



## Elimination of Cd (II) from Wastewater using Nickel (II) Tungstate Nanoparticles as Adsorbents: Adsorption Isotherm Study

D.Suresh<sup>1\*</sup>, G. Vijay Swaroop Singh<sup>2</sup>, T. Appa Rao<sup>3</sup>, M. Rajeswara Rao<sup>4</sup>, B. Dharma Rao<sup>5</sup>, P. Seetharam<sup>6</sup>

<sup>1</sup>Dept. of Chemistry, Sri YN College (A), Narsapur, West Godavari, AP-534275, India

<sup>2</sup>Dept. of Chemistry, Sri DNR Govt. Degree College, Palakol, West Godavari, AP-534260 India

<sup>3</sup>Dept. of Chemistry, Dr. VS Krishna Govt. Degree College (A), Visakhapatnam, AP-530013, India

<sup>4</sup>Dept. of Physics, Dr. VS Krishna Govt. Degree College (A), Visakhapatnam, AP-530013, India

<sup>5</sup>Dept. of BS & HSS, College of Engineering, Jawaharlal Nehru Technological University Gurajada Vizianagaram, AP-535003, India

<sup>6</sup>Bio Enviro Chemical Solutions, Visakhapatnam, AP-530017, India

(Received: 07 October 2023

Revised: 12 November

Accepted: 06 December)

### KEYWORDS

Wastewater treatment; adsorption; toxic metals; tungstates.

### ABSTRACT:

The removal of heavy metal ions from wastewaters, using efficient adsorbing nanoparticles, has been always an interesting area of research towards remediation of environmental pollutants. In this regard, toxic metal like cadmium (Cd) was preferred to be removed from selected wastewater samples using Nickel tungstate ( $\text{NiWO}_4$ ) nanoparticles (NPs), acting as adsorbents. The NPs were synthesized using a facile sol-gel method and the calcinated sample was characterized using XRD, SEM-EDS and FTIR techniques. These results have displayed the formation of the NPs in wolframite structure. Using atomic absorption spectrophotometer (AAS), the adsorption capacity of the NPs was estimated using various supporting experimental factors like effect of NPs weight (20 mg  $\text{L}^{-1}$ ), contact time (30 min), pH (5.0) and concentration of the metal ion solution (7 ppm). Further, Freundlich adsorption isotherm was applied on the results and it was noted that the rate of adsorption was in accordance with the empirical relation. The developed methodology has followed the Pseudo-first kinetics, indicating the efficacy of the method. All the results were compared with few standard scientific reports and it was observed that NPs were effective in removing the Cd(II) ions.

### 1. Introduction

Over the decades, natural water sources were being exploited with the discards of various heavy metal ions [1-2]. Along their widespread to water resources, their toxic nature has also affected the aquatic ecosystem through the food chain [3-5]. Metals contributing for this large scale environmental damage majorly, Pb (II), Cr (VI), Cu (II), Cd (II), Hg (II) etc [5]. Among these toxic metals, United states Environmental Protection Agency (USEPA), has declared the hazardous effects of Cd (II) disposals [6]. Excess levels of the metal ion concentration, beyond its threshold limit value (TLV,  $0.005\text{mg}\cdot\text{dm}^{-3}$ ), can cause carcinogenic conditions in human beings [6]. Higher levels of exposure ( $>\text{TLV}$ , up to  $1.0\text{mg}\cdot\text{dm}^{-3}$ ), could also to death conditions [7]. When it enters the body, it can be transported through

various modes and is accumulated in the kidneys [8], liver, and gut [9]. Exposure to the metal ions also causes renal and hepatic dysfunction, pulmonary edema, testicular damage, osteomalacia, and harm to the adrenals and hemopoietic system [10]. Along with its cytotoxic effects, the metal ion was also proven human carcinogen (International Agency for Research on Cancer classification, Group I) [11]. Occupational or environmental cadmium exposure has been reported to cause various forms of cancers in humans [12]. It has also been established that the metal ion can decrease the cellular viability and could inject neurodegenerative diseases, Alzheimer's and Parkinson's diseases [13, 14].

On the other side, the metal ion is acting an important constituent of several engineering materials and



electronic devices [15]. It is acting as a corrosive agent, stabilize in PVC products and as one of the electrode in Ni-Cd batteries [16]. Contaminated soils are the richest source of cadmium [17]. In many areas, the soil is mainly contaminated due to volcanic eruptions and hence, it causes soil erosion, abrasion of rocks etc. [17]. Various adsorbents were used in the elimination of these hazardous metal ions from the wastewaters [18], and one such material, whose adsorption capacity has been not investigated so far, are the tungsten oxides ( $\text{AWO}_4$ ,  $\text{A}=\text{M}^{+2}$ ;  $\text{M}$ =alkaline earth metal or transition metal ion). These  $\text{AWO}_4$  type divalent transition metal compounds have been reported to be useful for humidity sensors [19], photocatalysts [20], photochromic [21] and as photoanodes [22]. They are capable of withstanding low pH environments and high temperatures, making them excellent choices for robust, nanostructured, inorganic frameworks.

