface of Mn(II) and Cd(II) ions and the solution concentration come to equilibrium with each other. The adsorbant dose of 0.25 g/L was therefore used in all subsequent experiments. The relationship between the amount of ZnO NPs and the amount of heavy metal adsorption is presented in (Fig. 8). The % removal of heavy metal ions from the aqueous solution was observed by ZnO NPs, 72 % and 77 % for Mn(II) and Cd(II), respectively.

Fig. 7: Effect of contact time on Mn(II) and Cd(II) adsorptions by ZnO NPs adsorbent; (500 and 550 mg/L initial Mn(II) and Cd(II) concentrations, respectively with 0.25 g adsorbent dose, temperature 30 °C and pH = 7).

Fig. 8: Effect of adsorbent dosage on removal of Mn(II) and Cd(II) ions, adsorbent dose up to 2 g, 350 rpm agitation, and pH = 7.
Effect of pH

(Fig. 9) demonstrates pH-based adsorption capacity for Mn(II) and Cd(II) ions, for 24 hrs. contact time at 500 and 550 mg/L as an initial Mn(II) and Cd(II) concentrations and solid/liquid ratio of 1 g/L. The removal of Mn(II) and Cd(II) from water by prepared adsorbent ZnO NPs was found to be highly dependent on the solution pH value, which affects the surface charge of the adsorbent and degree of ionization and speciation of the adsorbent. The highest adsorption capacity was noted of the ZnO NPs for Cd(II) ion. As the pH of the sorption solution increased the interaction with Mn(II) and Cd(II) ions is favorable, leading to enhance the adsorption capacity until Mn(II) and Cd(II) ions tend to hydrolyze. After pH= 6.0, the adsorption capacity increases remarkably. The implications of Mn(II) and Cd(II) hydrolysis at higher solution pH are: (i) due to a lower residual charge, Mn(OH)\(^+\) and Cd(OH)\(^+\) species have less affinity to the ZnO NPs surface compared to Mn(II) and Cd(II) ions; and (ii) at higher pH values, precipitation of Mn(OH)\(_2\) and Cd(OH)\(_2\) or electrostatic repulsion of negative species by ZnO NPs (the negatively charged surface) can prevent the uptake of Mn(II) and Cd(II) ions.

Adsorption isotherms

Experimental isotherms are important for the description of sorption capacity to help assess the feasibility of the process for a given adsorbent. The isotherm plays a critical role in the predictive modeling procedures for the design of sorption systems and analysis. Among these models, the most used to describe the adsorption process in water treatment were developed by Langmuir, Freundlich, and Temkin. Experimental and calculated data were listed.

Langmuir isotherm

In this study, the plot of \( C_e/Q_e \) versus \( C_e \) yields a straight line shown in (Fig. 10), and calculated values are listed in Table 4. The results revealed that the adsorption process suited well to the Langmuir model with \( R^2 \) values of 0.9998, 0.9998, and 0.9981 for ZnO NPs. Better fitted Langmuir isotherm model suggested the homogenous adsorption of Mn(II) and Cd(II) cations with the adsorption active site of equal affinity. The separation factor, \( R_L \), values determined from the Langmuir model for Mn(II) and Cd(II) removal were in the range of 0.031-0.018 suggesting that the removal of Mn(II) and Cd(II) was favorable.

Fig. 9: Effect of pH on adsorption of Mn(II) and Cd(II) by ZnO NPs adsorbent, (500 mg/L and 550 mg/L initial Mn(II) and Cd(II) concentrations respectively, 0.25 g adsorbent dose, temperature 30 °C, 24 hrs.).

