

Zinc oxide-urea formaldehyde nanocomposite film as low-cost adsorbent for removal of Cu(II) from aqueous solution

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ABSTRACT

Copper is widely used in different industries and found its significant loss during the manufacturing and processing. The lost Cu is discharged in the effluent, thus adsorption of heavy metals is an important technology for treatment of wastewater containing different types of selected heavy metals. In this study, nanosize (~95 nm) zinc oxide was prepared through KNO₃-NaNO₃ eutectic melt at 450 °C. The obtained ZnO was encapsulated in urea-formaldehyde (UF) resin during acid catalysed polymerization process. The characterization of ZnO and ZnO-UF were made by X-ray diffraction (XRD), Scanning electron microscope (SEM) and Infra red spectroscopic (FT-IR) techniques. The prepared ZnO encapsulated in urea-formaldehyde resin casted in the form of film (~0.5 mm thickness) was used to remove 80% Cu (II) content from aqueous solution in 15 minutes. Further, the adsorption process was investigated and data was explained with Langmuir adsorption isotherm model. Copyright © 2015 VBRI press.

Keywords: Nanocomposite; eutectic melts; Cu removal; isotherm model.



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Introduction

Heavy metals removal from industrial wastewater is a challenging task for scientists, due to multi-facet contamination of water bodies [1-3]. The heavy metals contamination in water bodies are mainly because of indiscriminate discharge of wastewater by small, medium and heavy scale industries. Toxic heavy metals of particular concern in treatment of industrial wastewaters are including Zn, Cu, Ni, Hg, Cd, Pb and Cr [4-7]. These metals are often detected in industrial waste waters of metal plating, mining activities, smelting, battery manufacture, tanneries, refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries, etc. [8-9]. Different techniques such as ion exchange, chemical precipitation, ultra filtration, electrochemical have been used for removal of metals from industrial wastewater employing different adsorbent materials [10-13]. The different adsorbent materials which are used for copper removals are listed in **Table 1**.

The listed materials in **Table 1** are ineffective to detect the metals at trace level and also economically infeasible due to their relatively high costs. Therefore, developing countries can't afford these composites. To overcome these challenging points, there is a need to investigate a cost effective and economical alternate materials as well as method for water purification [14].

Table 1. Different adsorbent used for copper removal.

Adsorbent	Decontamination efficiency	Contact time	References
Tea waste	21.02 mg/gm	-----	[15]
Chitosan bead	129.6 mg of Cu(II)/g	3 hours	[16]
Black tea waste	43.18 mg g ⁻¹	10 min.	[17]
Silk fibroin/nylon-6 blend	32% to 77 %	1-2 hours	[18]
Magnesium hydroxyapatite/ferroferic oxide nano-composites	305 mg/g	90 minute	[19]
Hardwoods Powder	165	2 hours	[20]
Graphene oxide–CdS composite	90%	-----	[21]

Nowadays innovation of nanotechnology has generated effective materials due to large surface area to volume ratio to remove the toxic metals [22]. Conversely, problem of stabilisation and agglomeration of nano scale materials restricted its effective and potential applications. The encapsulation of nanoparticle in polymers matrix has been reported, to solve these problem [14, 23-24]. Numerous nano materials stabilised polymer matrix are reported for water purification but their dispersion in a polymer matrix still needs intensive investigation [25]. Yan *et al.* have extensively reviewed the significance of the stabilisation of nanoparticles and for their different potential applications [26]. Polymer nanocomposites have efficient capacity to purify heavy metal containing wastewater, if the properties of nanocomposite constituents will be synergized [27]. The present work reports the synthesis of nano size ZnO by a simple scalable eutectic melt method. The prepared Zinc oxide has been used to prepare its nano nanocomposite with urea formaldehyde by *in-situ* polymerization and chemical functionalisation method. The prepared resins were used for removal Cu(II) ion from aqueous solution. The mechanism of copper sorption over the nanocomposites, sorption kinetic, and sorption isotherm were discussed. The objective of this work is to examine the use of ZnO-UF nanocomposite for the effective removal of Cu(II) ion from aqueous solutions and propose a mechanism of chemical interactions between the Cu(II) ions and nanocomposite along with synergistic effect of ZnO and UF resins.

