

Adsorption of Nickel ions Ni(II) from aqueous solution by using the Nb₂O₅/CdS nano composites.

Nada Y Fairouz

University of Babylon, College of Science-Department of Chemistry/Hilla- Iraq.

Abstract : Nowadays, development of materials based on coupled photocatalysts in sorption process for removal of heavy metal ions from waste water has been considered by many researchers. In this study, new coupled catalysts Nb₂O₅/CdS was prepared by the wet commixing method at different ratios of (0.75:0.25, 0.6:0.4, 0.5:0.5, 0.85:0.15, 0:1, 1:0, Nb₂O₅:CdS). Calcination was tested at different temperature 200 °C, 500 °C and 800 °C for 4 hours. The prepared powder was characterized by X-ray diffraction. The result showed that (0.85:0.15) percentage at 800 °C has higher activity than other ratio at different temperature. Furthermore, the mass for the catalyst, initial of concentration for Ni (NO₃)₂, effect of temperature, effect of PH.

The experimental data for the Ni cation was analyzed by isotherms and kinetics equation in which the isotherm of the cation and Nb₂O₅/CdS was fitted well with the Freundlich and Langmuir models, respectively. The kinetic study followed pseudo-second order mode, finally the prepared nanocomposite can be used as a good adsorbent for metal cation from waste water.

Keywords : couple Nb₂O₅/CdS nanocomposite, wet commixing method, heavy metal ion Ni (II) removal, Adsorption photodegradation.

Introduction

Nowadays, removal of heavy metal ions from waste water is an important environmental concern, owing to a vast industrial discharge of different toxic material, and particularly metal ions into environment several methods such as precipitation, cementation ion exchange and membrane processes, electro-deposition, solvent extraction, adsorption, etc. have been used for removal of hazardous metal ions¹.

Most of these methods suffer from several disadvantages such as high reagent and energy requirements, in complete heavy metal ion removal generation of toxic sludge, and long desorption time. In particular adsorption method has provided a feasible option, both effectively and economically for removal of pollutants from waste water². In this regard, various materials such as zeolites, activated carbon, clays, agricultural wastes biomass and polymers were introduced as adsorbents^{3,4}.

The pollution of water with toxic organic compounds, heavy metal ions and dyes imposes ecological and public problem due to hazardous and irrecoverable effects of such pollutants on human health and the environment⁵⁻⁸. Adsorption is a convenient separation process, in which the adsorbed compounds may refer to organic, mineral or natural source⁹⁻¹².

Nb is in group 5 transition element niobium-oxygen mainly exists in the form of stoichiometric oxides such as NbO, Nb₂O₃, NbO₂ and Nb₂O₅. It gives a n-type semiconducting property with a band gap of about

3.4 eV. ⁽¹⁰⁾Nb₂O₅ exhibits a variety of crystalline allotropes, with orthorhombic (T-Nb₂O₅), pseudo-hexagonal (TT-Nb₂O₅), tetragonal (M-Nb₂O₅) and monoclinic (H-Nb₂O₅).¹³

CdS is a group II–VI semiconductor, and as such, CdS nanoparticles have generated great interest due to their unique size-dependent chemical and physical properties. CdS has a band gap energy of 2.42 eV at room temperature, and it shows great potential for uses in photochemical catalysis, solar cells, nonlinear optical materials and various luminescence devices.^{14,15}

Experimental

Materials

Chemical materials used in this work is Niobium pentoxide Nb₂O₅, Cadmium sulphide CdS, Ni(NO₃)₂ and other inorganic chemicals including HCL, NaOH solution and all solvents were purchased from Merck (Germany).

Preparation and characterization of couple Nb₂O₅/CdS

Nb₂O₅/CdS composite was prepared by the wet commix method, that involved using Nb₂O₅ with CdS powders as initial materials, and adding 10ml of distilled water, then mixed by Magnetic stirrer hot plate three hours after that drying in the oven at 100⁰c for one hour, the calcination of this was provided using Furnace at 800⁰c for 4 hours. The prepared Nb₂O₅/CdS was characterized by x-ray diffraction (XRD), FTIR spectroscopy.

Adsorption experiments:

Adsorption of heavy metal cation Ni⁺² was performed by mixing 0.1g (optimum amount) of synthesized nano-adsorbent (Nb₂O₅/CdS) with 100ml of metal ion solution 500ppm in the flask with a magnetic stirrer at temperature (23⁰C) for 60 min. The PH of solution was adjusted with 1M of HCL, NaOH solution using PH meter. The nano adsorbents were separated by centrifuge, and the concentration of cation Ni⁺² before and after adsorption was measured by Uv-visible spectrophotometer.

In addition, the adsorption isotherms were investigated by comparing the Freundlich, Langmuir and Temkin isotherm models with the experimental data. Also the kinetic studies were conducted using the pseudo-first and pseudo-second order. The adsorption amount q_t (mg/g) was calculated using the following equation

