



Removal of Ni(II), Cd(II) from aqueous solutions by sorption onto Copper Oxide Nanomaterials

Sayyed Hussain^{1*}, Kiran Pakhale¹,
Chandranayan Waghmare¹, Milind Ubale²

¹Post Graduate Department of Chemistry, Sir Sayyed College, Aurangabad
431001.M.S.(India)

²Post Graduate Department of Chemistry, VasantraoNaik College, Aurangabad
431001.M.S. (India).

Abstract : In this work, Copper Oxide nanoparticles were examined and compared for their ability in removing Ni (II) and Cd (II) from aqueous solutions. Batch operations were conducted with different process parameters such as contact time, nanoparticles concentration, initial arsenic concentration and pH. Results revealed that Copper Oxide Nanoparticles(CON) presented an outstanding ability to remove both Ni(II) and Cd(II). Removal efficiency was enhanced with increasing the contact time but reduced with increasing initial Ni(II) and Cd(II) concentrations and pH. It could be concluded that Copper Oxide nanoparticles showed remarkable potential for Ni(II), Cd(II) removal from aqueous solution e.g. contaminated water. The adsorption kinetics fitted well with pseudo-second-order model and the adsorption data obeyed the Langmuir equation. The adsorption isotherm data could be well described by the Freundlich equation. Results of this study suggest that CON show potential for developing a simple process for field applications to remove Ni(II), Cd(II) from aqueous systems.

Key words : Ni(II), Cd(II), Copper Oxide nanoparticles(CON), Adsorption, Isotherm.

Introduction:

As Water pollution is increasing worldwide due to rapid growth of industry, increased human population, providing clean water to human population is becoming more and more challenging task to do, which results into various studies to remove hazardous materials like bacteria, heavy metals from aqueous solutions and wastewater. The toxic metal ions dissolved can eventually reach the top of the food chain and thus become a risk factor for human health.^[1]

The conventional technologies for the removal of heavy metal ions from aqueous solution include chemical precipitation, ion exchange, reverse osmosis, electrochemical treatment and adsorption.^[2] Among the different treatments described above, adsorption technology is attractive due to its merits of efficiency, economy and simple operation. A variety of adsorbents, including clays, zeolites, dried plant parts, agricultural waste biomass, biopolymers, metal oxides, microorganisms, sewage sludge, fly ash and activated carbon have been used for heavy metal ions removal.^[3-6]

However the problem with these methods is that the toxic metal is transferred from liquid medium to solid waste which themselves has novel disposal challenge whereas use of nanoparticles facilitates recovery of

both.

Compared to the traditional adsorbents, nanoparticles possess quite good performance owing to high efficient specific surface area and the absence of internal diffusion resistance.^[7]

The objectives of this research were to investigate adsorption capacity, reaction kinetics and the effects of pH, contact time, change in temperature, initial concentration of metal ions and amount of adsorbent dosage on Ni(II), Cd(II) removal by performing batch experiments. Results from this study can be used to assess the utility of Copper Oxide nanoparticles for heavy metal removal, in particular Ni(II), Cd(II) adsorption, at the field scale.

Materials and methods:

Laboratory batch experiments were carried out to study the adsorption of Ni(II),Cd(II) on Copper oxide nanoparticles (CON).

2.1 Adsorbent Selected:

The adsorbent selected for the present work was CopperOxide nanoparticles. The 99.9% pure form of Copper oxide nanoparticles (CON) made available directly from the manufacturer MKnano Sales of MK Impex Corp. Canada of desired particle size (20-30 nm).This adsorbent been used throughout the experimental work. The particle size of adsorbent selected for these experiments were on the basis of their settlement at the bottom of the system, so that the portion of the solution could be taken out conveniently from the supernatant liquid. The experiments were performed at room temperature($30\pm 5^{\circ}\text{C}$) using 50 ppmNi(II), Cd(II) solution.

2.2 Preparation of metal ion solution:

The Ni(II), Cd(II) metal ion solution as a model pollutant from industries was prepared. The chemicals were all of Analytical grade and used without further purification. The solutions were prepared in doubly distilled water.TheNi(II) solution was prepared byusingNiSO₄, Cd(II) solution was prepared by using CdSO₄in doubly distilled water.The prepared solutions were standardized as per literature.^[8] Also, HCl and NaOH were used for adjusting pH of solutions.