Experimental

Materials and methods

KNO₃ (99.5 %), NaNO₃ (99 %), ZnSO₄·5H₂O (AR grade) from E. Merck, Urea (99%) and Formaldehyde (AR grade) from NOVA chemical were procured and used without further purifications. The doubled distilled water was used throughout the investigations.

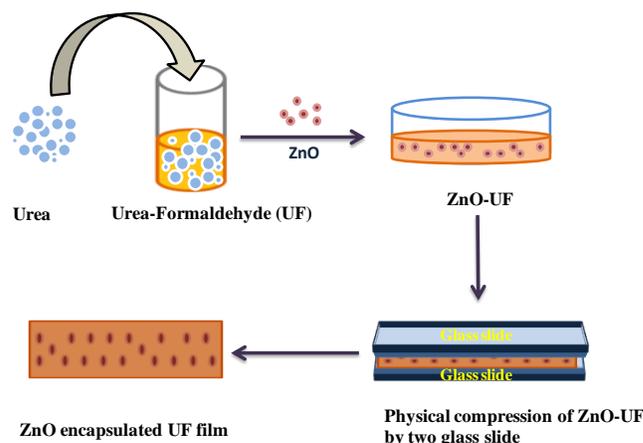
Preparation of ZnO nanoparticles

Nano sized ZnO nanoparticles were prepared by nitrate eutectic melt, as described earlier [28]. In a typical experiment, 3.0 gm anhydrous ZnSO₄ was mixed with 5 gm NaNO₃-KNO₃ (45:55) eutectic mixture and homogenized properly by mortar and pestle. The followed the mixture was heated at 450 °C in a muffle furnace for 1 h, where a white product (i.e. ZnO) was obtained. The product was

washed with distilled water and then dried at 100 °C in a vacuum oven for 3 hours.

Preparation of ZnO encapsulated UF film

Formaldehyde and urea were mixed in molar ratio of 2:1 (w/w) in 200 ml round bottom flask and stirred magnetically at 60 °C for 30 min. In this mixture 100 mg of ZnO and 0.5 ml H₂SO₄ were added with continuous stirring. After some time (~15 minutes) a white precipitate settled down. The precipitate was washed with distilled water and pressed between two ordinary glass plates where a thin film (thickness ~0.5 mm) was formed. In another experiment UF resin without ZnO was prepared by the above methods and a film without ZnO was used for controlled experiment. **Scheme 1** illustrates the overall scheme for structuring the ZnO encapsulated UF thin film.



Scheme 1. Schematic representation of the preparation of ZnO encapsulated UF thin film.

Instrumentation

Zinc oxide and nanocomposite were characterised by X-ray Diffractometer (XRD) using Rigaku Rotaflex (RAD/Max-200B) using Cu K alpha radiation with λ value 1.5405 Å wave length and 2° per minute scanning speed. Fourier transform infrared spectroscopy (FTIR) spectra were recorded using the Perkin Elmer (RK-1310) spectrometer in KBr media to investigate the chemical interactions in nanocomposite. The average particle size and morphology of the samples were examined by (SEM) (ZEISS Scanning Electron Microscope) after gold coating. The study about the copper removal was carried out by UV-2501 PC (Shimadzu Corporation, Japan) UV spectrometer.

Removal of Cu(II) from aqueous solution

CuSO₄ solution (200 ppm) in distilled water was prepared and divided into two equal parts (100 ml each) and kept in two different beakers. In one beaker 1sq cm UF film was dipped which acted as a reference and in the second beaker ZnO-UF nanocomposite film of 1 sq cm dimension was placed and stirred for one minute. After, then 2 ml solutions from both the beakers were taken out at an interval of 5, 10, 15 and 20 min and UV-visible spectra were recorded in the wavelength range of 600 - 1100 nm with the help of UV-

Visible spectrophotometer. From the absorbance at the λ_{max} , concentrations of Cu (II) were calculated using Lambert -Beers law [29].

