

Removal of Cu Metal ion from Contaminated Water by Guar Gum Nanocomposite



Vidhya Raj

Research Scholar,
Deptt. of Chemistry,
Government Science College,
Jabalpur, India

Abstract

Water pollution by heavy metals represents a serious problem around the world. Among various treatment techniques for water remediation, adsorption is an effective and versatile method due to the low cost, effectiveness and simplicity. Guar gum was hydrophobically modified by condensation with dimer acid by microwave irradiation. Hydrophobically modified guar gum Nanocomposite was used for adsorption for metal ion remediation. Products were characterized by FTIR spectroscopy; SEM images showed that morphological surface changes happen after Cu adsorption, Zetasizer, viscosity and XRD.

Keywords: Guar Gum, Dimer Acid, Nanocomposite, Hydrophobically Modified Guar Gum.

Introduction

International program on chemical safety by World Health Organization has listed heavy metals and other many metals (Cu^{2+} , Mn^{2+} , Cr^{2+} , Hg^{2+} , Zn^{2+} , Ni^{2+}) added to these are dangerous, hazardous and can cause a lot of inconvenience to the humanity, Heavy metal contamination represents a major problem around the world due to industrial waste waters discharged into natural water bodies (Fu & Wang, 2011). [1]

Review of Literature

Mining activities, agricultural runoff, industrial and domestic effluents are mainly responsible for the increase of the metals released into the environment. Contact with a higher amount of these pollutants can cause harmful effects on human health, such as abnormal urine, hypertension, staining of skin, abdominal pain, nausea, dizziness, asthma, itching, blurred vision and carcinogenic effects. [2] There are numerous methods currently employed to remove and recover the metals from our environment. These include chemical oxidation and reduction, membrane separation, liquid extraction, carbon adsorption, ion exchange, electrolytic treatment, electro precipitation, coagulation, flotation, evaporation, hydroxide and sulfide precipitation, crystallization, etc. Amongst these methods, adsorption is the most efficient technique for the removal of pollutants from wastewater (Forgacs, et al., 2004; Zhao, et al., 2015; Srivastava & Sillanpää, 2017). Adsorption is always used because its process is relatively simple, non-toxic and biodegradable properties combined to its high adsorption capacity of heavy metals makes this polysaccharide an excellent option to be used in treatment of polluted effluents. To our knowledge, the abundant reaction sites and functional groups on novel-nanomaterials surfaces have led them as typical adsorbents for efficiently removing heavy metal ions, and the possible mechanism could attribute to adsorption reaction. [3]

Recently, specific adsorbent is much developed; it contains ligands which interact specifically with metal ion derived from supporting solid modification from inorganic material (like silica) or polymer. [4] The results obtained demonstrate the ability of modified guar gum nanocomposite to remove Copper from water. [5] Adsorption properties and equilibrium data, commonly known as adsorption isotherms, describe how pollutants interact with adsorbent materials and so, are critical in optimizing the use of adsorbents. Then, it is important to establish the most appropriate correlation for the equilibrium curve. In this study, isotherms were used for fitting the experimental data: Langmuir equation, Freundlich model, Temkin model and D-K-R model. [6] The goal of this study were

Hydrophobically modified guar gum nanocomposite as a sorbent for Cu removal, Since this polysaccharide is abundant in nature and has a low cost of preparation, it has been selected as a possible biosorbent for Copper removal from contaminated water. [7,8]

Aim of the Study

Utilization of green chemistry for environmental pollution remediation renewable resource based guar gum and dimer acid (derived from castor oil) were processed by microwave synthesis to yield hydrophobically modified guar gum for remediation of Cu (II) from aqueous solution.

Experimental

Materials

Guar gum (GG), molecular weight 2.2×10^5 , was supplied by Agro gums, Ahmedabad, Gujarat, India. Dimer acid (DA) (composition: 98% dimer +2% trimer) was supplied by Jayant oil mills, Mumbai, India. *p*-toluenesulphonic acid (PTSA) and polyvinyl alcohol (PVA) molecular weight 1,25,000 were purchased from Research Lab Fine Chem. Industries, Mumbai, India. Dodecyl benzene sulphonic acid (DBSA) and other reagents were purchased from E. Merck, Mumbai, India. Deionized (DI) water from Millipore water purification system model Elix-3 was used in all the preparations and measurements. All the materials and reagents were used as received.

Methods

Synthesis of Hydrophobically modified guar gum (HMG)

The emulsion of Dimer acid 2.0 g in 10% NaOH (15 mL) was thoroughly mixed with of finely powdered guar gum 2.0 g and 4.0 g for sample coded as HMG, 0.008 g *p*-toluene sulphonic acid (PTSA) and 0.04 g dodecyl benzene sulphonic acid (DBSA). The homogenous reaction mixture thus obtained was irradiated in a domestic Kenstar microwave oven initially at power 60 four times for 30 sec each time, then for 1 min (thrice).