In this regard, it was planned to synthesize Nickel tungstate ( $\text{NiWO}_4$ ) NPs and their role as adsorbents was investigated towards the removal of Cd(II) ions from the aqueous solutions. The supporting experimental factors were determined, along with the studies of adsorption isotherm and kinetic profiles.

## 2. Experimental

### Material and Methods

Nickel (II) Chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ), Sodium tungstate ( $\text{NaWO}_4$ ), glacial acetic acid were procured from Sigma Aldrich (99 % pure) for the synthesis of Nickel tungstate NPs. Cadmium (II) chloride ( $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ ) procured from Merck (98% pure, India) and the same was used as the metal ion solution for the adsorption studies. All the chemicals were used without further purification and the experimental solutions were prepared using double distilled water.

### Synthesis of Nickel tungstate NPs

The NPs were prepared using solid-state metathesis, followed by ball milling methods. Ni(II) Chloride and sodium tungstate,  $\text{NaWO}_4$  were added to each other in

1:1 mole ratio and the mixture was taken in an agate mortar. Then the mixture was grinded to about 4- 5 hours in the presence of 1 mL of ethanol solvent. In the due course of grinding, the color of the mixture was observed to change into the characteristic color of Ni(II) ions. After collecting the finally obtained paste, it was then dried under hot plate neat  $70\text{-}80^\circ\text{C}$  and then the solid powder was calcinated near  $500^\circ\text{C}$  for about 2 hours. The pure solid powder was washed several times with distilled water, in order to separate the by-product, sodium chloride. The residue was dried near  $70^\circ\text{C}$  and the finally obtained Nickel tungstate powder was characterized.

### Characterization

The synthesized nickel tungstate NPs were characterized using **X-ray diffractometer** in the range of  $2\theta = 5\text{-}10^\circ$  by step scanning on the Rigaku D/MAX-2500 diffractometer (Rigaku Co., Japan) with Cu-K $\alpha$  radiation ( $k = 0.15406 \text{ nm}$ ) operated at 40 kV and 100mA. SEM images of the samples were taken using a Philips XL 30 **SEM** scanning electron microscope (FEI-Philips Company, Hillsboro). **Fourier Transform Infra Red** spectral (FT- IR) data was recorded from BRUKER ALPHA FT-IR with Opus 6.1 version using KBr pellets at  $400\text{-}4500 \text{ cm}^{-1}$  region. **Atomic absorption spectrophotometer** (AAS) (iCE FIOS, Thermo Fischer Scientific, Focal length: 250 mm, Diffraction grating: 1800 lines/mm, bandwidth variable from 0.1 to 2.0 mm) was used to record the concentration of the metal ion in its aqueous solution, before and after contact with the  $\text{NiWO}_4$  NPs.

## 3. Results and Discussion

### a. XRD spectra

The diffraction peaks at  $2\theta = 15.61^\circ, 19.27^\circ, 23.9^\circ, 24.9^\circ, 30.9^\circ, 36.57^\circ$  and  $54.62^\circ$  related to  $d_{010}$ ,  $d_{100}$ ,  $d_{011}$ ,  $d_{110}$ ,  $d_{111}$ ,  $d_{002}$  and  $d_{202}$  diffraction planes respectively were assigned in XRD patterns with Nickel tungstate NPs as shown in figure 1 (JCPDS No. 15-0755).

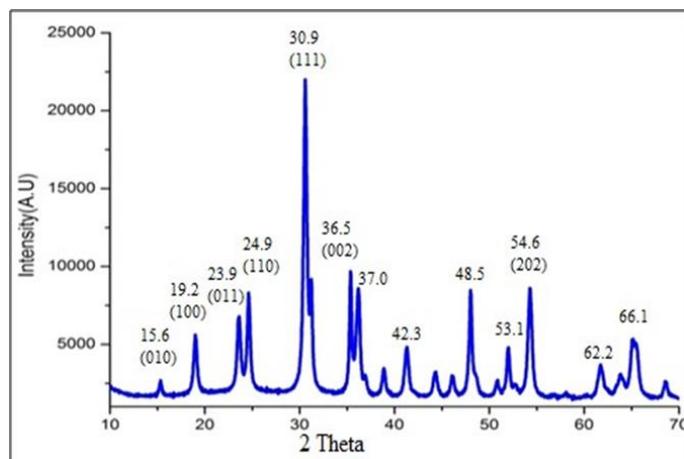
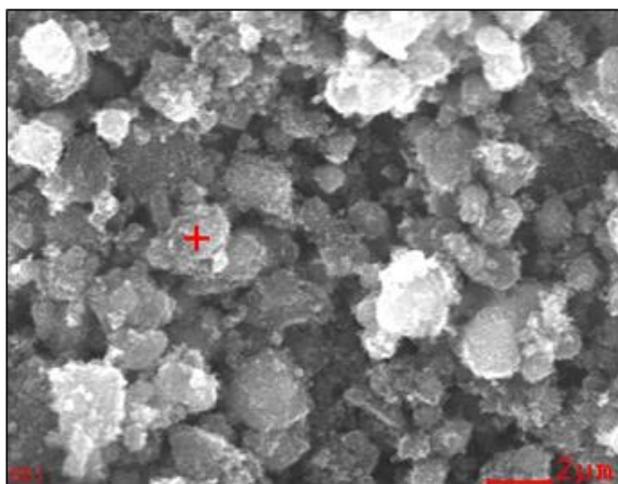
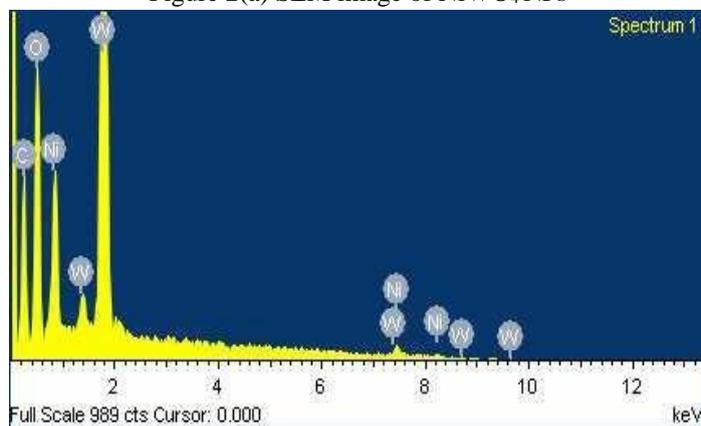