Adsorption and isotherm study

Extent of adsorption, determines the capacity of an adsorbent for a given concentration of the adsorbate. The adsorption studies of Cu(II) ions on ZnO-UF nanocomposite was carried out at room temperature by changing the amount of adsorbent, keeping the volume and concentration of the metal solutions constant. Copper removal capacity by nanocomposite was calculated by using following relation (eqn-1).

$$\text{Metal removal capacity (MRC)} = \frac{C_i - C_f}{M} \times V \quad \text{---(1)}$$

Where, C_i = initial Cu (II) concentration in the solution (gm / L); C_f = Cu(II) concentration in the solution after removal (gm /L); V =volume of the solution (liter); M = the weight of the nanocomposite. Further, isotherm studies were carried out with different initial concentrations of Cu(II) (50–150 ppm) at ambient temperature ~ 25 °C. The amount of Cu (II) adsorbed (mg/g) was calculated by mass balance eqn.-2.

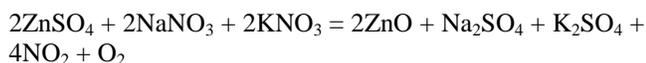
$$q = \frac{C_0 - C_{eq} \times V}{W} \quad \text{---(2)}$$

Where, q is the adsorbent capacity (mg/g); C_0 is the initial concentration of Cu (II) in ppm; C_{eq} is the final or equilibrium concentration of Cu(II) in ppm; V is the volume of experimental solution(l); and W is the dry weight of nanocomposite (gm). For this purpose a volume of 50 ml of Cu(II) solution with a concentration in the range 50–150 mg/dm³ was placed in a 125 ml conical flask. A known weight of nanocomposite has been added to the solution and then shaken at a constant speed of 100 rpm. After shaking the flasks for 15 min, the nanocomposite was separated by filtration through a whatman filter paper no 1. The filtrate was analysed for the remaining copper ion concentration by method described earlier.

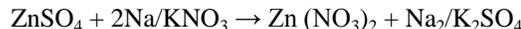
Results and discussion

Synthetic mechanism

Different methods both physical and chemical have been used to prepare zinc oxide nano structure using different precursor salt. Generally, a precursor salt heated at appropriate temperature to yield ZnO. *Singh et al.* [30] has reported the formation of transition metal oxide in eutectic melt at lower temperature. *Shukla et al.* [31] has reported that heating of salt at lower temperature yields smaller particles. In this method, ZnSO₄ reacted with the eutectic mixture in the following way.



The reaction may proceed as shown in **Scheme 2** [32]. Solid ZnSO₄ was surrounded by molten nitrates, where exchange reactions took place as given below-



The reaction proceeds via diffusion. Once Zn (NO₃)₂ is formed, it decomposes in the following way-



Scheme 2. Schematic representation of the decomposition of ZnSO₄ in NaNO₃-KNO₃ eutectic mixture.

Further, urea and formaldehyde polymerises by acid catalysis in a controlled condition. In the present case presence of zinc oxide supports the in situ acid catalysed polymerisation due to lewis acidic behaviour of ZnO and also entered in the resin matrix and ZnO-UF nanocomposite was formed quickly than pure UF resin.

Characterization

Powder XRD patterns of ZnO and ZnO-UF nanocomposites are shown in **Fig. 1**. All of the diffraction peaks of ZnO were indexed to hexagonal structure of zinc oxide, which are well consistent with the respective JPCDS card No.: 36-1451. The full width half maxima at 111 peak of ZnO were used to calculate the crystallite size using Scherrer formula (Eq. 3) [33, 34].

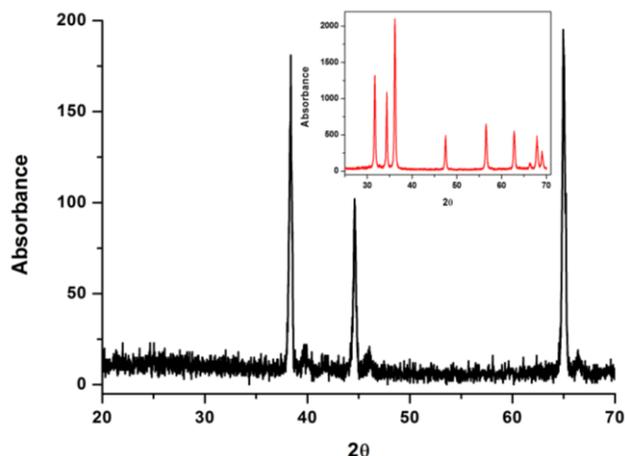


Fig. 1. X-ray diffraction pattern of ZnO-UF nanocomposite. Inset; XRD of ZnO nanoparticle.