The results showed that the removal of Mn(II) and Cd(II) ions increased significantly as the pH increased up to 7. It was noticed that when the pH value is higher than 5, the adsorption amount increased dramatically, which was attributed to the fact that heavy metal ions started to precipitate leading to the reduction of the metal ions in the aqueous solution at higher pH value, pH increases may change the phase structure and the stoichiometry of the forming phases.
Freundlich isotherm

The Freundlich isotherm is usually used for heterogeneous surface energy systems (non-uniform distribution of sorption heat). The log $q_e$ vs log $C_e$ plot allows determining the Freundlich constants. The results of Freundlich adsorption isotherm models are shown in (Fig. 11). The adsorption constants and the correlation coefficients are also listed in Table 4. If a value of $1/n$ is below one, it indicates a normal adsorption process. On the other hand, $1/n$ being above one indicates the cooperative adsorption process. In this study the $1/n$ values lie between 0 and 1; this indicates a normal adsorption process of Mn(II) and Cd(II) adsorption onto ZnO NPs adsorbent. Also, $n$ value lies between one and ten; this indicates a favorable adsorption process. As given in Table 4, the values of $R^2$ have been recorded 0.9877, and 0.9656 for ZnO NPs adsorbent of Mn(II) and Cd(II) respectively. This indicates that the Freundlich isotherm was not the best fit for the sorption process of Mn(II) and Cd(II) onto the surface of the adsorbent. Therefore, the removal of Mn(II) and Cd(II) ions onto ZnO NPs surface proceed with some heterogeneity inactive sites.

Fig. 11: The plot of log $q_e$ versus log $C_e$ for estimation of correlation coefficient; $R^2$ of the Freundlich model.

Temkin isotherm

Temkin model which assumed that the adsorption heat would decrease by increasing the adsorbent mass was also used to analyze adsorption data, shown in (Fig. 12). According to calculated Temkin parameters A and B, Table 4, values were found to be 1.77 L/g, 59.90 J/mol, 10.40 L/g and 51.07 J/mol, in the case of ZnO NPs for Mn(II) and Cd(II) respectively, indicating that the heat of sorption refers to a physical process. Due to a weak interaction between Mn(II) and Cd(II) ions and prepared ZnO NPs surfaces. Furthermore, the $b_T$ values recorded 0.042, and 0.048 KJ/mol for Mn(II) and Cd(II) onto ZnO NPs adsorbent, respectively, which confirmed that the removal occurred through physisorption process.

Comparing $R^2$ values in Table 4, it is found that the highest values were recorded for the Langmuir isotherm model. Therefore, Langmuir isotherm was the best fitted in sorption. The adsorption isotherms are followed in an order: Langmuir > Freundlich > Temkin.

Adsorption performance evaluation

A comparison of the sorption performance of prepared nano-adsorbent with other reported adsorbents for some cations was shown in Table 5. In the Table 5 are some nanomaterials prepared by different methods. Moreover, it has a high cost compared to the ZnO NPs under study, which can be prepared in more quantities with less cost. The synthesized ZnO NPs is considered to has the outstanding capability to adsorb Mn(II) and Cd(II) cations compared to various nano-adsorbents to remove other cations from aqueous solution (Table 5). The adsorption capacity of ZnO NPs for both Mn(II) and Cd(II) cations were 391.6 and 437.2 mg/g. The excellent adsorption capacity of the synthesized nanomaterial, in this study, was attributed to the high specific surface area and dispersion of ZnO NPs sample.
Table 4: Isotherm parameters for Mn(II) and Cd(II) removal onto ZnO NPs

<table>
<thead>
<tr>
<th>Cations</th>
<th>Isotherm models</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Temkin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(II)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_m = 397$</td>
<td>$K_L = 0.054$</td>
<td>$R_L = 0.031$</td>
<td>$R^2 = 0.9997$</td>
<td>$K_F = 107$</td>
</tr>
<tr>
<td>Cd(II)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_m = 427$</td>
<td>$K_L = 0.091$</td>
<td>$R_L = 0.018$</td>
<td>$R^2 = 0.9988$</td>
<td>$K_F = 152$</td>
</tr>
</tbody>
</table>

Table 5: Different nanocomposites-based metal oxides used as adsorbents for metal ions removal from aqueous solution