Figure.1. XRD spectra of nickel(II) tungstate NPs

**b. SEM-EDS analysis-**

The SEM image of the NPs was shown in figure 2(a). It shows that the morphology of  $\text{NiWO}_4$  and obviously reveals that the micro structured NPs have a rough surface, with various irregular particles anchored on its

surface. Further, the EDS spectrum (figure 2b) and elemental composition demonstrates the presence of Ni, W, O and C which confirms the proper formation of  $\text{NiWO}_4$ .

Figure 2(a) SEM image of  $\text{NiWO}_4$  NPsFigure.2(b). EDS spectra of  $\text{NiWO}_4$  NPs



### c. FTIR spectra

Tungstates ( $\text{ABO}_4$ ), generally exhibits the characteristic stretching absorption bands in the region  $900\text{--}400\text{ cm}^{-1}$  [22]. The low frequency band was assigned to the deformation mode of  $\text{WO}_4$  tetrahedral. It is clear that the weak absorption bands with the maxima at  $873\text{--}870\text{ cm}^{-1}$  can be assigned to the stretching mode of W–O bonds in joints with  $\text{WO}_4$  tetrahedral. However, the broad absorption bands with their maxima located

around at  $693\text{--}688\text{ cm}^{-1}$  could be attributed to stretching and bending vibrations of W–O bonds in  $\text{WO}_4$  which is shown in figure 3.

The absorption bands occurring at less than  $600\text{ cm}^{-1}$  ( $525\text{ cm}^{-1}$ ) was assigned to the deformation modes of W–O bonds in  $\text{WO}_4$  tetrahedral or the deformation modes of W–O bonds in  $\text{WO}_4$  tetrahedral or the deformation modes of W–O–W bridges [23].

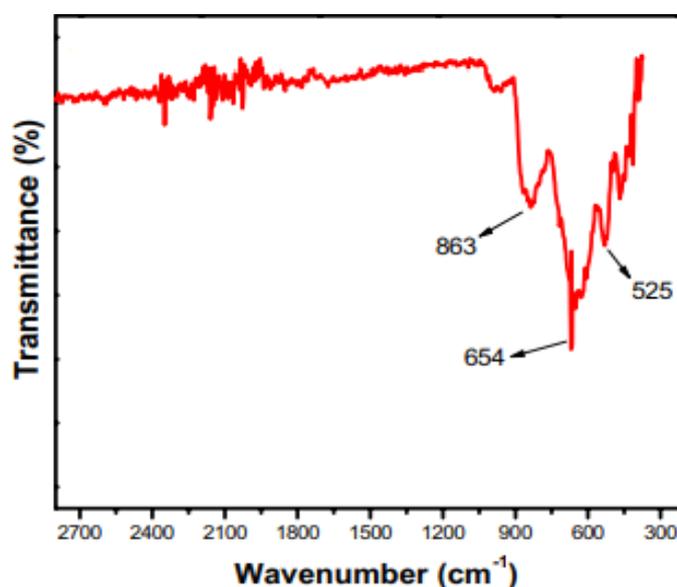


Figure.3. FTIR spectra of  $\text{NiWO}_4$  NPs

### d. Analysis of heavy metal ions elimination from waste waters

The sample solutions for the experimental study were prepared by using 0.1 N solutions of the salt solution. The concentration of the Cd(II) ion was measured using AAS and the % removal of the metal was calculated using equation 1 [24].

$$\% \text{ Removal of metal ion} = \frac{A-B}{A} \times 100 \dots [1]$$

Where, A and B are the concentrations of the metal ion, before and after treatment with the NPs under established conditions. Each experimental solution (50 mL) was taken in 250mL beaker and a known weight of NPs (mg) was added to it. The mixture was kept under magnetic stirring for a fixed time (min) and the resultant suspension was centrifuged (5000 rpm),

filtered and the obtained supernatant liquid was analyzed with AAS, to find out the % removal of the respective metal ion in its solution.