$$T = \frac{K\lambda}{\beta \cos \theta} \quad \text{---(3)}$$

where, T is the average size of the crystallite, K is a dimensionless shape factor, λ is the X-ray wavelength, β is the line broadening at full width at half maximum intensity (FWHM) and θ is the Bragg's angle. The crystallite size of ZnO was found to be ~ 95 nm. The diffraction pattern of ZnO nanoparticles given in **Fig. 1** while inset, which shows the crystalline nature. However, the 101 reflection peak of ZnO is present in the X-ray diffraction pattern of nanocomposite but with reduced intensity. However the crystallinity of zinc oxide was reduced with the dominant amorphous nature of UF. This result divulges the formation ZnO-UF nanocomposites.

SEM photographs of ZnO and ZnO-UF nanocomposite are shown in **Fig. 2(A)** and **(B)** respectively. **Fig. 2(A)** confirmed the formation of nanosized ZnO with ~ 95 nm size. The value was found nearly the same as calculated by XRD. **Fig. 2(B)** shows homogeneous encapsulation of nanosized ZnO in UF resin in the nanocomposite.

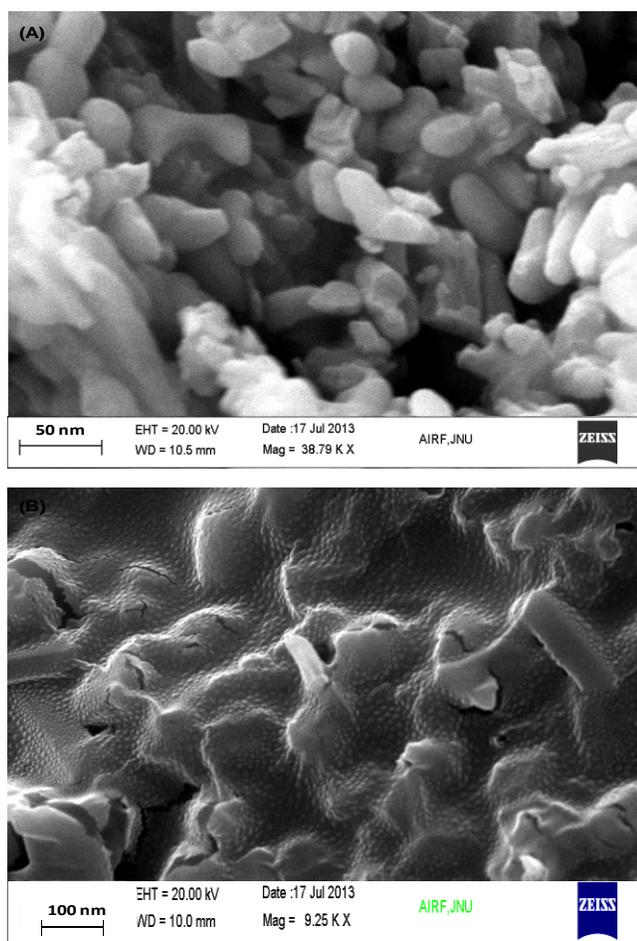


Fig. 2. SEM picture of (A) ZnO and (B) ZnO-UF nanocomposite.

IR spectra of UF and ZnO-UF nanocomposite are shown in **Fig. 3** and the conclusive peak positions are tabulated in **Table 2** along with their functional group [35]. The IR spectra of UF is showing peaks at 3431, 2917, 1638, 1288, 1176, 1069, 1007, 888, 851, 614, 575, and 454 cm^{-1} while in the case of nanocomposite these respective peaks shifted to 3409, 2905, 1646, 1281, 1191, 1058, 1001, 881, 844, 609, 562, and 444 cm^{-1} . The spectra of UF attributed the presence of NH and CO groups in the range 3500-3200 and 1650 cm^{-1} -1550 cm^{-1} . The vibrational

frequencies for CH_2OH , CH_3 and CN groups appeared in the range 1400 cm^{-1} to 1300 cm^{-1} [36]. The shifting in band position of NH, CH and CO in case of UF towards lower wavelength indicates that ZnO interacts with UF with a very weak force at NH sites, because ZnO is lewis acid in nature while NH is lewis base. This interaction indicates that lewis basic nature of NH-CO-NH group [37] of urea interacts with lewis acid ZnO and increase the cross link density in the CH chain. The chemical interaction also stabilizes ZnO nanoparticles in polymer matrix.