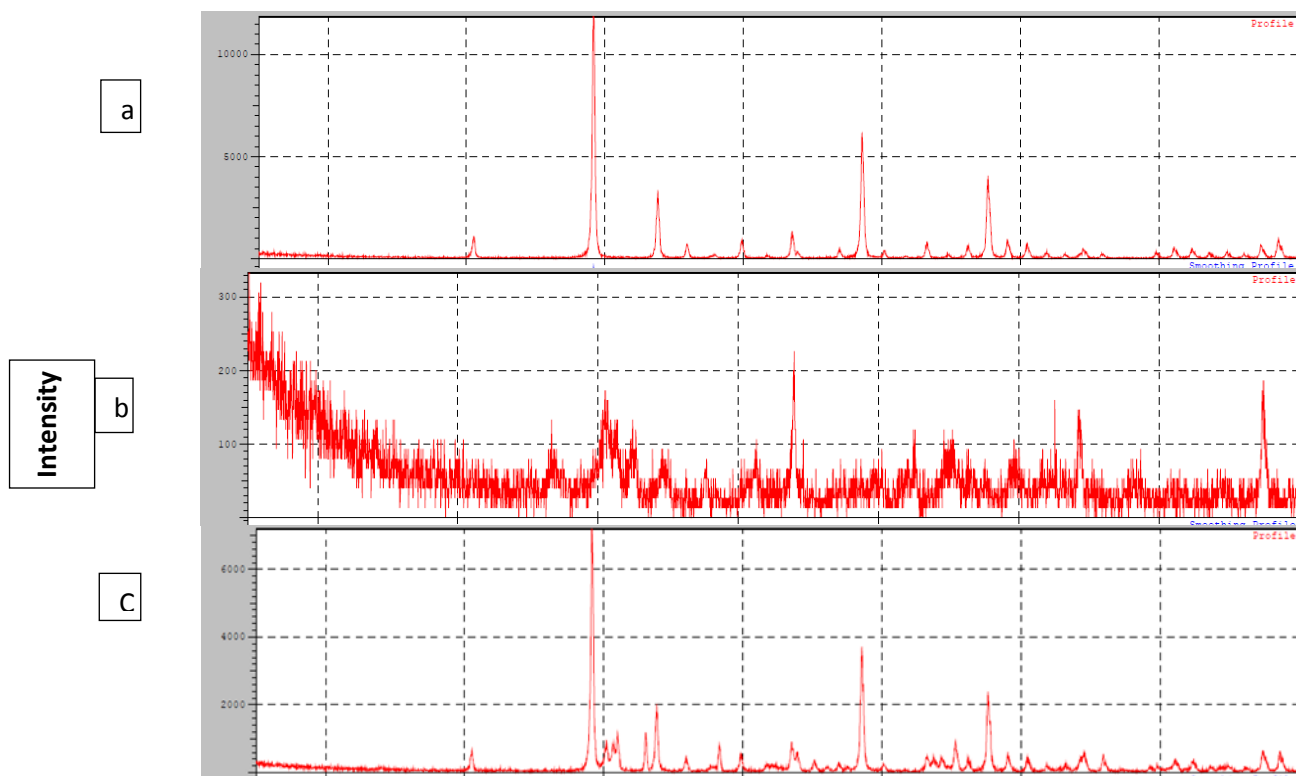
$$Q_t = (C_0 - C_t) V \dots \dots (1)$$

Where C_0 and C_t are the concentration of cation Ni⁺² in the solution before and after adsorption period of time m/L respectively, m (g) is the mass of nano-adsorbent and, V (L) is the volume of the cation Ni⁺² solution.

Result and Discussion

X-ray diffraction patterns

The formation and crystalline nature of nano adsorbents are also supported by XRD patterns. The Nb₂O₅ and CdS are characterized by x-ray diffraction (XRD), and compared with couple Nb₂O₅/CdS. Figure 1.a. show different peaks of Nb₂O₅ apparent in the shape of the spectrum represent 2θ at (29.1993, 48.5727, 57.6540, 33.8265, 43.5250, 78.6291, 20.5662, 39.8886). Figure 1b. Shows different peaks apparent of CdS in the spectrum represent 2θ at (77.3992, 43.9213, 30.5576, 31.1819, 64.3029, 32.5703, 34.7182, and 41.2730). While in figure 1c. of (Nb₂O₅/CdS) show that different peaks, at 2θ (29.1805, 48.5498, 57.6326, 33.8154, 33.0343, 31.0088, 55.2794, 38.3226, 65.9035) notes appear peaks in spectrum at 2θ (33.0343, 31.0088, 55.2794, 38.3226, 65.9035) not found in two initial material (Nb₂O₅, CdS)



2 Theta

Figure 1: X-ray diffraction spectrum of: A. Niobium pentoxide Nb₂O₅ B. CdS. couple Nb₂O₅/CdS.

The average crystallite size of the nanocomposite can be calculated by using the Debye–Scherrer equation¹⁶, results are shown in table 1.

$$D = K \lambda / FWHM \cos \theta$$

Where D, represent the average particle size, K is a dimension shape factor 0.9, λ = is X-ray wavelength, FW is the full width at half the maximum.

and θ is Bragg angle.

According to Scherer equation .our results demonstrated that the mean diameter of nano particles in the photocatalyst was estimated to be 45.48nm.

Table 1 : Particle Size of Niobium Oxide, CdS and Couple Nb₂O₅/CdS.

Catalyst	2Theta (deg.)	FWHM (deg)	Average Particle Size/nm
Nb ₂ O ₅	29.1993	0.22060	37.25
	48.5727	0.19910	43.86
	57.6540	0.20860	43.58
	33.8265	0.22800	36.47
	43.5250	0.21620	39.60
	78.6291	0.22400	46.04
	20.5662	0.22000	36.86
CdS	39.8886	0.20660	41.00
	77.3992	0.44000	23.17
	43.9213	0.54000	15.87

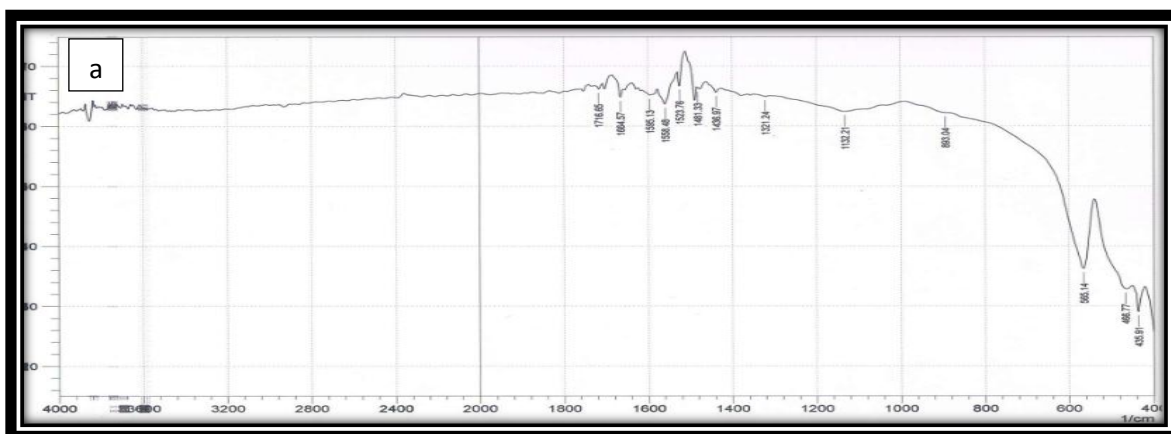
	30.5576	0.61000	13.50
	31.1819	0.52000	15.87
	64.3029	0.44000	21.35
	32.5703	0.30000	27.60
	34.7182	0.32000	26.05
	41.2730	0.28000	30.39
Nb₂O₅/CdS	29.1805	0.20730	39.71
	48.5498	0.19960	43.72
	57.6326	0.20690	43.86
	33.8154	0.20280	41.12
	33.0343	0.16050	51.91
	31.0088	0.19520	42.38
	55.2794	0.19780	45.44
	38.3226	0.17160	49.14
	65.9035	0.18200	52.10

Fourier Transition for Infrared spectrum (FT-IR)

FTIR analysis was carried out on a Bruker Tensor 27 spectrometer (Bruker, Karlsruhe, Germany) ($\text{KBr} \times \text{m}^{-1}$). The FTIR spectra of nanoparticles were shown in fig.2(a,b,c). Study of the double prepared catalyst was achieved by using Fourier Transform Infrared (FTIR). All spectra were recorded at the wavenumber ranged from 400-4000 cm^{-1} . Figure 2.a is characteristic of the sample niobium pentoxide Nb_2O_5 that show the peaks at (435.91, 466.77, 565.14, 893.04, 1132.21, 1321.24, 1436.97, 1481.33, 1523.76, 1558.48, 1595.13, 1664.57, 1716.65, 3741.90) (3741.90 cm^{-1} return to absorption water band in the sample, and bending band at 1716.65 cm^{-1} while the spectral appears the vibration modes assigned to Nb-O in the spectral range (910-850) cm^{-1} for Nb-O¹⁷.

