# A brief study on zinc oxide based nanosorbents and adsorptive removal of heavy metal ions Naveen Chandra Joshi<sup>1</sup>\*, Nishant Kumar<sup>2</sup>, Ajay Singh<sup>2</sup>

Department of Chemistry, Uttaranchal University Dehradun, Uttrakhand, India

Received: 18-01-2020 / Revised: 28-02-2020 / Accepted: 08-03-2020

#### Abstract

The liquid waste streams releases from industrial sectors contain numerous inorganic and organic pollutants. These pollutants may be heavy metals and synthetic dyes. Metal oxide based nanomaterials have been used in the removal of such pollutants from waste water by using adsorption techniques. The adsorption based removal of heavy metals is found good alternative over other conventional methods. ZnO nanoparticle based adsorbents have been utilised in the removal different heavy metal ions from waste water. These adsorbents are generally prepared by the incorporation of organic or inorganic materials with ZnO nanoparticles. In this brief review, we will be discussed about different ZnO based nanomaterials which potentially utilised in treatment of waste water containing heavy metals.

Keywords: Heavy metals, Adsorption, ZnO nanoparticles, Waste water treatments.

#### Introduction

activities The human such industrialisations, agriculture, urbanisations and domestic activities release a large number of inorganic and organic pollutants. Heavy metals are one of them and common heavy metals included lead, cadmium, mercury, chromium, copper, iron, zinc etc. Such metals are not biodegradable, not metabolised and not decomposed [1]. These heavy metals are also important for living organisms but under the concerned limits but many of them are highly hazardous to living organisms even at very low concentrations. The methods such as chemical precipitation, reverse osmosis, ion exchange, solvent extraction, electrochemical and adsorption have been used in the removal of heavy metals from water or waste water [2].

# \*Correspondence Dr. Naveen Chandra Joshi Department of Chemistry, Uttaranchal University Dehradun, U.K.,India. E-Mail: drnaveen06joshi@gmail.com

Among all conventional methods, adsorption process is cost effective, efficient and applicable in the large scale operations of waste water treatments [3,4]. Nanotechnology has offered applications of nano sized materials in the fields of physical, chemical, biological and environmental sciences [5]. Nanotechnology is mainly related to the synthesis, characterisations and exploration of materials in the nano range (1–100 nm)[6].Due to many specific physical and chemical properties, the nanomaterials such as zinc oxide (ZnO), carbon nanotubes (CNTs), magnesium oxide (MgO), ferric oxide (Fe<sub>3</sub>O<sub>4</sub>), graphene, manganese oxide (MnO<sub>2</sub>) and titanium oxide (TiO<sub>2</sub>) have played the major roles in the treatment of waste water containing different heavy metals [7,8].

#### ZnO nanoparticleand adsorption

The zinc oxide (ZnO) nanoparticles serve as nanosorbent due to its good adsorptive properties, nontoxicity, chemical, thermal and mechanical stability [9]. The use of zinc oxide nanoparticles and their composites may have some disadvantages such as colloidal stability, agglomeration and lack of separating and recovering properties [10-14]. The adsorption study of heavy metals on the surface of nanosorbents in the laboratory scale is usually carried out under the batch system. The batch system includes contact time, pH, concentrations, dosage and temperatures. The optimized conditions found from the batch experiments can be applicable in the large scale removal processes of heavy metal ions from contaminated water [15-18]. The suitability of metal adsorption for a particular isotherm model indicates type of adsorption and it is an important step to find out a suitable isotherm model for design purposes. Various isotherm models such as Langmuir, Freundlich, Temkin, RedlichPatterson (R-P), Dubbin-Radush (D-R), Sips, Toth and Khan Isotherm models have been used to correlate the experimental results of adsorption [19-29] (Table:1). The kinetics of adsorption of heavy metals on to nanosorbents is an essential part in the better applicability of optimized batch conditions, rate and the mechanism of sorption. The four identified kinetic models for such studies are pseudo first order kinetic model, pseudo second order kinetic model, elovich kinetic model and intra particle diffusion [15,16] (Table:2).