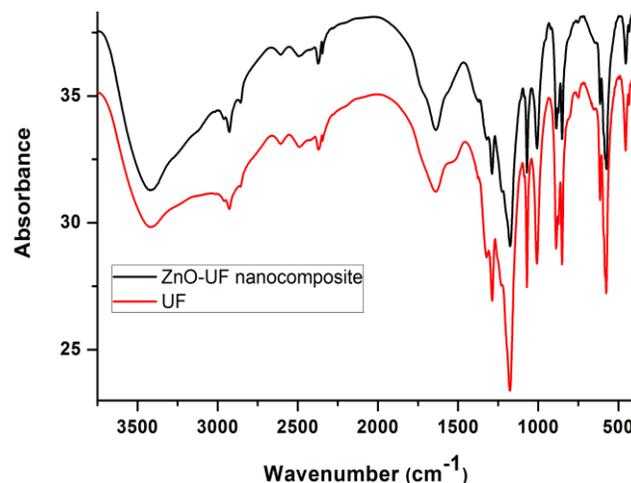


Fig. 3. FT-IR spectra of UF and ZnO-UF nanocomposite.

Table 2. FTIR data of UF and ZnO-UF nanocomposite.

UF (cm^{-1})	ZnO-UF nanocomposite (cm^{-1})	Expected vibrations
3431	3409	N-H
2917	2905	CH
1638	1646	CO
1069	1058	CO bending
851	844	C-O-C

Copper decontamination

In 100 ml copper sulphate solution of 200 ppm concentration, 1 sq.cm ZnO-UF nanocomposite film was introduced and stirred gently. The absorption spectra were recorded at different intervals of time and are shown in **Fig. 4**.

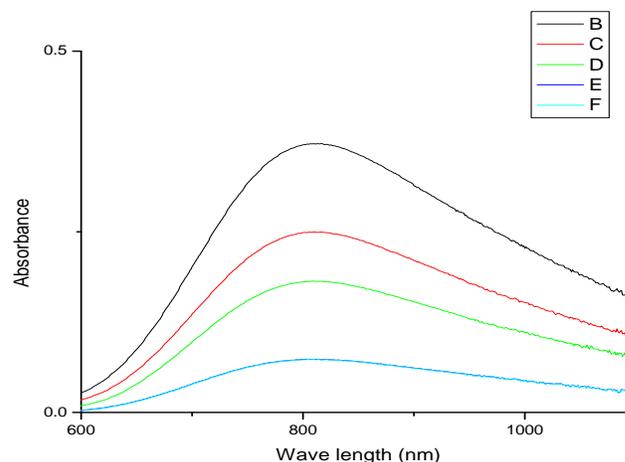


Fig. 4. UVvis spectra of CuSO_4 recoded at different time (B= initial, C=5 min, D= 10 min, E= 15 min and F 20 min.) interval in the presence of ZnO-UF nanocomposite.

The spectra indicated the decrease in intensity of the absorption band with time due to removal of Cu^{2+} ions from the solution in the presence of ZnO-UF nanocomposite. A plot of absorption intensity at λ_{max} with time is shown in **Fig. 5**. The curve indicated the decrease in absorbance from 0.375 to 0.075 within 15 minutes due to adsorption of Cu(II) on ZnO-UF nanocomposite. Further, absorbance was used to calculate the concentration of Cu^{2+} ions using Lambert-Beer's law and the result is given in **Table 3** [38]. The data shows that 80% Cu^{2+} was removed within 15 minutes.