### i. Effect of weigh to NPs

The composition of the NPs (adsorbent) is an important factor to be considered, in determining its catalytic role [25]. The composition of the NPs (mg) towards the removal of the metal ion, was studied by varying the weight the NPs from 5 mg to 30 mg  $\text{L}^{-1}$ . It was noticed that the removal of the metal has increased with increase in the catalyst weight (mg) from 5 to 20 mg  $\text{L}^{-1}$  of the solution (figure 4). However, at higher weights of the catalyst, from 20 mg  $\text{L}^{-1}$ , the removal efficiency has decreased. At higher catalyst weights, the particles could agglomerate and, causes less catalytic activity [25]. This leads to decreased adsorption of the metal ions on the surface of the  $\text{NiWO}_4$  NPs.

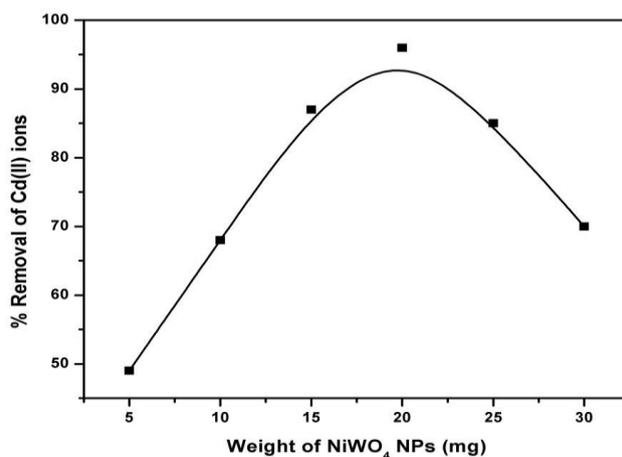


Figure.4. Effect of NPs weight

### ii. Effect of concentration of the metal ion aqueous solution

Rate of adsorption is affected by the concentration of the adsorbate solution, and hence the studies were performed by varying the concentration of the adsorbate solution from 1 to 10 ppm with a fixed weight of adsorbent (20 mg). As seen from figure 5, the

rate of adsorption has increased up to 7 ppm of the metal ion concentration. However, this tendency has declined from thereafter, showing a less removal efficiency until 10 ppm. Hence, it was noticed that the % removal of Cd(II) ions on the surface of the NiWO<sub>4</sub> NPs was effective near 7 ppm concentration of the metal ion.

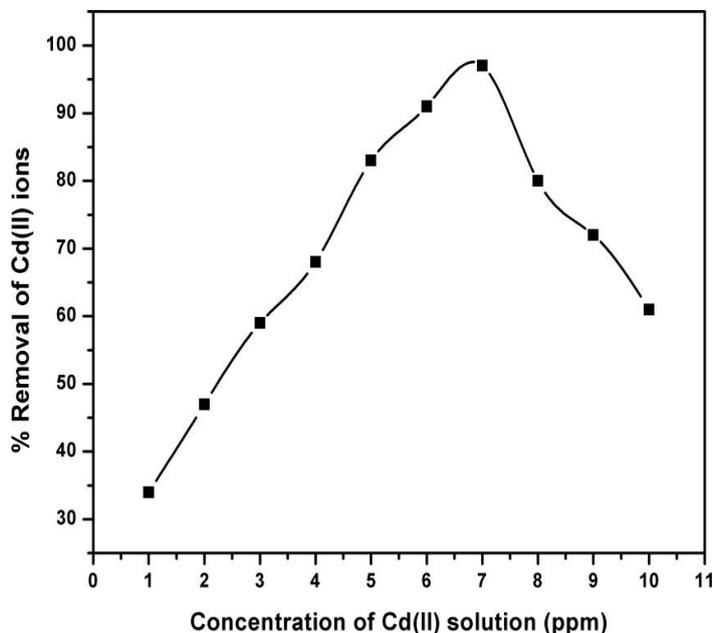


Figure.5. Effect of Cd(II) solution concentration

### iii. Effect of contact time

In this experimentation, the effect of contact time was determined by maintained the above optimal conditions. The time of contact was studied by fixing the time intervals in the range of 10 to 50 min with a difference of 10 min at each trial. As displayed in figure 6, with increase in contact time of the metal ion

solutions with the NPs, the % removal of the metal ions has increased upto 30 min of contact time. However, after 30 min, the removal tendency has decreased with the NPs. Hence, the results revealed that the effective removal of the metal ions was observed at 30 min of contact time with the synthesized NiWO<sub>4</sub>NPs.