Type of isotherms	Mathematical equation	Parameters
Langmuir	$C_e/Q_e = 1/K_l x + C_e/K_l$	Kı, x
Freundlich	$\mathbf{Q}_{\mathbf{e}} = \mathbf{K}_{\mathbf{f}} \cdot \mathbf{C}_{\mathbf{e}}^{-1/n}$	K <sub>f</sub> , 1/n
Temkin	$Q_e = y + z \ln C_e$	y, z
Redlich Patterson (R-P)	$Q_e = K_{rp}C_e/1 + \alpha. C_e^{\beta}$	K <sub>rp</sub> , α, β
Dubbin-Radush (D-R)	$Q_e = Q_d exp\{RT \ln (1 + 1/C_e)^2 / -2E^2\}$	$Q_{d,}E$
Sips	$Q_e = Q_s b C_e^{1/n} / 1 + S C_e^{1/n1}$	$Q_{s}, 1/n_{1}, b$
Toth	$Q_e = Q_t C_e / (K_t + C_e^{1/n})$	$Q_{t, 1/n_2}$
Khan	$O_e = (O_k B_k c_e) / (1 + B C_e)^{Ak}$	$O_k B_k A_k$

**Table:1 Isotherm models** 

\*Terms:  $C_e = Equilibrium concentration of metal ions (mg/L), Q_e= Amount of metal sorbate per gram of sorbent (mg/g), K<sub>1</sub> = Adsorption capacity, x = Energy of adsorption, K<sub>f</sub> = Adsorption capacity, 1/n = Adsorption intensity, y = Binding constant at equilibrium time, z = Heat of sorption, K<sub>rp</sub> = Binding capacity (L/g), <math>\alpha$  = Redlich Patterson constant,  $\beta$  = Exponent lies between 0 and 1, Q<sub>d</sub>= Adsorption capacity, E = Energy of adsorption, Q<sub>s</sub> = Adsorption capacity, n<sub>1</sub> = Sips exponent, b = Energy of adsorption, Q<sub>t</sub> = Adsorption capacity, n<sub>2</sub> = Toth model exponent, Q<sub>k</sub>= Adsorption capacity, B<sub>k</sub> = Khan model constant and A<sub>k</sub>= Khan model exponent.

#### **Table:2 Kinetic models**

Kinetic models	Mathematical equations	Parameters
Pseudo first order	$\ln (Q - Q') = (\ln Q) - (k * t)$	K
Pseudo second order	$\frac{t}{Q} = \frac{1}{k'} * Q + Q$	k
Elovich	$Q = k_E t^{1/2 +} I_e$	Ι
Intra particle diffusion	$Q = m + n \ln t$	m, n

\*Terms: Q and Q'= Adsorption capacity at equilibrium and at time t, k and k' = pseudo-first and second order rate constant in min<sup>-1</sup> and g/mol/min, I = the intra particle diffusion and m and n=initial adsorption rate (mg/g/min) and desorption constant.

### **Current studies**

Various ZnO nanoparticles based adsorbent have been utilised in the removal of heavy metal ions from waste water. Joshi and Singh [16] have synthesised zinc oxide based nanosorbent (ZOBN) by using the leaves extract of Shorearobusta (Sal). This adsorbent was efficiently used in the removal of Pb2+ and Cd2+ ions from waste water. The ZOBN was well characterised by using FTIR, UV-Visible, XRD, FESEM and EDX methods. The adsorption efficiencies of Pb2+ and Cd<sup>2+</sup> ions have been found 52.5% and 35.5% at contact time 60 min, 92.9% and 89.9% at pH 6 and 45.1% and 39.9% at temperature 60°C, respectively.Sani et al. [29] has reported the utilisation ZnO/talc nanocomposite in the removal of Pb<sup>2+</sup> ions from waste water. The ZnO/talc nanocomposite has been characterised by using the analytical techniques. The data of adsorption have been best fitted to pseudosecond-order kinetic model, Freundlich and the Langmuir isotherm models. The maximum lead adsorption capacity of ZnO/talc nanocomposite was found as 48.3 mg  $g^{-1}$ .