2.3 Adsorption experiments:

Laboratory batch experiments were carried out to study the adsorption of Ni(II),Cd(II) on Copper oxide nanoparticles (CON).A known amount of (CON) was added to 50 ppm of the corresponding Ni(II), Cd(II) solution over a period of time on a shaker at 120 rpm. After the aqueous phase was separated, the concentration of Ni(II), Cd(II) in the solution was determined spectrophotometrically (shimatzu-1211) at their respective wavelengths i.e. λ_{max} .

The adsorption of Ni(II),Cd(II) was investigated at pH range of 3-11. The initial pH of the solution was adjusted by using 0.1 M HCl or 0.1 M NaOH. The effects of contact time (0,5,10,15,30,and 40 min), initial concentration of Ni(II),Cd(II) (20,50,100,150 ppm) and amount of adsorbent dosage (0.1, 0.2, 0.3, and 0.4 g) were also examined throughout the experiments at $30\pm 5^{\circ}\text{C}$ and 120 rpm shaking speed. The amount of Ni(II),Cd(II) removal was calculated from the difference between Ni(II),Cd(II) take and that remained in the solution.

Results and discussion:

3.1.Effect of initial pH:

The percentage of cadmium (II) and Nickel(II) ion removed by CON as a function of equilibrium

solution pH is shown in Fig. 1. Because pH affects the surface charge of adsorbents, which influence the adsorption of charged ions. Under different pH conditions, the removal efficiency of Cadmium ions and Nickel ions by the CON was measured. As presented in Fig. 1, the removal efficiency increased when the initial pH varied from 3 to 5, then at higher pH removal efficiency decreased with increasing solution pH. At low pH values, high concentration of H^+ ions in acidic solutions would also compete with metal cations for the active binding sites on the adsorbent. Which results into decrease in adsorption capacity. At $pH > 5$ values the adsorbent would carry negative charge which increases electrostatic attraction between the adsorbent and metal cation, hence increase adsorption capacity. However when pH of the solution further increases metal ions would precipitate and reduce the extent of adsorption.^[9] Thus, the optimal pH for Ni(II), Cd(II) ions removal was found to be 6.0. At pH 3 and 4, competition between H^+ ions and metal cations could thus explain the weak adsorption in acid medium. In pH 5 and 6, cadmium adsorption was increased because of OH^- enhancement. Decrease of cadmium adsorption at $pH > 6$ was due to formation of dissolved hydroxyl groups.^[10]

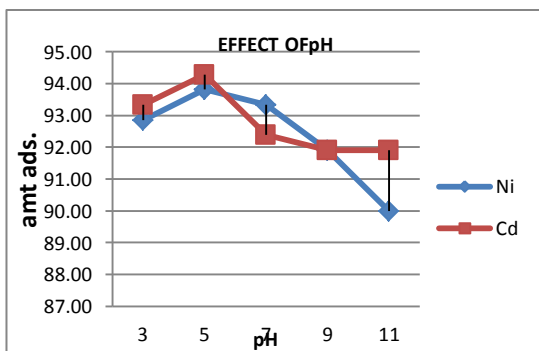


Fig.1.

3.2. Effect of contact time:

The variation in the amount adsorbed as a function of time for Cd and Ni is shown in Fig.2. The removal efficiency increases rapidly in initial stage and it decreases slowly after some time because large number of available sites are occupied by the metal ions with time in the first 30 min. Then the adsorption curve reached equilibrium after this time.^[11]

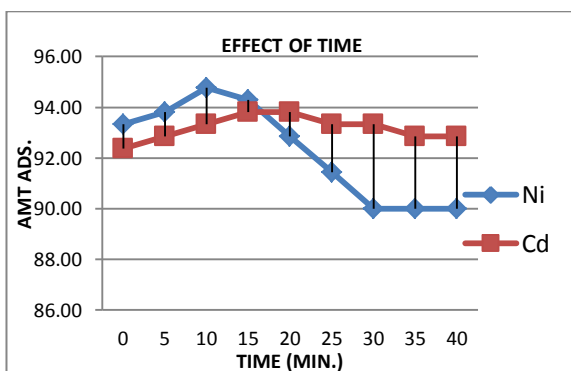


Fig.2.