Figure 2. b. Appear the peaks at (499.56, 597.93, 1109.07, 1390.68, 1425.40, 1587.42, 1602.85, 1764.87, 2243.21, 2436.09, 2908.65, 3427.51, 3485.37,). the peaks (3485.37 and 3427.51 cm^{-1}) are returning to stretching and bending vibration for two water band these peaks indicate the hydroscopic character of the sample (CdS)

Figure 2.c. Appear the peaks at (422.41, 470.63, 565.14, 893.04, 999.13, 1058.92, 1126.43, 1226.73, 1516.05, 1548.84, 1600.92, 1653.00, 1707.00, 1774.51, 2362.80). the peak at 1600.92 cm^{-1} also can see in spectrum of CdS but in the couple appear less intensity, the peak at $565.14, 893.04 \text{ cm}^{-1}$ return to the initial material Nb_2O_5 , the new peaks observe at (422.41, 470.63, 999.13, 1058.92, 1126.43, 1226.73, 1516.05, 1548.84, 1653.00, 1707.00, 1774.51, 2362.80).



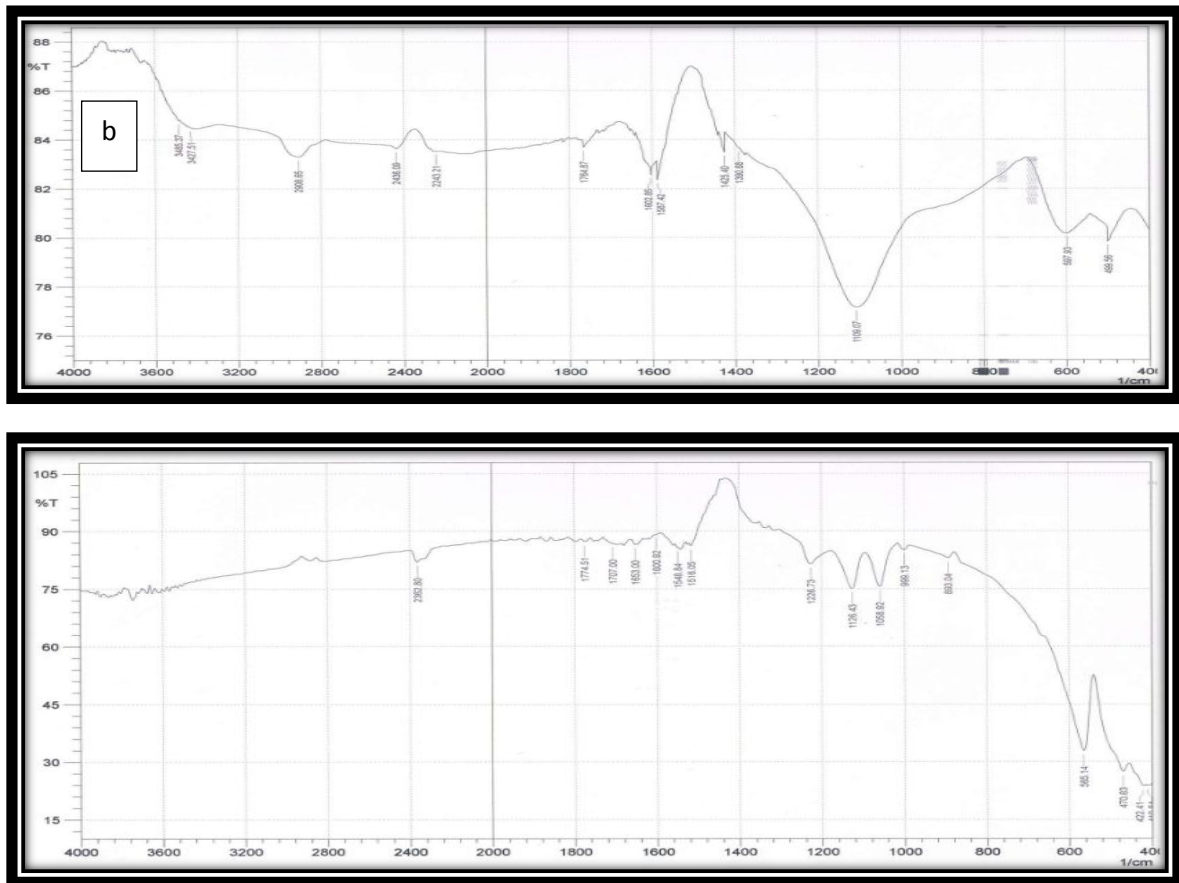
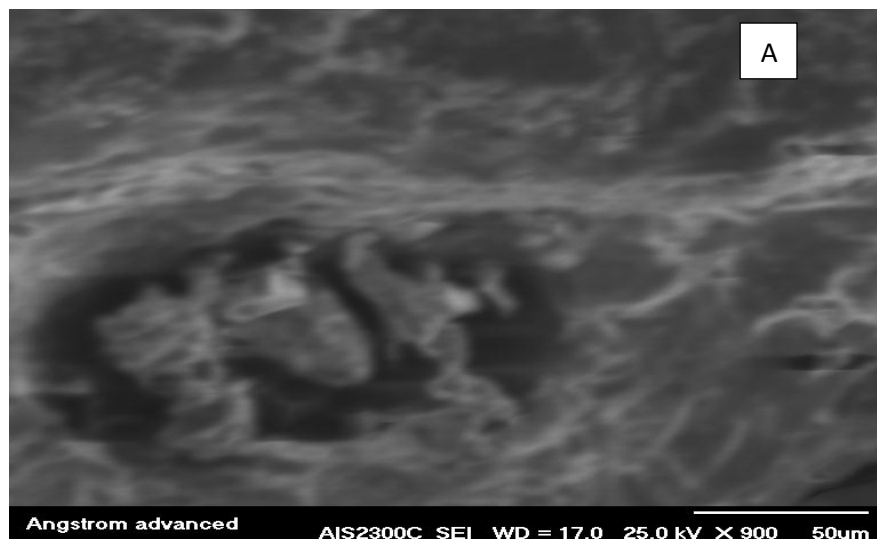
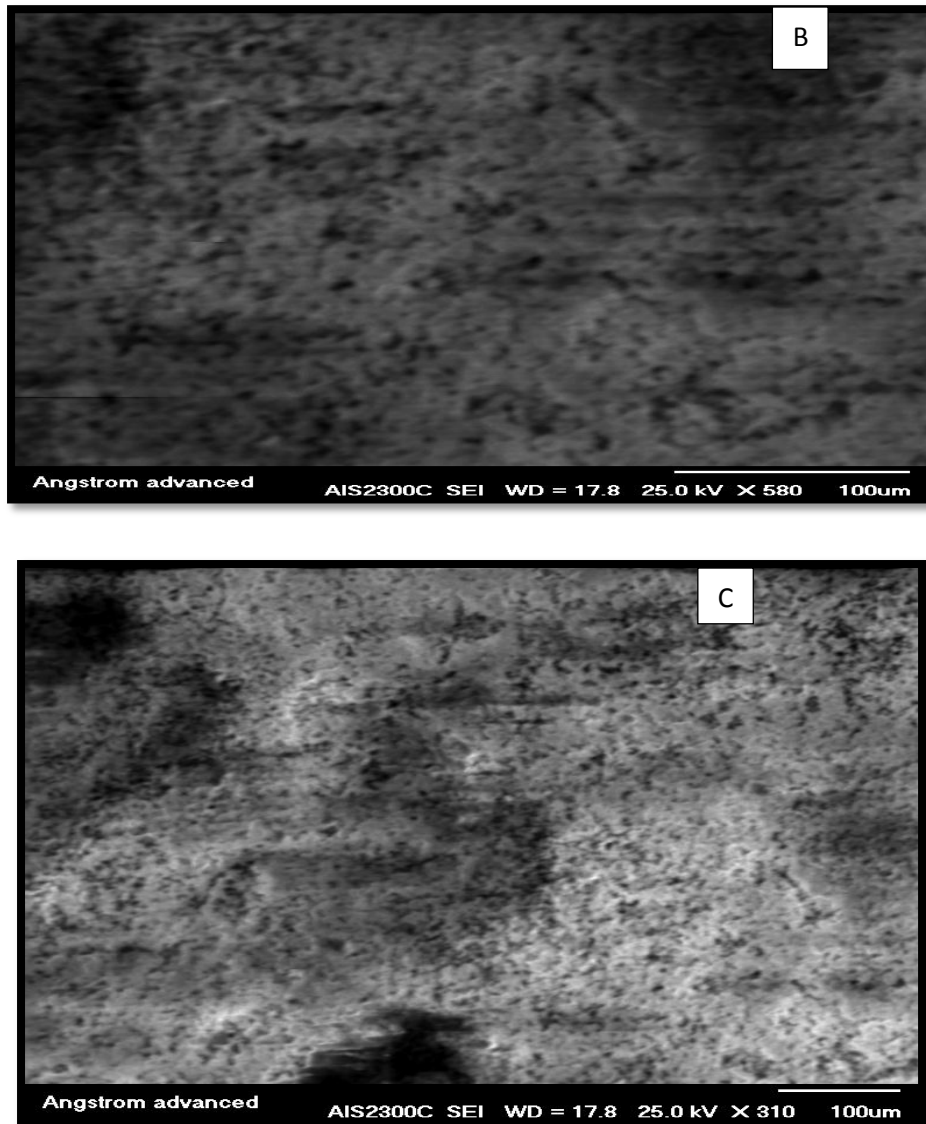