Kumar et al. [30] considered the synthesis, characterisation and utilisation of ZnO-NiObased nanocomposite as an adsorbent for the removal of Pb<sup>2+</sup> and Cd<sup>2+</sup>ions from waste water. The adsorption capacity was calculated as1519.7 mgg<sup>-1</sup>for this material. adsorption The process showed chemisorption which was demonstrated by the pseudosecond order kinetic model. Yuvaraja et al [31] reported ZnO nanorods for the removal of As (III) from waste water. The ZnOnanorods have been characterised by using by XRD, FT-IR spectroscopy, SEM, and TGA. The maximum As<sup>3+</sup> ionsadsorption capacity of ZnOnanorodshas been found to be 52.63 mg/g at pH 7, adsorbent dose 0.4 g, contact time 105 min, and temperature 323 K. Sani et al [32]have incorporated ZnO nanoparticles into the layers of montmorilloniteand utilised in the removal of copper and lead ions from waste water. The experimental data were indicated that this incorporated material can be best utilised in the removal of copper and lead ions under large scale treatments of waste water.Alswata and coworkers[33]have utilised the ZnO/Zeolite nanocomposite in the removal of lead and arsenic ions from the waste water. The maximum adsorption efficiencies of lead and arsenic ions have been recorded as 93% and 89%, respectively, at pH4, 0.15 g and 30 min.

# Conclusions

This paper investigated the adsorptive performances of ZnO based nanosorbents for heavy metal ions from waste water. The adsorption study was adequately given with applying batch parameters, isotherms and kinetics. The recent study was comprised of the work of some researchers based on the adsorption of heavy metal ions by using ZnO based nanomaterials.

# References

- NP Khumalo, SD Mhlanga, AT Kuvarega, GD Vilakati, BB Mamba, DS Dlamini, Adsorptive removal of heavy metals from aqueous solution by graphene oxide modified membranes, International Journal of Scientific & Engineering Research, 2017;8:4.
- SK Gunatilake, Methods of Removing Heavy Metals from Industrial Wastewater, J Multidiscip Eng Sci Stud, 2015; 1:12–18.
- J Wang, B Chen, Adsorption and coadsorption of organic pollutants and a heavy metal by graphene oxide and reduced graphene materials, Chem Eng J, 2015; 281:379–388.
- NC Joshi, A chodhary, Y Prakash, A Singh, Green Synthesis and Characterization of α-Fe2O3 Nanoparticles using Leaf Extract of Syzygiumcumini and their Suitability for Adsorption of Cu(II) and Pb(II) Ions, Asian Journal of Chemistry, 2019;31:1809-1814.
- NC Joshi, Y Prakash, Leaves extract-based biogenic synthesis of cupric oxide nanoparticles, characterizations, and antimicrobial activity, Asian J Pharm Clin Res, 2019;12:288-291.
- 6. V Yadav, Nanotechnology, big things from a tiny world: a review, AEEE, 2013;3(6):771–778.
- 7. V Parihar, M Raja, R Paulose, A brief review of structural, electrical and electrochemical

properties of zinc oxide nanoparticles, Rev Adv Mater Sci, 2018;53:119-130.

- H Sadegh,Gomaa, AM Ali, VK Gupta, ASH Makhlouf et al., The role of nanomaterials as effective adsorbents and their applications in wastewater treatment, J NanostructChem,2017; DOI 10.1007/s40097-017-0219-4.
- MM Ibrahim, S Asal, Physicochemical and photocatalytic studies of Ln3+- ZnO for water disinfection and wastewater treatment applications. J Molecular Structure, 2017; 1149:404–413.
- Z Rafiq, R Nazir, D Shahwar, MR Shah, S Ali, Utilization of magnesium and zinc oxide nanoadsorbents as potential materials for treatment of copper electroplating industry wastewater, J Environ ChemEng, 2014; 2:642–651.
- AC Martins, AL Cazetta, O Pezoti, JRB Souza, T Zhang, EJPilau, TAsefa, VC Almeida, Sol-gel synthesis of new TiO2/activated carbon photocatalyst and its application for degradation of tetracycline, Ceram Int, 2017; 43(5):4411– 4418.
- I Voigt, H Richter, M Weyd, K Milew, R Haseneder, C Günther, V Prehn, Treatment of oily and salty mining water by ceramic nanofiltration membranes., ChemIng Tech, 2019; 91(10):1454–1459.
- 13. L Rafati, MH Ehrampoush, AARafati, M Mokhtari, AH Mahvi, Fixed bed adsorption column studies and models for removal of ibuprofen from aqueous solution by strong adsorbent nano-clay composite, J Environ Health SciEng, 2019;1–13.
- 14. S Mustapha, MMN damitso, AS Abdul kareem, Application of TiO2 and ZnO nanoparticles immobilized on clay in wastewater treatment: a review, Appl Water Sci, 2020; 10, 49.
- NC Joshi, N Malik, A Singh, Synthesis and Characterizations of Polythiophene–Al2O3 Based Nanosorbent and Its Applications in the Removal of Pb2+, Cd2+ and Zn2+ Ions, J Inorg Organomet Polym, 2020; 30: 1438–1447.