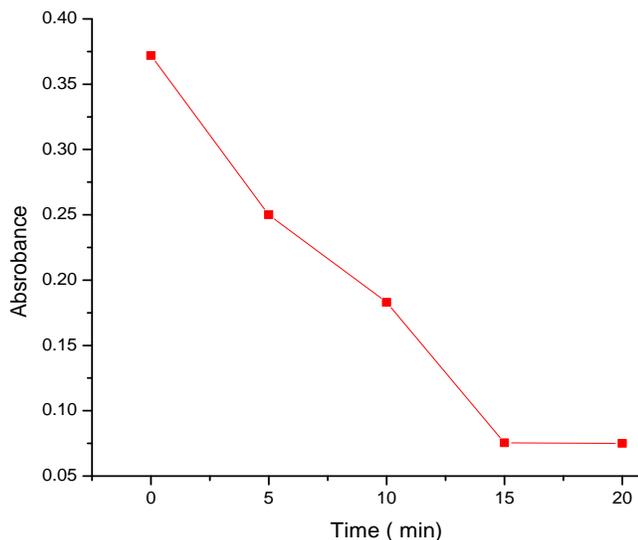


Fig. 5. Change in absorbance of copper solution at different time intervals.

Table 3. Concentration of copper solution at different time intervals.

Time (Min)	0	5	10	15	20
Conc. (ppm)	200	134	98	40	40

The Cu^{2+} ion removal capacity was determined at different pH and the results are shown in **Fig. 6**. The data clearly revealed that nanocomposite is effective for removal of Cu^{2+} ions in acidic media.

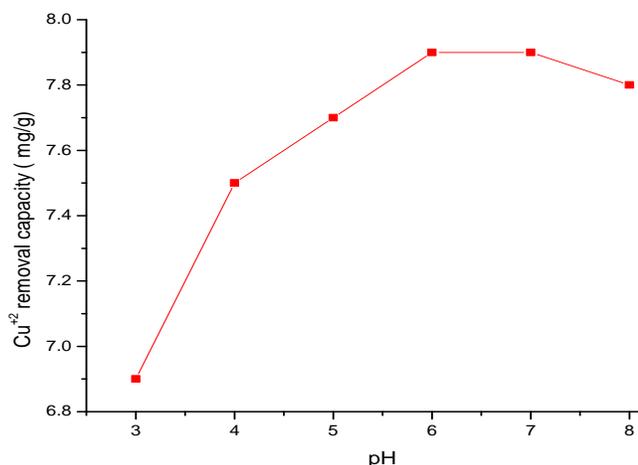
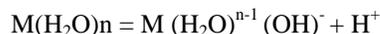
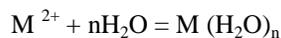
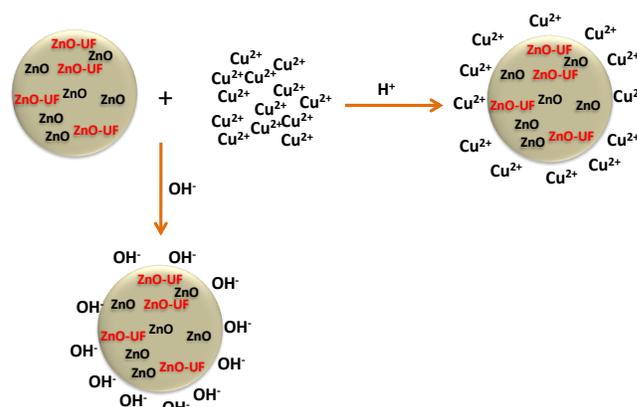


Fig. 6. Cu removal capacity of ZnO-UF nanocomposite at different pH.

The increase in pH above 7.8 reduces the adsorption capacity of the nanocomposite. Apparently in basic medium, copper solution becomes turbid and hence adsorption and removal tendency of Cu^{2+} ions are reduced. The decrease in removal of Cu(II) at higher pH may be due to solvation and hydrolysis of metal ion as explained in the following reactions :



The solvation and hydrolysis process lead the metal ion to form soluble hydroxylated complexes that compete for active sites and decreases the extent of adsorption. The adsorption of Cu^{2+} in acidic and basic medium can be also understood from **Scheme 3**. In basic medium the adsorption capacity is reduced. The film is surrounded by hydroxyl groups and hinders the approach of Cu^{2+} ions at the surface of ZnO-UF nanocomposite and hence in basic medium the adsorption capacity of nanocomposite is reduced. Also in basic medium there are no free Cu^{2+} ions to be adsorbed.



Scheme 3. Adsorption of Cu^{2+} ions on the surface of ZnO-UF nanocomposite in acidic and basic media.