Figure 2: FTIR Spectrum for a. Niobium pentoxide (Nb₂O₅) b. CdS and c. Couple of Nb₂O₅/CdS

Scanning Electron Microscope SEM :

The particles were irregular in shape and mostly present in aggregates. The size of the particles was varied from 70-80nm .





Figures 3. A) Nb₂O₅, B) CdSand C) Nb₂O₅/CdS.

Figures show the images of SEM there are no obvious induced surface porosity and there is no evidence of agglomeration indicating good dispersion without observable aggregation.

Photocatalytic experiments

Effect adsorbent dose

Adsorbent doses used was (0.02gm, 0.05gm, 0.1gm ,0.15gm) at time of 60 min with initial concentration of Ni(NO₃)₂ 2000mg/L at room temperature (23 °C), and the obtained data are shown in Fig3. The figure shows that the removal percentage increases with increasing adsorbent dose due to increased surface area and the available of a more adsorption number of active sites.^(18,19), but at a high amount of the catalyst more than 0.1g the removal percentage was decreased due to an accumulation that is causing an increase in the particle size and decrease in specific surface area which leads to decrease in the number of surface active sites¹⁸⁻²¹.

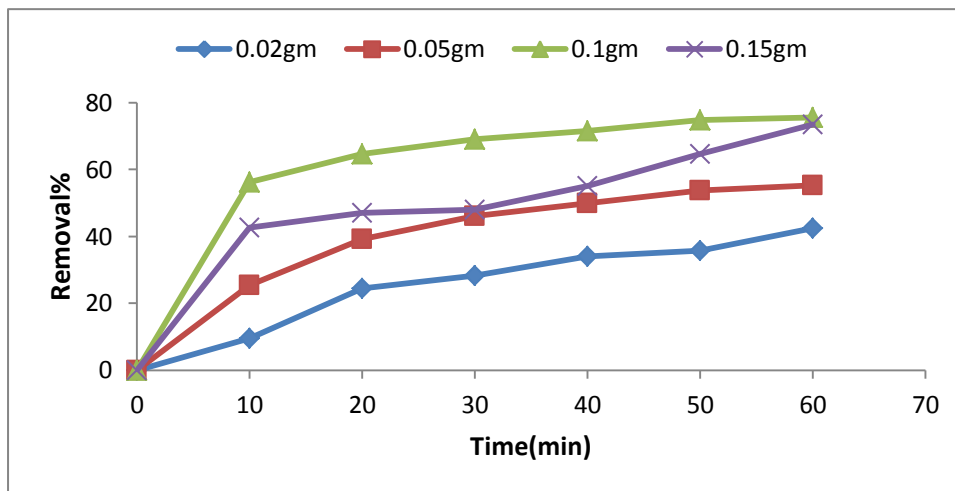


Fig.(4) Effect of adsorbent dosage on percentage removal of Ni(NO3)2.