3.3. Effect of initial metal ion concentration:

Effect of initial metal ion concentration on adsorption capacity of CON is shown in Fig.3. Solutions of different initial concentrations 20,50,100,150 ppm.were used to investigate the effect of initial concentration on removal of Cd(II) and Ni(II) from aqueous solution. Sorbent used was 0.2 gm at $pH = 6$.

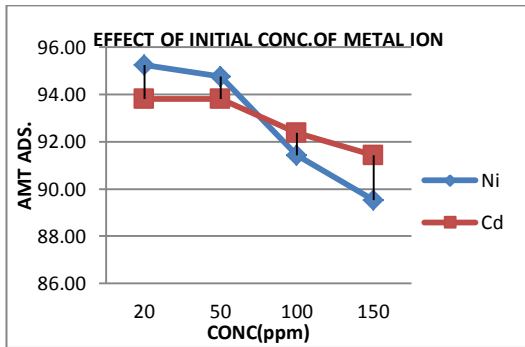


Fig.3.

At low initial solution concentration, the surface area and the availability of adsorption sites were relatively high, and the Ni(II), Cd(II) ions were easily adsorbed. At higher initial solution concentration, the total available adsorption sites are limited, thus resulting in a decrease in percentage removal of Ni(II), Cd(II) ions.^[12]

3.4. Effect of adsorbent dosage:

The metal removal efficiency increased with increase in adsorbent doses, as the total surface area as well as the exchangeable adsorption sites also increased. However the number of adsorption sites per gram of adsorbent did not increase proportionally with adsorbent dose, some of the adsorption sites might also remain unsaturated during the reaction process, in addition increase in adsorbent dose also led to decrease in equilibrium metal concentration, so the driving force for the metal adsorption decreased. Thus a regular drop in unit adsorption observed.^[13] The amount of adsorbent, which was varied from 0.1 to 0.4 g while keeping the Ni(II), Cd(II) concentration as 50 ppm (Fig. 4). This was because of the availability of more binding sites for complexation of Ni(II), Cd(II) ions.

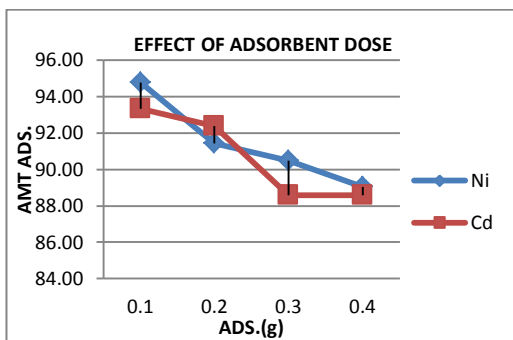


Fig.4.

3.5. Effect of temperature:

The effect of different temperature on adsorption indicates slow increase in adsorption at lower temperatures and decrease in adsorption at higher temperature with rise in temperature from 10°C to 80 °C (Fig.5). This effects may attribute to a negative temperature co-efficient of solubility of the solute or to a steep simultaneous decrease of real adsorption of solvent.

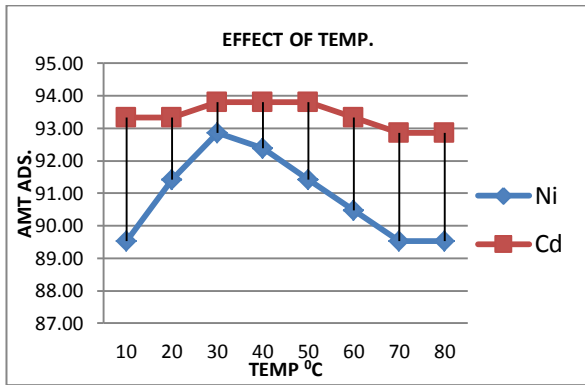


Fig.5.