- NC Joshi, ASingh, Adsorptive performances and characterisations of biologically synthesised zinc oxide based nanosorbent (ZOBN),Ground water for Sustainable Development, 2020;10:100325.
- NC Joshi, VRangar, R Sati, E Joshi, A Singh, Adsorption Behavior of Waste Leaves of Quercus Leucotrichophora for the Removal of Ni2+ and Cd2+ Ions from Waste Water, Orient J Chem, 2019;35(2) 591-596.
- NC Joshi, NS Bhandari, S Kumar, Biosorption of copper (II), iron (II) and zinc (II) from synthetic waste water using Banjh leaves as low cost adsorbent, Environ. Sci.: An Indian Journal, 2011; 6:148-153.
- OJ Redlich, DL Peterson, A useful adsorption isotherm, Journal Physical Chemistry, 1959; 63: 1024–1026.
- I Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, Journal of American Chemical Society, 1918; 40: 1361– 1403.
- 21. MM Dubinin, The potential theory of adsorption of gases and vapors for adsorbents with energetically non-uniform surface, Chemical Review, 1990; 60:235-266.
- 22. MM Dubinin, LVRadushkevich, Equation of the characteristic curve of activated charcoal, Chem Zentr, 1947; 1: 875–890.
- 23. HMF Freundlich, Over the adsorption in solution, Journal Physical Chemistry, 1906; 57: 385–470.
- 24. MI Tempkin, VPyzhev,Kinetics of ammonia synthesis on promoted iron catalysts, Acta Physiochim URSS, 1940; 12:217-222.
- 25. R Sips, On the structure of a catalyst surface, Journal Chemical Physics, 1948; 16: 490–495.
- 26. J Toth, State equations of the solid gas interface layer, ActaChemAcad Hung, 1971; 69: 311–317.
- AR Khan, IR Al-Waheab, A Al-Haddad, Generalized equation for adsorption isotherms for multicomponent organic pollutants in dilute aqueous solution, Environmental Technology, 1996;17: 13–23.
- 28. KV Kumar, Linear and non linear regression analysis for the sorption kinetics of methylene

blue onto activated carbon, Journal of Hazardous Materials, 2006; B137: 1538-1544.

- 29. HA Sani, MB Ahmad, TASaleh, Synthesis of zinc oxide/talc nanocomposite for enhanced lead adsorption from aqueous solutions, RSC Adv, 2016; 6:108819-108827.
- 30. KY Kumar, HB Muralidhara, YANayaka, H Hanumanthappa, MSVeena, SRK Kumar, ZnO-NiO nanocomposites as highly recyclable adsorbent for effective removal of Pb(II) and Cd(II) from aqueous solution, International Conference on Advanced Nanomaterials & Emerging Engineering Technologies, 2013;95-101.
- 31. G Yuvaraja, C Prasad, YVijaya et al., Application of ZnO nanorods as an adsorbent material for the

**Conflict of Interest: None Source of Support: Nil**  removal of As(III) from aqueous solution: kinetics, isotherms and thermodynamic studies, Int J IndChem, 2018; 9:17–25.

- 32. HASani, MB Ahmad, MZHussein, N Azowa Ibrahim, A Musa, TA Saleh, Nanocomposite of ZnO with montmorillonite for removal of lead and copper ions from aqueous solutions, Process Safety and Environmental Protection, 2017;109: 97-105.
- 33. AA Alswata, MB Ahmad, NM Al-Hada, HM Kamari,MZB Hussein, N Azowa Ibrahim, Preparation of Zeolite/Zinc Oxide Nanocomposites for toxic metals removal from water, Results in Physics, 2017; 7: 723-731.