Adsorption isotherm

Successful representation of the dynamic adsorptive metal decontamination from solution onto an adsorbent is dependent upon a good description of the equilibrium separation between the two phases. An equilibrium is established when the amount of copper being adsorbed onto the ZnO-UF nanocomposite is equal to the amount being desorbed. The equilibrium solution of Cu(II) concentration remains constant. Plotting solid-phase concentration against liquid-phase concentration graphically depicts the equilibrium adsorption isotherm. Several theories of adsorption equilibrium have been used to describe these isotherms [39]. **Fig. 7** shows the amount of copper adsorbed per unit weight of nanocomposite as a function of nanocomposite dosage per liter at adsorption time. The experiment was performed until the concentration of copper in solution did not significantly change. Because the decrease in the dissolved metal concentration is due to both precipitation and adsorption, the precipitation as found in the blank was not significant. At the end of the experiment, a net absorption of copper was found to vary from 20.5 %

to 82.5.4% with an increasing dose of nanocomposite. For, determination of adsorption isotherm, amount of copper adsorbed per unit mass of nanocomposite was plotted against the equilibrium Cu concentration.

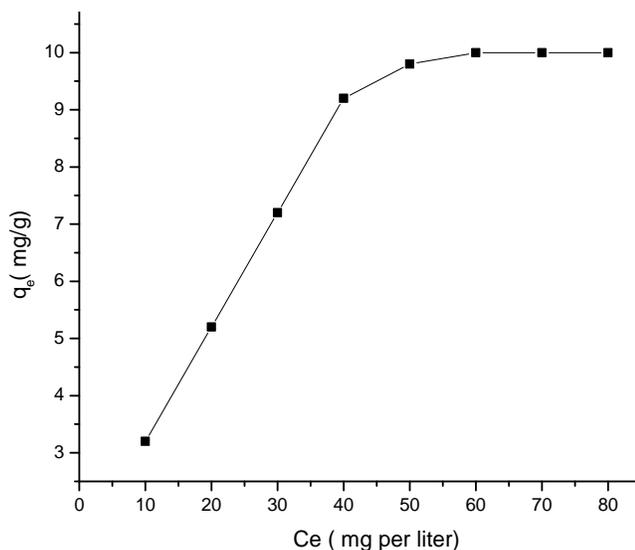


Fig. 7. Verification of Langmuir adsorption isotherm.

The graph shown **Fig. 7** indicates that upto certain value of C_e , q_e varied linearly and after that it became almost constant. It may be because Cu(II) ions interacts with Zn centers of nanocomposite due to difference in their electronegativity. According to the assumption of Langmuir model a plot of C_e (nanocomposite present per liter) versus q_e Cu(II) adsorbed per gram of nanocomposite should be a straight line with a slope $(1/b)$ and an intercept as $1/K_b$ for surface adsorption with homogenous sites and form a monolayer [40]. Thus, graph in **Fig. 7** reveals that initially Langmuir model was obeyed and at higher concentration the surface saturated and deviated from the model. Further, comparison of the results obtained from this study to the previously reported [41-43] about percentage removal of Cu(II) on various adsorbents and time of removal, it can be stated that our findings are comparatively well for effective copper decontamination.

Conclusion

Nano size zinc oxide nanoparticle has been prepared by heating zinc sulphate in nitrate eutectic melt. The prepared ZnO nanoparticle was encapsulated *in situ* in UF. The prepared ZnO-UF nanocomposite was used for efficient and cost effective removal of Cu^{2+} ions from the solution with 80 % copper removal capacity within 15 minutes. The significant adsorption of Cu(II) ion by ZnO-UF nanocomposite was found in the pH range of 6.6 to 7.0 and followed Langmuir-type adsorption isotherms. The study synchronizes the surface active sites of ZnO and stability UF resins to polymerization kinetics. The synergistic effect reveals its significance in nano technology to effectively monitor and remove heavy metal from water. From the perspective of nanocomposite utilization, effective copper (II) adsorption capacity of this low-cost adsorbent, made this potentially applicable for future practical applications. Owing to the properties of ZnO-UF nanocomposites, they

may play central role for the removal of other heavy metals. This study also proves the importance of UF and further open a new scenario for the application of UF as good stabilizer to develop the nanocomposites.

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