Effect of Initial Concentration

Used initial Ni(NO₃)₂ concentration and effect on removal efficiency at constant adsorbent dose 0.1gm, 23°C, and time at 60 min. It was also found that the removal efficiency decreased as the initial concentration increased, as shows in fig.4 the removal percentage is decreased due to reduced surface area and saturated the active sites²².

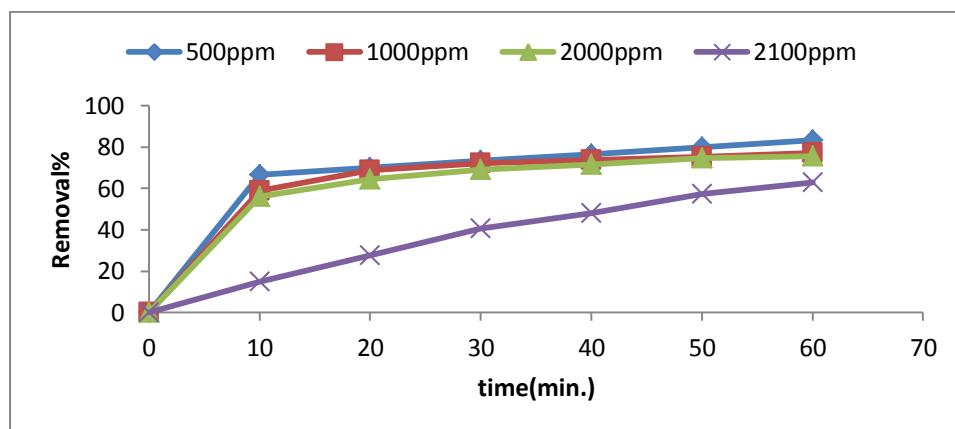


Fig.(5) Effect of initial concentration on removal efficiency.

Effect of temperature

The effect was studied of temperature on removal of Ni(NO₃)₂ using catalyst at different temperature ranging from (15-30C°). Figure5, shows the effect of temperature on the removal of Ni(NO₃)₂ at a fixed initial concentration 500 ppm and 0.1gm Nb₂O₅\CdS catalyst, and indicates that removal percentage of Ni(NO₃)₂ increases with increase of temperature because an increase in the mobility of the adsorbate molecules and the presence of the pores on the surface of the adsorbent particles. Noted similar observations and they suggested that the increase in temperature increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle. This is due to the total volume and the possibility of the adsorbent pores, an increase of the number of active sites for the adsorption as well as an increase in the mobility of the adsorbate molecules.²³

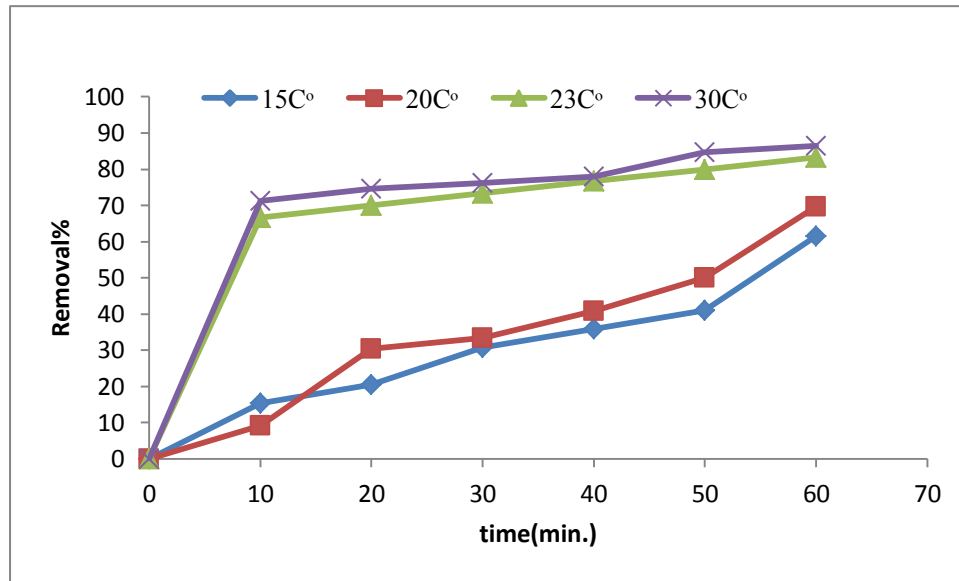


Figure 5. Effect of temperature on removal efficiency

Effect of pH

The pH of the ion solution affects the surface charge of the adsorbent, the degree of ionization of the materials, and the dissociation of adsorbate on the active sites of the adsorbent. The percentage removal of ion at different pH values is plotted in Fig 6. The percentage removal increased when pH was increased from 2 to 3. In low pH value, binding sites are generally protonated or positively charged (by the hydronium ions). Thus, repulsion occurs between the metal cation and the adsorbent at a higher pH value; binding sites start deprotonating, and makes adsorbent available for metal binding. In general, cation binding increases as pH increases²⁴.

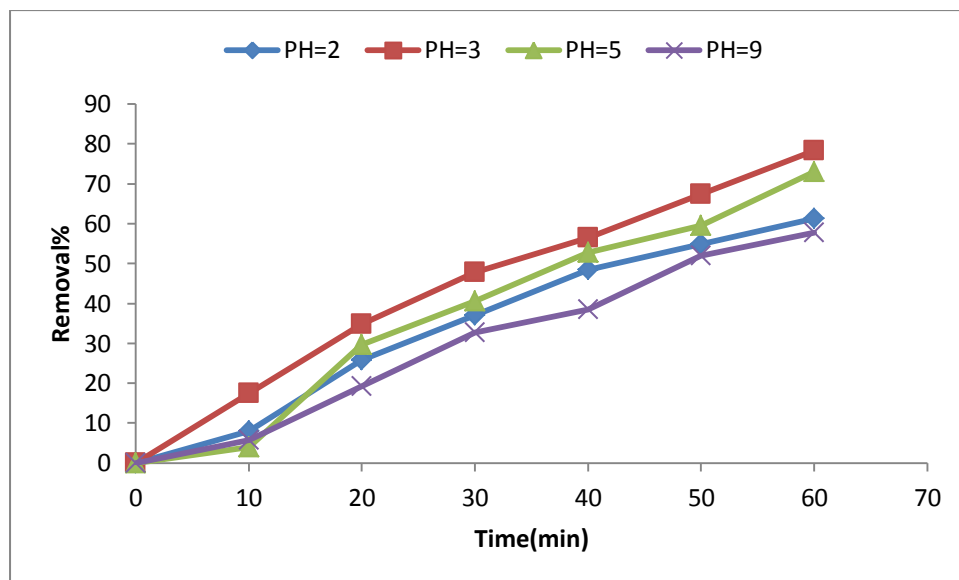


Figure 6. Effect of PH on removal efficiency

Adsorption isotherms

The adsorption isotherms designate how solute interact with the sorbent ,leading to finding the best equilibrium position in the adsorption process .several isotherm models can be used to investigate adsorption data. In the present work ,the adsorption isotherm were studied by the Langmuir, Freundlich and Temkin