Kinetic study:

4.1. Adsorption kinetics:

Kinetic modeling not only allows estimation of sorption rates but also leads to suitable rate expressions characteristic of possible reaction mechanisms. In this respect, kinetic models including the pseudo-first-order kinetics model, pseudo-second-order kinetics models were investigated. The experimental kinetic results fitted to the two models are the pseudo second-order model gives the best fit with more R² which is less than 1, therefore, pseudo second-order model could be used for prediction of the kinetics of adsorption of Ni(II), Cd(II) on the CON nanoparticles.

Adsorption isotherm models:

An adsorption isotherm is a graphical representation of amount of substance adsorbed against the residual concentration of the adsorbate and adsorbent doses. It is important to describe how solutes interact with adsorbents and to compare adsorption capacities of different adsorbents. Adsorption data was analyzed using Langmuir and Freundlich isotherm in order to find the adsorption capacity of CON.

5.1. Langmuir Isotherm:

The Langmuir isotherm (1918) assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place at that site. As such the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved. It is represented by equation.(1) [14-16]

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + C_e/Q^0 \text{-----(1)}$$

Where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of solute in the bulk solution (mg/L), Q⁰ is the monolayer adsorption capacity (mg/g) and b is a constant related to the free energy of adsorption.

The linear plot of C_e/q_e (C_e/X/m) vs C_e shows that the adsorption obeys Langmuir adsorption model.(Fig.6.)

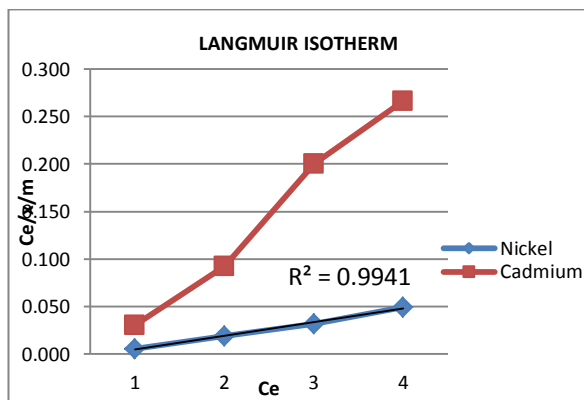


Fig.6.

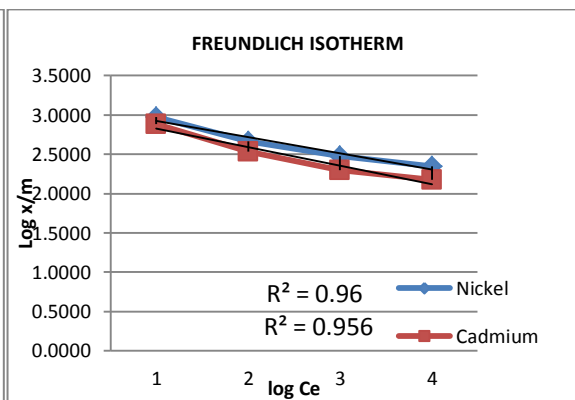


Fig.7.

5.2. Freundlich Isotherm:

The Freundlich isotherm (1906) is applicable to both monolayer (chemisorption) and multilayer adsorption (physisorption) and is based on the assumption that the adsorbate adsorbs onto the heterogeneous surface of an adsorbent. It is represented by the equation (2).^[14,17]

$$\text{Log} \frac{x}{m} = \text{Log} k + \frac{1}{n} \text{Log} C_{eq} \text{-----}(2)$$

Where, C_{eq} is the equilibrium concentration (mg/L) and x/m is the amount adsorbed per unit mass of adsorbent (mg/g). Plotting $\log x/m$ vs. $\log C_{eq}$ a straight line was obtained with a slope of $1/n$, and $\log k$ is the intercept. (Fig.7.)

Conclusion:

The results of this study suggest that Ni(II), Cd(II) adsorption process by Copper Oxide nanoparticles was kinetically rapid and follow the pseudo-second-order rate. Nanoparticles provide an efficient technique for the removal of toxic heavy metals from wastewater. This study investigated the removal of Ni(II), Cd(II) using CON as novel sorbents. Metal removal depended on the pH of the medium and maximum adsorption occurred at pH 6. A second order model described the kinetic data well. The Freundlich and Langmuir isotherm fitted equilibrium data. Results showed that CON had a much higher metal adsorption capacity.