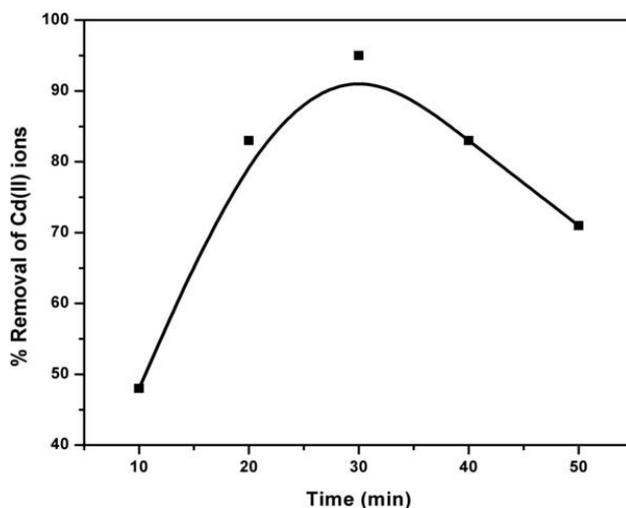


Figure.6. Effect of contact time

#### iv. Effect of pH

The pH of a solution, is an important aspect to be considered in the process of catalysis [26]. Therefore, the adsorption of Cd(II) ions on the surface of the tungstate NPs was studied by varying the pH of the solution from 2.0 to 7.0. A known weight of the adsorbent ( $10 \text{ mg L}^{-1}$ ) was dispersed in the Cd(II)

solution (10 ppm) and the adsorption studies were conducted. It was observed that the rate of removal of the adsorbate, has increased from pH 2.0 to 5.0, and then it shown a steady decline up to pH 7.0. Hence, the % removal of the ion was maximum at around pH 5.0 (figure 7).

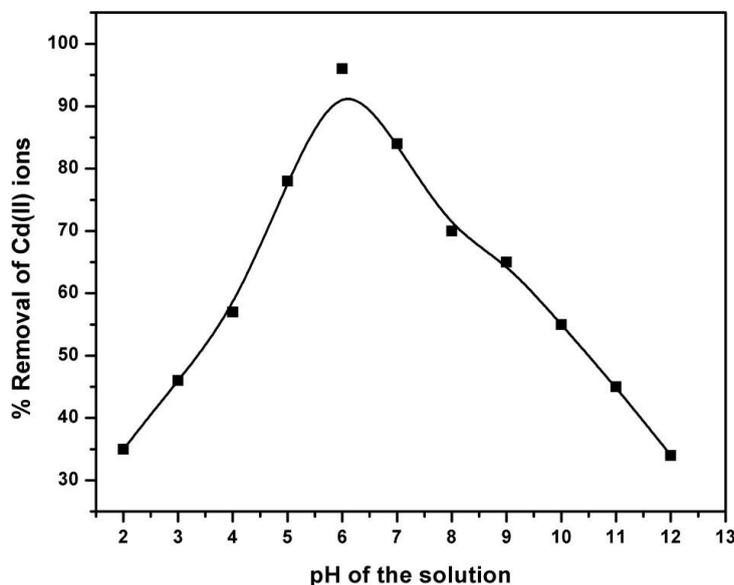


Figure.7. pH effect on the Cd(II) solution

#### v. Adsorption isotherm

An adsorption isotherm was applied by establishing a graphical relation between the amount of the adsorbate getting adsorbed on the surface of the adsorbent against the equilibrium concentration of the adsorbate at a given temperature [27]. In the present work, Freundlich model was adopted to authenticate the results of the

rate of adsorption of Cd(II) on the surface of the  $\text{NiWO}_4$  NPs [28, 29]. The model can describe the exponential distribution of active centers on the catalyst surfaces [30]. It describes the multilayer adsorption phenomenon and equation 2 shows its linear expression [31].

$$\ln q_e = \ln C_e + \ln K_F \dots [2] \quad n$$



Where  $\ln q_e$  and  $\ln C_e$  denotes the equilibrium adsorption capacity of the adsorbent ( $\text{mg g}^{-1}$ ) and the equilibrium concentration of the adsorbate ( $\text{mg L}^{-1}$ ) respectively. The adsorption capacity of the NPs was observed from the  $\ln K_F$  (Freundlich constant), and  $(1/n)$  represents the slope indicating the surface heterogeneity. A linear plot was observed in the present

studies (figure 8), which was observed to obey the equation 2. A better adsorption capacity was found to be observed with the NPs ( $\ln q_e = 175 \text{ mg/g}$ ), and with these results it was confirmed that the  $\text{NiWO}_4$  NPs can act as catalytic nano-adsorbents removing toxic heavy metals like  $\text{Cd(II)}$  ion.