models .The Langmuir model is often used to describe the equilibrium adsorption isotherm of homogeneous system which is presented by the following equation in the linear form.²⁵

$$C_e/Q_e = 1/Q_m K_L + C_e/Q_m \dots\dots(2)$$

Where C_e and Q_e are the equilibrium concentration (mg/l) and equilibrium adsorption capacity (mg/g) respectively, Q_m is the maximum metal ion adsorption capacity (mg/g) and K_L is the Langmuir constant related to the adsorption energy (L/mg) .the isotherm constant were calculated from the plot between C_e/Q_e and C_e .

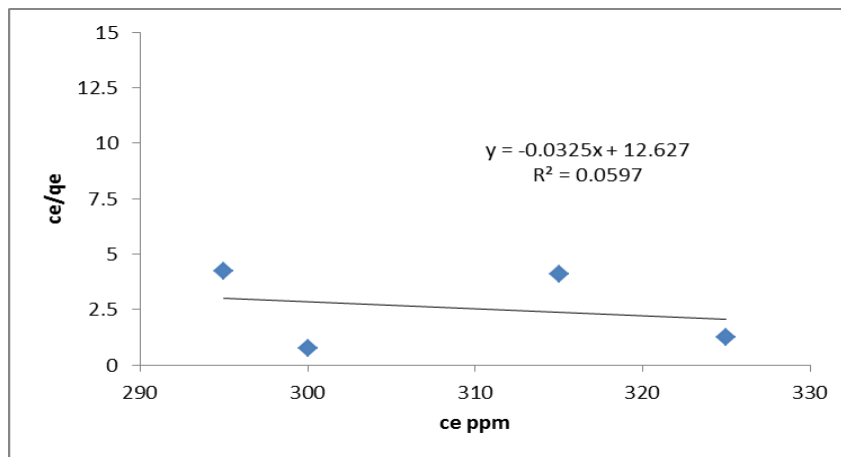


Figure 7 : Langmuir isotherm for adsorption of Ni(II)

The Freundlich adsorption isotherms is the oldest equation and its use indicates the heterogeneity of adsorption sites the Freundlich equation²⁶

$$\text{Log } Q_e = \log k_f + 1/n \log c_e \dots\dots(3)$$

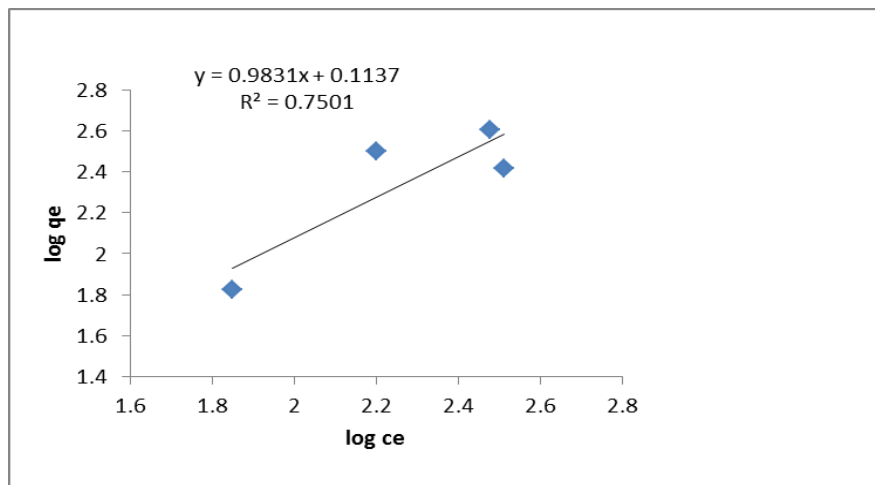


Figure 8 : Freundlich isotherm for adsorption of Ni(II)

Where k_f is a constant related to the adsorption capacity and $1/n$ is an experimental parameter related to the adsorption intensity which defines the affinity of the process to be a chemisorptions $n < 1$ of a physisorption $n > 1$.the Q_e and c_e already were mentioned. The Temkin isotherm takes into account of indirect adsorbate – adsorbate interactions on adsorption isotherms .The temkin isotherm model is given by the following equation⁽²⁷⁾

$$Q_e = B \ln A + B \ln C_e \dots\dots(4)$$

Where B and A (l/mg) are temkin constant .the B and A isotherm constants were Calculated from the plot between Q_e and $\ln C_e$.

By comparing the R^2 Vlues of these isotherm for the tested metal ion,the most appropriate and suitable equation can be obtained for the fitting the experimental data .

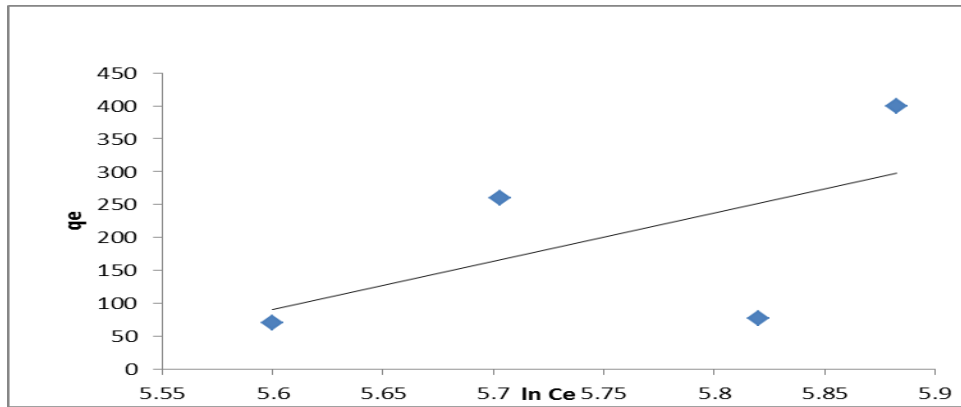


Figure 9: Temkin isotherm for adsorption of Ni(II)