<table>
<thead>
<tr>
<th>Nanomaterials</th>
<th>Adsorption capacity (mg/g)</th>
<th>Analyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2/graphene oxide</td>
<td>72.8</td>
<td>Cd(II)</td>
</tr>
<tr>
<td></td>
<td>65.6</td>
<td>Pb(II)</td>
</tr>
<tr>
<td>Fe3O4/chitosan/graphene oxide</td>
<td>76.9</td>
<td>Pb(II)</td>
</tr>
<tr>
<td>Phosphonium-coated MNPs</td>
<td>50.5</td>
<td>As(V)</td>
</tr>
<tr>
<td></td>
<td>32.2</td>
<td>Cr(VI)</td>
</tr>
<tr>
<td>SiO2/graphene</td>
<td>113.6</td>
<td>Pb(II)</td>
</tr>
<tr>
<td>Fe-Mn binary oxide-biochar</td>
<td>95.2</td>
<td>Cd(II)</td>
</tr>
<tr>
<td>Co–Al–Fe</td>
<td>130</td>
<td>As(III)</td>
</tr>
<tr>
<td></td>
<td>76</td>
<td>As(V)</td>
</tr>
<tr>
<td>ZnO NPs (Current study)</td>
<td>391.6</td>
<td>Mn(II)</td>
</tr>
<tr>
<td></td>
<td>437.2</td>
<td>Cd(II)</td>
</tr>
</tbody>
</table>

**Thermodynamics study**

To investigate the sorption process of Mn(II) and Cd(II) in-depth, the typical thermodynamic parameters are determined. The calculated thermodynamic parameters, Figure 13, are listed in Table 6. In general, the value of $\Delta H^o < 0$ indicated that the sorption process was an exothermic reaction. As the temperature increased the value of $\Delta G^o$ increased. The positive value of $\Delta G^o$ under various temperatures denoted that the reaction was a nonspontaneous process. From Table 6, the $\Delta G^o$ value of ZnO NPs adsorbent are negative indicating that the two reactions are a spontaneous and thermodynamically feasible process. As illustrated in (Fig. 13), a higher temperature enhances the adsorption reaction, and the values of $\Delta H^o$ are positive. In a work, Ren et al. noticed that the adsorption capacity of the graphene/MnO$_2$ composite increased from 46 to 60 mg/g when the reaction temperature from 298 K to 318 K. In this study, at 313 K the adsorption capacity of ZnO NPs nanoparticle is observed to be 1.2 times higher than for those recorded at 298 K. The $\Delta S^o$ of two adsorbents are positive, indicating that the randomness at the adsorbent / Mn(II) or Cd(II) solution interface increased as the process progressed. The values of $\Delta H^o$ were ranged from 37 to 41 kJ/mol, illustrating that physisorption existed for the adsorption of Mn(II) and Cd(II) on the prepared adsorbent.

**Fig. 13:** Effect of temperature (K) in adsorption of Mn(II) and Cd(II) by ZnO NPs adsorbent. (500, 550 mg/L initial Mn(II) and Cd(II) concentration respectively, 0.25 g adsorbent dose, temperature 30 °C, 24hrs.).
Table 6: Thermodynamic parameters for Mn(II) and Cd(II) adsorption by ZnO NPs as adsorbent.

<table>
<thead>
<tr>
<th>Ions</th>
<th>Temperature (K)</th>
<th>$K_d$ (L/mg)</th>
<th>$\Delta G^o$ (kJ/mol)</th>
<th>$\Delta H^o$ (kJ/mol)</th>
<th>$\Delta S^o$ (J/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(II)</td>
<td>298</td>
<td>1.41</td>
<td>-1.00</td>
<td>41.98</td>
<td>144.88</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>2.06</td>
<td>-1.81</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>2.67</td>
<td>-2.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>2.93</td>
<td>-2.73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd(II)</td>
<td>298</td>
<td>1.83</td>
<td>-1.47</td>
<td>37.58</td>
<td>131.90</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>2.66</td>
<td>-2.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>3.21</td>
<td>-2.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>3.28</td>
<td>-3.08</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Conclusion