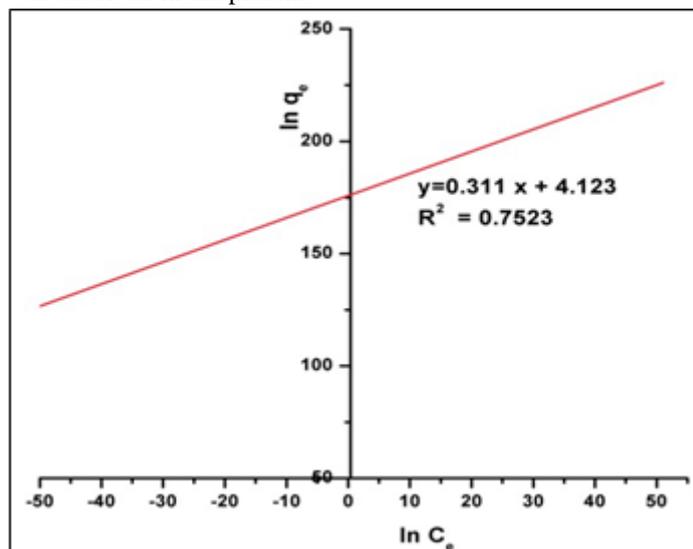


Figure.8. Linear plot of Freundlich adsorption isotherm

#### vi. Adsorption kinetics

In the phenomenon of adsorption, the study of kinetics plays an important role in understanding the rate of adsorption of the adsorbates on the surface of the adsorbent [32]. For liquid-solid phase based adsorption systems, pseudo-first order kinetic model can be applied, to describe the adsorption phenomenon [33]. According to this model, the equation 3 describes its kinetic expression [34].

$$\frac{dq_e}{dt} = K(q_e - q_t) \quad [3]$$

The integral form is expressed as equation 4:  $\log(q_e - q_t) = \log q_e - kt/2.303 \dots$  [4]

$$\log(q_e - q_t) = \log q_e - \frac{kt}{2.303} \dots [4]$$

Where,  $q_e$  and  $q_t$  represents the equilibrium adsorption capacity of the adsorbent ( $\text{mg/g}$ ), and the adsorption capacity ( $\text{mg g}^{-1}$ ) in a time  $t$  (min) respectively. The rate constant of the pseudo first-order adsorption model was denoted by  $k$  ( $\text{min}^{-1}$ ). By applying the pseudo first order kinetics on the established results, it was found

that the rate constant ( $k$ ) was obtained as  $2.3 \times 10^{-2} \text{ min}^{-1}$ , with linearity.

It was observed that the  $\text{NiWO}_4$  NPs were effective in removal of the  $\text{Cd(II)}$  ions and the results were obtained on par with few reported adsorbents, as shown in Table 1. Kumar et al., have performed the adsorption studies with Mesoporous  $\text{ZnO}$  nano-rods for the removal of  $\text{Cd(II)}$  ions [35]. It was found that the adsorption capacity of these adsorbents was nominal. Nano titania particles were used as the adsorbents by Lianget. al, and observed that the adsorption capacity was nearly  $8 \text{ mg/g}$  [36]. Except with  $\text{Fe}_3\text{O}_4\text{-ZnO}$  NPs, developed by Singh et al., [37], whose % removal tendency was very less, remaining adsorbents shown in the Table 1 [38-41] have shown maximum removal efficiency. The % removal of  $\text{Cd(II)}$  ions by the  $\text{NiWO}_4$  NPs was observed to 95 %, indicating the capability of the NPs in removing the toxic metals from aqueous solutions and wastewaters as well.

**Table1.** Comparison of adsorption capacity of  $\text{NiWO}_4$  NPs with some adsorbents for the removal of  $\text{Cd(II)}$

| Adsorbent                         | Results   | Reference |
|-----------------------------------|---|-----------|
| Mesoporous $\text{ZnO}$ nano-rods | Adsorption capacity = $147.25 \text{ mg. g}^{-1}$ | [35]      |



|   |   |              |
|---|---|--------------|
| Nano-TiO <sub>2</sub>   | Adsorption capacity=<br>7.9mg.g <sup>-1</sup>                     | [36]         |
| Fe <sub>3</sub> O <sub>4</sub> -ZnONPs  | % Removed=22%   | [37]         |
| EDTA-functionalized<br>magnetic mesoporous silica<br>(MMS-EDTA)                     | % Removed=95%   | [38]         |
| Humicacid-Fe <sub>3</sub> O <sub>4</sub>  | % Removed=95%   | [39]         |
| Fe <sub>3</sub> O <sub>4</sub> @APS@AA-co- CA<br>Fe <sub>3</sub> O <sub>4</sub> NPs | % Removed=90%   | [40]         |
| Amine-Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @ meso-<br>SiO <sub>2</sub>  | % Removed=91%   | [41]         |
| NiWO <sub>4</sub> NPs   | Adsorption capacity= 175<br>mg.g <sup>-1</sup> .<br>% Removed=95% | Present work |

#### 4. Conclusion

The elimination of Cd(II) ions from aqueous solutions was conducted in the presence of NiWO<sub>4</sub> NPs. The process was found to be effective at pH near 5.0, with 20 mg of the NPs weight. At 30 min of contact time and 7 ppm concentration of the Cd(II) solution, the rate of adsorption was found to be effective in the removing the Cd(II) ions from the solution (95% removed). The results have obeyed the Freundlich adsorption isotherm and pseudo-first order kinetics, perfectly. Hence, it was concluded the NiWO<sub>4</sub> NPs were efficient adsorbents in the removal of toxic metal ions from wastewaters.

#### Acknowledgement

The authors are thankful to their college management, for providing the research facilities to undertake the research work.