Adsorption Kinetics

The kinetic study of adsorption processes expresses important data about the efficiency of adsorption .the adsorption kinetics of metal ion Ni^{2+} with Nb_2O_5 CdS nanocomposites were studied by two kinetic model :pseudo first and pseudo second order models .for the equation (5,6) respectively.²⁸

Pseudo first order model

$$\log (Q_e - Q_t) = \log Q_e - (k_1 / 2.303) t \dots\dots\dots(5)$$

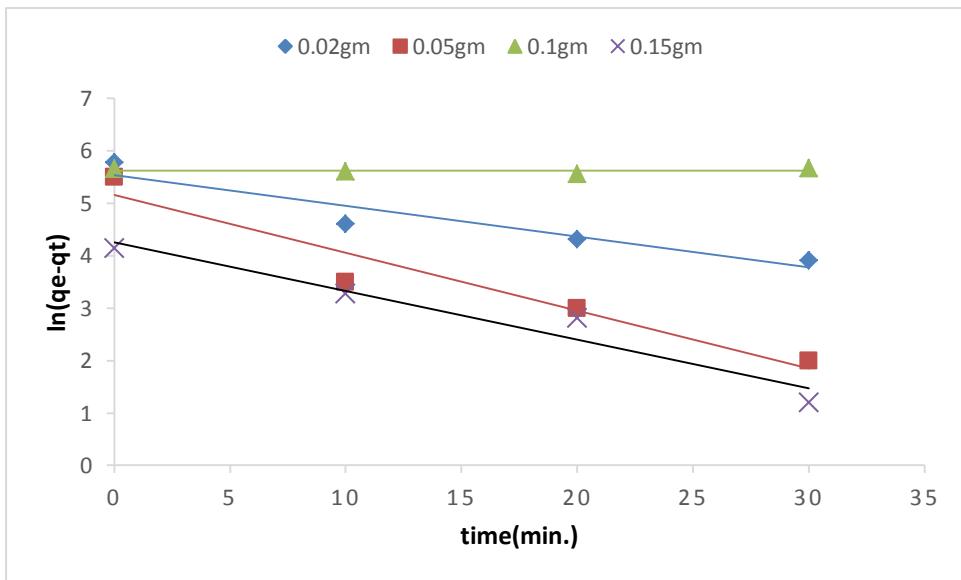


Fig.10. Pseudo first order

Pseudo second order model

$$t/Q_t = (1/k_2 Q_e^2) + (1/Q_e)t \dots\dots\dots(6)$$

where Q_t (mg/g) is adsorption capacity of the metal ion on an adsorbent at time t (min.), Q_e (mg/g) is the adsorption capacity at equilibrium , k_1 (min⁻¹) and k_2 (g.mg min⁻¹) , R^2 is correlation coefficient .are the kinetic parameters of these models were calculated and given in the figures and tables .

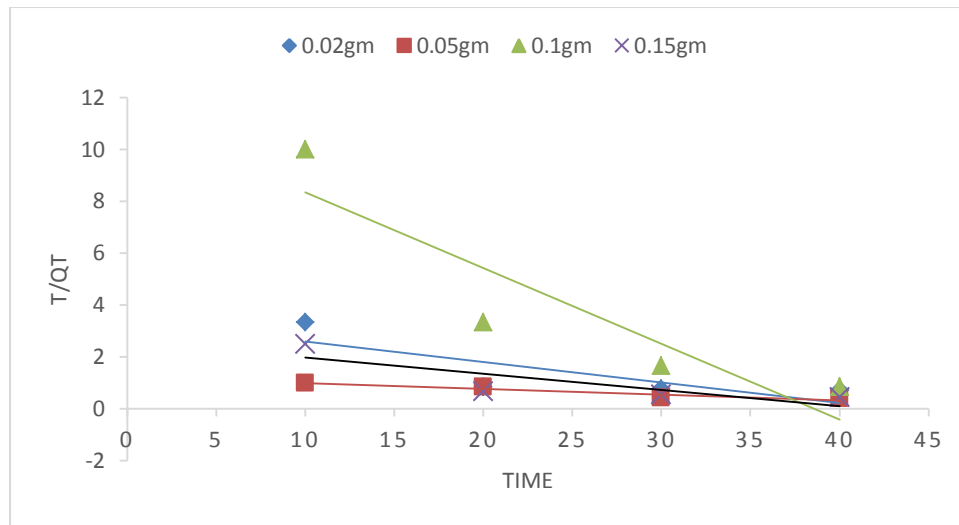


Fig.11.Pseudo second order

Table2: Adsorption constants for pseudo first ,second order isotherms and Langmuir, Freundlich, Temkin.

Weight(gm)	model Pseudo second order			
	qeexp.(mg\g)	qecal.(mg\g)	K2(min1-)	R2
0.02gm	400	3.42	0.007	0.8193
0.05gm	260	45.04	0.0004	0.9014
0.1 gm	70	12.62	0.001	0.6368
0.15gm	76.66	16	0.0014	0.6851
Weight(gm)	Pseudo first order model			
	qeexp.(mg\g)	qecal.(mg\g)	K1(min1-	R2
0.02gm	400	276.44	0.0589	0.0002
0.05gm	260	253.99	0.05	0.8973
0.1 gm	70	172.25	0.1101	0.931
0.15gm	76.66	70.17	0.0929	0.9437
Adsorption isotherms	parameters	Ni ²⁺		
langmuir	Q m	30.769		
	K _L	3.502		
	R ²	0.0597		
Freundlich	k _f	1.120		

	n	1.01
	R^2	0.7501
Temkin	A	239
	B	732.44
	R^2	0.3351

From the results that are summarized in Table 2,3, it can be seen that the value of the correction factor (R_2) that are obtained from Freundlich model is higher than that for Langmuir isotherm. This means that, this process is agreed with Freundlich model. The value of (n) that represents the number of adsorbed layers is (1.01) in this case adsorption processes were followed Freundlich adsorption isotherm.

The value of the correction factor (R_2) that are obtained from pseudo second order is (0.636-0.9014) higher than R_2 for pseudo first order, this means that followed pseudo second order.

Conclusion

In summary, the excellent photocatalyst nano-composite was synthesized successfully by wet commixing method the nano-adsorbents were characterized by FTIR, XRD. The results confirmed that the new catalyst was nanocomposite and the average particle size is equal to (45.48nm) and FTIR bands were new and shifted from their location in the modified catalyst Nb₂O₅/CdS than their location in separately CdS and Nb₂O₅ respectively.