In this study, the preparation and characterization of ZnO NPs have been investigated. Parameters of the precipitation conditions like pH, component ratio, and aging temperature have been studied in detail. Precipitates obtained from different conditions were characterized by several techniques like UV-visible spectrophotometer, photoluminescence spectroscopy, SEM, TEM, XRD, and FT-IR. ZnO NPs showed an absorption peak at 362 nm with a wide direct bandgap (3.39 eV). PL spectra showed the emission peak at 420 and 325 nm excitation wavelengths for ZnO NPs. The average crystallite sizes for the ZnO NPs nanoparticle were calculated by the XRD line broadening method and confirmed with TEM and SEM micrographs summations. The calculated average crystallite sizes of ZnO NPs were with average lengths of 19.71 nm. TEM observations showed that the as-produced ZnO NPs is spherical with different diameters in the range 22.2–27.8 nm. Furthermore, the produced nanomaterial show exceptional adsorption capability for Mn(II) and Cd(II) removal from water, the adsorption capacities were found to be 391.6 and 437.2 mg/g for Mn(II) and Cd(II) respectively. The adsorption isotherms could be well described by the Langmuir, Freundlich, and Temkin isotherm models. Thermodynamically, the adsorption processes were spontaneous, endothermic, and physical in nature, for ZnO NPs. The high removal efficiency of Mn(II) and Cd(II) by ZnO NPs with its exceptional adsorption capability suggests that the ZnO NPs has great potential applications in environmental protection.

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تحضير حبيبات أكسيد الزنك النانوية باستخدام بولي إيثيلين جليكول بطريقة تحكم الميكروويف

عبدالهادي سليمان عبد الهادي 1 – جمال عبدالعزيز جودة 1 – عبد الرحمن مصطفى حامد 1 – محمد عبد الرحمن أبو سعيد 1 – محمد عبد المطلب 1

1 قسم الكيمياء، كلية العلوم، جامعة الأزهر، فرع أسيوط، أسيوط 71524، مصر
2 معهد بحوث التكنولوجيا المتقدمة والمواد الجديدة، مدينة البحث العلمي والتطبيقات التكنولوجية، برج العرب الجديدة، الإسكندرية 21934، مصر

تم تحضير جسيمات أكسيد الزنك النانوية (ZnO NPs) باستخدام بعض العوامل المؤثرة مثل البولي إيثيلين جليكول (PEG) كعامل ثبت عند درجة حرارة مختلفة. كانت أفضل الظروف لتحضير أكسيد الزنك النانوية عند درجة حرارة 11 وتركيز 0,1 مول (pH) 7,5. تأكد من البولي إيثيلين جليكول مع وزن جزيئي 20000 ودرجة حرارة 60 درجة مئوية. تم استخدام تقنيات مختلفة مثل الأشعة تحت الحمراء (FTIR)، والتحليل المصريي الإلكتروني (UV-Vis)، والنيوترون الأمامي (XRD)، ومناقشة التدفق (SEM)، لمعرفة أن أكسيد الزنك النانوية (UV-Vis) من الواضح أن طيف أكسيد الزنك النانوية من الوضع أثناء تحليل المجهري الإلكتروني. أظهر ذروة امتصاص عند 269 و 362 نانومتر مع فجوة نطاق مباشرة تبلغ 0.3 فولت. ظهرت باستخدام مقياس معايير الضوئي (PL) للاكسيد الزنك النانوية ذروة انبعاث عند 420 نانومتر. كان المتوسط الأحادي المحسوس لحبيل أكسيد الزنك النانوية باستخدام تقنية توزيع الخطي في 19.71 من الوزن.

أن أكسيد الزنك النانوية المحضر (TEM) ونانومتر. أظهرت صور المجهري النانوية للضوء كروية بأقطار مختلفة في المدى 22.2 - 27.8 نانومتر. على ذلك، فإن أكسيد الزنك النانوية المحضر لديها قدرة امتصاص ممتازة لإزالة بعض الكاتيونات من الماء. كانت سعت الامتصاز 391.6 والكتيونات (Cd (II) و Mn (II)) من التوالي، وصورة نمطية (Themkin) و فورنليش (Langmuir) والديناميكية الحرارية، ظهرت عمليات امتصاص أكسيد الزنك النانوية تقليدية ومهما للحرارة وذات الجدة بواسطة أكسيد الزنك النانوية ونظام الاستدامة على الامتصاص إلى أن أكسيد الزنك النانوية يمكن أن تكون لها تطبيقات محتملة كبيرة في حماية البيئة.