#### Conflict of interest

The authors no conflict of interest

#### References

- Singh, S., Barick, K. C., Bahadur, D., Functional Oxide Nanomaterials and Nanocomposites for the Removal of Heavy Metals and Dyes. *Nanomaterials and Nanotechnology*, 2013, 3, 1-19.
- Amin, M. T., Alazba, A. A., Manzoor, U., A Review of Removal of Pollutants from Water/Wastewater Using Different Types of Nanomaterials. *Advances in Materials Science and Engineering*, 2014; Article ID 825910, 1-24.
- Silver, S., The Bacterial View of the Periodic Table: Specific Functions for All Elements. *Microbes and Environments*, 1998, 13, 177-192.
- Liu, X., Hu, Q., Fang, Z., Zhang, X., Zhang, B., Magnetic chitosan nano composites :a useful recyclable tool for heavy metal ion removal. *Langmuir*, 2009, 25, 3-8.
- Muzammil, A., Miandad, R., Muhammad, W., Gehany, F., Barakat, M. A., Remediation of wastewater using various nanomaterials. *Arabian Journal of Chemistry*, 2019, 12, 4897–4919.
- Kazantzis, G., Blanks, R., A mortality study of cadmium exposed workers. In: Edited Proceedings of the Seventh International Cadmium Conference, New Orleans.150-157. London: Cadmium Association.1992.
- Giuseppe, G., Maria, S. S., Graziantonio L, Alessia C, Alessia C, The Effects of Cadmium Toxicity. *International Journal of Environmental Research and Public Health*, 2020, 17(3782), 1-24.
- Satarug, S., Dietary Cadmium intake and its effects on kidneys. *Toxics*2018, 6, 15. Tinkov, A. A., Gritsenko, V. A., Skalnaya, M. G., Cherkasov, S. V., Aaseth, J., Skalny, A. V. Gut as a target for cadmium toxicity. *Environ. Pollut.* 2018, 235, 429–434.
- Tinkov, A.A.; Filippini, T.; Ajsuvakovae, O.P.; Skalnaya, M.G.; Aasethf, J.; Bjørklundh, G.; Gatiatulinai, E.R.; Popova, E.V.; Nemereshinai,



- O.N.; Huangk, P.T.; et al. Cadmium and atherosclerosis: A review of toxicological mechanisms and a meta-analysis of epidemiologic studies. *Environ. Res.* 2018, 162, 240–260.
10. IARC. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans- Beryllium, Cadmium, Mercury, and Exposures in the Glass Manufacturing Industry. In Summary of Data Reported and Evaluation; International Agency for Cancer Research-World Health Organization: Geneva, Switzerland, 1997; Volume 58.
  11. Mezynska, M., Brzóśka, M.M., Environmental exposure to cadmium—A risk for health of the general population in industrialized countries and preventive strategies. *Environ. Sci. Pollut. Res.* 2018, 25, 3211–3232.
  12. Tamás, M.J., Fauvet, B., Christen, P., Goloubino, P., Misfolding and aggregation of nascent proteins: A novel mode of toxic cadmium action in vivo. *Curr. Genet.* 2018, 64, 177–181.
  13. Saturnino, C., Iacopetta, D., Sinicropi, M.S., Rosano, C., Caruso, A., Caporale, A., Marra, N., Marengo, B., Pronzato, M.A., Parisi, O. I., et al. N-Alkyl carbazole derivatives as new Tools for Alzheimer's disease: Preliminary Studies. *Molecules* 2014, 19, 9307–9317.
  14. Rahimzadeh, M.R., Rahimzadeh, M.R., Kazemi, S., Moghadamnia, A.A., Cadmium toxicity and treatment: An update. *Caspian J. Intern. Med.* 2017, 8, 135–145.
  15. Genchi, G., Carocci, A., Lauria, G., Sinicropi, M.S., Catalano, A., Nickel: Human health and environmental toxicology. *Int. Environ. Res. Public Health*, 2020, 17, 679.
  16. Casado, M., Anawar, H.M., Garcia-Sanchez, A., Santa Regina, I., Cadmium and zinc in polluted mining soils and uptake by plants (El Losar mine, Spain). *Int. Environ. Pollut.* 2008, 33, 146–159.
  17. Jinyue, Y., Baohong, H., Jinggang, W., Beiqian, T., Jingtao, B., Na, W., Xin, L., Xin, H., Nanomaterials for the Removal of Heavy Metals from Waste water. *Nanomaterials*, 2019, 9, 1-39.
  18. Bhattacharya, A. K., Biswas, R. G., Hartridge, A., Environment sensitive impedance spectroscopy and dc conductivity measurements on NiWO<sub>4</sub>. *J. Mater. Sci.* 1997, 32, 353-356.
  19. Guangli, H., Yongfa, Z., Synthesis and photocatalytic performance of ZnWO<sub>4</sub> catalyst. *Mater. Sci. Eng. B*, 2007, 139, 201-208.
  20. Kuzmin, A., Purans, J., Kalendarev, R., Pailharey, D., Mathey, Y., XAS, XRD, AFM and Raman studies of nickel tungstate electrochromic thin films. *Electrochim. Acta*, 2001, 46, 2233-2236.
  21. Pandey, P. K., Bhave, N. S., Kharat, R. B., Structural, optical, electrical and photovoltaic electrochemical characterization of spray deposited NiWO<sub>4</sub> thin films. *Electrochim. Acta*, 2006, 51, 4659-4664.
  22. El-Sheikh S. M., Rashad, M. M., Novel Synthesis of Cobalt Nickel Tungstate Nanopowders and its Photocatalytic Application, *J Clust Sci*, 2015, 26, 743-757.
  23. Wang, X., Pei, Y., Lu, M., Lu, X., Du, X., Highly efficient adsorption of heavy metals from wastewaters by graphene oxide-ordered mesoporous silica materials. *J Mater Sci*, 2015, 50, 2113–2121.
  24. Sekhar, R. S., Douglas, S. P., Graphene oxide - Nanotitania Composites for Efficient Photocatalytic Degradation of Indigo Carmine. *J. Chin. Chem. Soc.* 2018, 65, 1423- 1430.
  25. Rahmanzadeh, L., Ghorbani, M., Jahanshahi, M., Effective removal of hexavalent mercury from aqueous solution by modified polymeric nano adsorbent. *J. Water Environ. Nanotechnol.*, 2016, 1, 1-8.
  26. Theodore, L., Ricci, F., Mass Transfer Operations for the Practicing Engineer; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2011.
  27. Putro, J.N., Santoso, S.P., Ismadji, S., Ju, Y.H., Investigation of heavy metal adsorption in binary system by nanocrystalline cellulose—Bentonite nanocomposite: Improvement on extended Langmuir isotherm model, *Microporous Mesoporous Mater.* 2017, 246, 166–177.
  28. Baseri, H., Tizro, S., Treatment of nickel ions from contaminated water by magnetite based nanocomposite adsorbents: Effects of thermodynamic and kinetic parameters and modeling with Langmuir and Freundlich isotherms. *Process Saf. Environ. Protect.* 2017, 109, 465–477.
  29. Wei, S., Chen, S., Shi, S., Li, X., Zhang, X., Hu, W., Wang, H., Adsorption of Cu(II) and Pb(II) on to diethylenetriamine-bacterial cellulose. *Carbohydr. Polym.* 2009, 75, 110–114.
  30. Freundlich, H. Over the adsorption in the solution. *J. Phys. Chem.* 1906; 57:385–470.
  31. Matouq, M., Jildeh, N., Qtaishat, M., Hindiyeh, M., Syouf, M.Q.A., The adsorption kinetics and modeling for heavy metals removal from waste