References:

1. Fu F, Wang Q (2011) Removal of heavy metal ions from waste waters :a review .j Environ Manage 92:407-418.
2. WanNghahWS ,Teong LC ,Hana Fiah MA (2011)adsorption of dyes and heavy metal ions by chitosan composites :a review Carbohydr Polym 83: 1446-1456.
3. Karami H (2013) heavy metal removal from water by magnetite nanorods ,ChemEng J. 219: 209-216.
4. Tirtom NV ,Dincer A,Beceriks,Aydemir T,Celik A(2012) hydrincrosslinked chitosan –clay composite beads in aqueous solution.ChemEng J. 197:379-386.
5. Aljeboree AM, ,Alkaim, A. F., and Al-Dujaili, A. H. (2015);Adsorption isotherm, kinetic modeling and thermodynamics of crystal violet dye on coconut husk-based activated carbon. Desalin. Water Treat. 53(13): 3656-3667.
6. Alkaim AF, Sadik Z, Mahdi DK, et al. (2015);Preparation, structure and adsorption properties of synthesized multiwall carbon nanotubes for highly effective removal of maxilon blue dye. Korean J. Chem. Eng. 32(12): 2456-2462.
7. Hassan MZ, Fairooz NY. (2016);Preparation, characterization of Ag₂O/Cr₂O₃ and investigation of the photocatalytic degradability on Congo red textile dye. International Journal of ChemTech Research. 9(8): 348-358.
8. Fairooz NY. (2016);Evaluation of new couple Nb₂O₅/Sb₂O₃ oxide for photocatalytic degradation of orange G dye. International Journal of ChemTech Research. 9(3): 456-461.
9. Al-Gubury HY, Fairooz NY, Qasim YM. (2016);Study physical properties of composite ZnO- Sb₂O₃ using liquid Impregnation Method. Journal of Chemical and Pharmaceutical Sciences. 9(4): 2570-2574.
10. Kareem A, Alrazak NA, Aljebori KH, Aljeboree AM, Aljboory HL, Alkaim AF. (2016);Removal of methylene blue dye from aqueous solutions by using activated carbon/ureaformaldehyde composite resin as an adsorbent. International Journal of Chemical Sciences. 14(2): 635-648.
11. Raheem RA, Al-Gubury HY, AljeboreeAM, Alkaim AF. (2016);Photocatalytic degradation of reactive green dye by using Zinc oxide. Journal of Chemical and Pharmaceutical Sciences. 9(3): 1134-1138.

12. Kamil AM, Mohammed HT, Alkaim AF, Hussein FH. (2016); Adsorption of Congo red on multiwall carbon nanotubes: Effect of operational parameters. *Journal of Chemical and Pharmaceutical Sciences*. 9(3): 1128-1133.
13. Kamil AM, Mohammed HT, Alkaim AF, Hussein FH. (2016); Adsorption of Congo Red on Multiwall Carbon Nanotubes: Equilibrium Isotherm and Kinetic Studies. *Int. J. Chem. Sci.* 14(3): 1657-1669.
14. Maity, R.; Chattopadhyay, K.K. Synthesis and optical characterization of CdS nanowires by chemical process. *J. Nanopart. Res.* 2006, 8, 125–130.
15. Zhang, Y.C.; Wang, G.Y.; Hu, X.Y. Solvothermal synthesis of hexagonal CdS nanostructures from a single-source molecular precursor. *J. Alloys Compd.* 2007, 437, 47–52.
16. Osuna Y, Gregorio –Jauregui KM, Gaina –Lozano J G (2012) chitosan coated magnited nanoparticles with low chitosan content prepared in one –step *J nanomater* 2012:1-7.
17. Mohamed FF, Allah PMA, Mehdi A, Baseem M. (2011); Photoremoval of Malachite Green (MG) using advanced oxidation process. *Research Journal of Chemistry and Environment*. 15(3): 65-70.
18. Ali MM, Fairooz NY. (2015); Preparing and characterizing study of the photocatalytic activity of new couple semiconductor Nb₂O₅/Sb₂O₃. *Research Journal of Pharmaceutical, Biological and Chemical Sciences*. 6(4): 1176-1182.
19. Malik P.K., and Saha S.K., 2003. Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst, *Sep. Purif. Technol*, 31: 241-250.
20. Ni Y, Ge X, Zhang Z, Liu H, Zhu Z, Ye Q. (2001); A simple reduction-oxidation route to prepare Co₃O₄ nanocrystals. *Materials Research Bulletin*. 36(13-14): 2383-2387
21. Wilson SJ. (1979); The dehydration of boehmite, γ -AlOOH, to γ -Al₂O₃. *Journal of Solid State Chemistry*. 30(2): 247-255.
22. Omran AR, Baiee MA, Juda SA, Salman JM, Alkaim AF. (2016); Removal of congo red dye from aqueous solution using a new adsorbent surface developed from aquatic plant (*Phragmites australis*). *International Journal of ChemTech Research*. 9(4): 334-342.
23. Al-Gubury HY, Fairooz NY, Aljeboree AM, Alqaraguly MB, Alkaim AF. (2015); Photocatalytic degradation n-undecane using coupled ZnO-Co₂O₃. *International Journal of Chemical Sciences*. 13(2): 863-874.
24. Hadi AG. (2016); Removal of Fe (II) and Zn (II) ions from aqueous solutions by synthesized chitosan. *International Journal of ChemTech Research*. 9(4): 343-349.
25. Murugesan A, Ravikumar L, SathyaSelvaBala V, Senthil Kumar P, Vidhyadevi T, Dinesh Kirupha S, kalaivani SS, Krithiga S, Sivanesan S (2011) Removal of Pb(II), Cu(II) and Cd(II) ions from aqueous solution using polyazomethineamides: equilibrium and kinetic approach. *Desalination* 271:199-208.
26. Shen W, Chen S, Shi S, Li X, Zhang X, Hu W, Wang H (2009) Adsorption of Cu(II) and Pb(II) onto diethylenetriamine-bacterial cellulose. *Carbohydrpolym* 75:110-114
27. Dada AO, Olalekan AP, Olatunya AM, Dada O (2011) Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms studies of equilibrium sorption of Zn²⁺ onto phosphoric acid modified rice husk. *J Appl Chem* 3:38-45
28. Ge F, Li MM, Ye H, Zhao BX (2012) Effective removal of heavy metal ions Cd²⁺, Zn²⁺, Pb²⁺, Cu²⁺ from aqueous solution by polymer-modified magnetic nanoparticles. *J Hazard Mater* 211-212:366-372.