References:

1. Rout K, Mohapatra M, Anand S. 2-Line ferrihydrite: synthesis, characterization and its adsorption behaviour for removal of Pb(II), Cd(II), Cu(II) and Zn(II) from aqueous solutions. Dalton Transactions. 2012; 41: 3302-3312.
2. Elouear Z, Bouzid J, Boujelben N, Feki M, Jamoussi F, Montiel A. Heavy metal removal from aqueous solutions by activated phosphate rock. J. Hazard. Mater. 2008; 156: 412-420.
3. Sharma YC. Thermodynamics of removal of cadmium by adsorption on an indigenous clay. Chem. Eng. J. 2008; 145: 64-68.
4. Tan GQ, Xiao D. Adsorption of cadmium ion from aqueous solution by ground wheat stems. J. Hazard. Mater. 2009; 164: 1359-1363.
5. Soltani RDC, Jafari AJ, Khorramabadi GhS. Investigation of cadmium (II) ions biosorption onto pretreated dried activated sludge. Am. J. Environ. Sci. 2009; 5: 41-46.
6. Tashauoei HR, Attar HM, Amin MM, Kamali M, Nikaen M, Dastjerdi MV. Removal of cadmium and humic acid from aqueous solutions using surface modified nanozeolite A. Int. J. Environ. Sci. Technol. 2010; 7: 497-508.
7. Kohler N, Sun C, Fichtenholtz A, Gunn J, Fang C, Zhang M. Methotrexate immobilized poly(ethylene glycol) magnetic nanoparticles for MR imaging and drug delivery. Small. 2006; 2: 785-792.
8. G. H. Jeffery, J. Bassett Mendnam, R.C.Denny; 'Vogels Text Book of Quantitative

- Chemical Analysis', 5, ELBS, Longman Group U.K.,(1999).
9. Barakat M.A.; Adsorption behavior of copper and cyanide ions at TiO₂ solution interface. *J of Colloid and Interface Sci.* 2005; 291(2), 345-352.
 10. Shih H, Dong H. Rapid removal of heavy metal cations and anions from aqueous solutions by amino-functionalized magnetic nano-adsorbent. *J. hazardous materials.* 2009; 163: 174–179.
 11. Ozmen M, Can K, Arslan G, Tor A, Cengeloglu Y, Ersoz M. Adsorption of Cu(II) from aqueous solution by using modified Fe₃O₄ magnetic nanoparticles. *Desalination.* 2010; 254: 162-169.
 12. Mehdi Bahrami, Boroomandnasab Saeed, Heidar Ali Kashkuli , Ahmad Farrokhian Firoozi, Ali-Akbar Babaei; Removal Of Cd(II) From Aqueous Solution Using Modified Fe₃O₄ Nanoparticles; Report and Opinion 2012;4(5)
 13. Leung PuiSize; Removal and recovery of Heavy metals by amorphous TiO₂ Nanoparticles and Calcium alginate immobilized TiO₂ Beds; The Hongkong Polytechnic University; 2009
 14. Sureshkumar Halnor, Maqdoom Farooqui and Milind Ubale; Removal of copper (ii) from aqueous solution and waste water by Prosopis juliflora leaf powder by adsorption; *I. J. of Application or Innovation in Engg & Management*; 2013:125-131.
 15. Boparai HK, Joseph M, O'Carroll D. Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles. *J. Hazardous Materials.* 2011; 186: 458-465.
 16. Langmuir I. The constitution and fundamental properties of solids and liquids. *Journal of the American Chemical Society.* 1918; 38: 2221– 2295.
 17. Yang CH. Statistical mechanical study on the Freundlich isotherm equation. *J. Colloid Interface Sci.* 1998; 208: 379–387.
 18. Bahrami M, Boroomandnasab S, Kashkuli H.A, Farrokhian Firoozi A, Babaei A.A. Removal Of Cd(II) From Aqueous Solution Using Modified Fe₃O₄ Nanoparticles. *Rep Opinion* 2012;4(5):31-40]. (ISSN: 1553-9873). <http://www.sciencepub.net/report>.