- water by Moringa pods. *J. Environ. Chem. Eng.* 2015, 3, 775–784.
32. CAVu, S., GuRdag, G.L., Noncompetitive Removal of Heavy Metal Ions from Aqueous Solutions by Poly[2-(acrylamido)-2-methyl-1-propanesulfonic acid-co- itaconic acid] Hydrogel. *Ind. Eng. Chem. Res.* 2016, 48, 2652–2658.
33. Farhan, A.M., Salem, N.M., Al-Dujaili, A.H., Awwad, A.M., Biosorption Studies of Cr(VI) Ions from Electroplating Waste water by Walnut Shell Powder. *Am.J. Environ. Eng.* 2012, 2, 188–195.
34. Kumar, K. Y., Muralidhara, H. B., Arthoba Nayaka, Y., Balasubramanyam, J., Hanumanthappa, H., Hierarchically assembled mesoporous ZnO nanorods for the removal of lead and cadmium by using differential pulse anodic stripping voltametric method. *Powder Technol.* 2012, 239, 208–216.
35. Liang, P., Shi. T, Q., Li, J., Nanometer-size titanium dioxide separation/ preconcentration and FAAS determination of trace Zn and Cd in water sample. *Int. J. Environ. Anal. Chem.*, 2004, 84, 315–321.
36. Singh, S., Barick K. C., Bahadur, D., Fe<sub>3</sub>O<sub>4</sub> embedded ZnO nanocomposites for the removal of toxic metal ions, organic dyes and bacterial pathogens. *J. Mater. Chem. A.* 2013, 1, 3325-3333.
37. Sinha, A., Jana, N.R., Functional, Mesoporous, super paramagnetic colloidsorbents for efficient removal of toxic metals. *Chem. Commun.* 2012, 48, 9272–9274.
38. Liu, J. F., Zhao, Z. S., Jiang, G. B., Coating Fe<sub>3</sub>O<sub>4</sub> Magnetic nano particles with humic acid for high efficient removal of heavy metals in water. *Environ.Sci.Technol.*,2008, 42, 6949–6954.
39. Ge, F., Li Meng-M., Ye H., Zhao Bao-X., Effective removal of heavy metal ions Cd<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> from aqueous solution by polymer modified magnetic nanoparticles. *J. Hazard. Mater.*, 2012, 211–212, 366–372.
40. Yuan, Q., Li, N., Chi, Y., Geng, W., Yan, W., Zhao, Y., Li, X., Dong, B., Effect of large pore size of multi functional meso porous micro sphere on removal of heavy metal ions. *J. Hazard. Mater.*, 2013, 254–255, 157–165.