Preparation of Nanocomposite (HMGNC) from HMG

A domestic Microwave oven make Kenstar model no. OM25FCD (frequency 2450 MHz) was employed for the preparation of guar gum Nanocomposite. 1 g of condensation product Gel was mixed with 1g AAm, 0.2g MBA, 0.02 KPS and 0.5 FE in water to obtain slurry by stirring for 1 h, and then microwave irradiated. For optimization of reaction conditions varying amounts of reaction components were irradiated at different powers, time duration and cycles. The product samples were obtained as porous agglomerated solid mass, which were dried at room temperature.

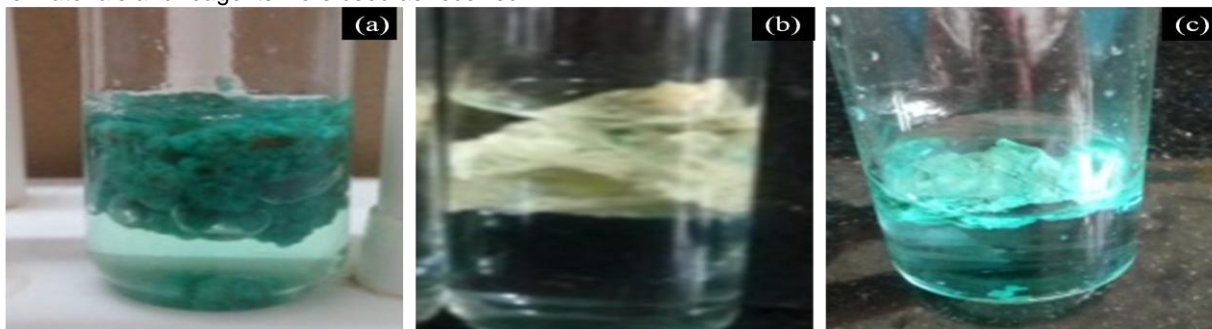


Fig.1. Cu adsorption images (a) HMGCu (b) HMGNC (c) HMGNCu

Characterization

Fourier transformation infra red (FTIR) spectra

The FTIR spectra of various samples were recorded on a SHIMADZU 8400-S FTIR

spectrophotometer in $4000-500 \text{ cm}^{-1}$ range as DRS in KBr dispersion.

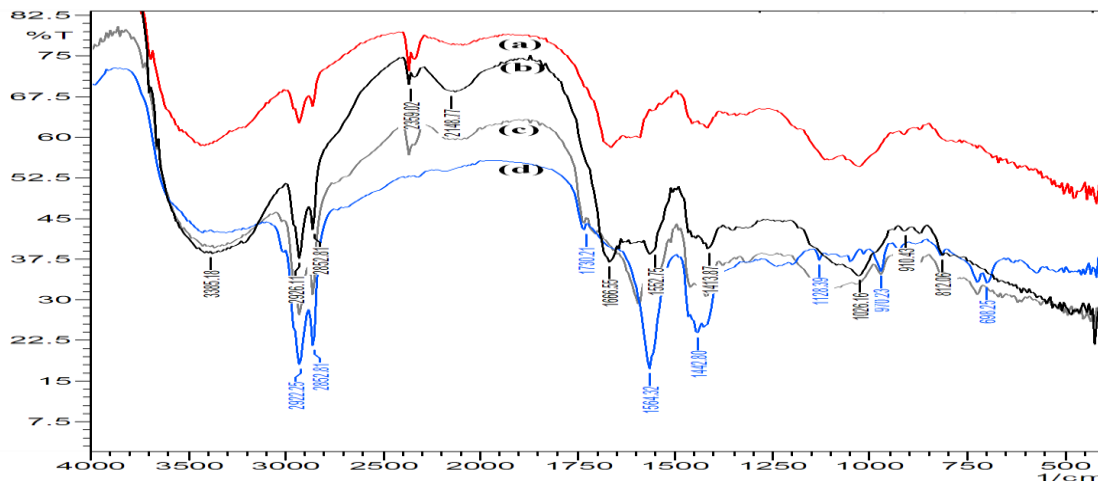


Fig.2. – FTIR spectra of (a) HMGNCu, (b) HMGNC, (c) HMG Cu (d) HMG

The comparison of FTIR spectra of HMGNC and Cu loaded HMGNCu sample are depicted in fig.2 it is infrared that ν OH intensity was increased in Cu loaded sample, thereby indicating by retaining water molecule also in the matrix. The FTIR spectroscopy is an important tool for identifying some characteristic functional groups, which can adsorb metal ions.

Particle size distribution measurement (DLS)

A sample solution of HMG with concentration of 1.0 % was prepared in Millipore water and the particle size was measured with a Malvern Instrument Zetasizer ZS90 by dynamic light scattering method. Particle size of HMG was found 135.6 d.nm. guar gum 1265 d.nm. and DA 210.7 and Zeta potential of condensation product were found 0.703 mV and guar gum -27.7 mV. So stability behaviour of the colloid is incipient instability.

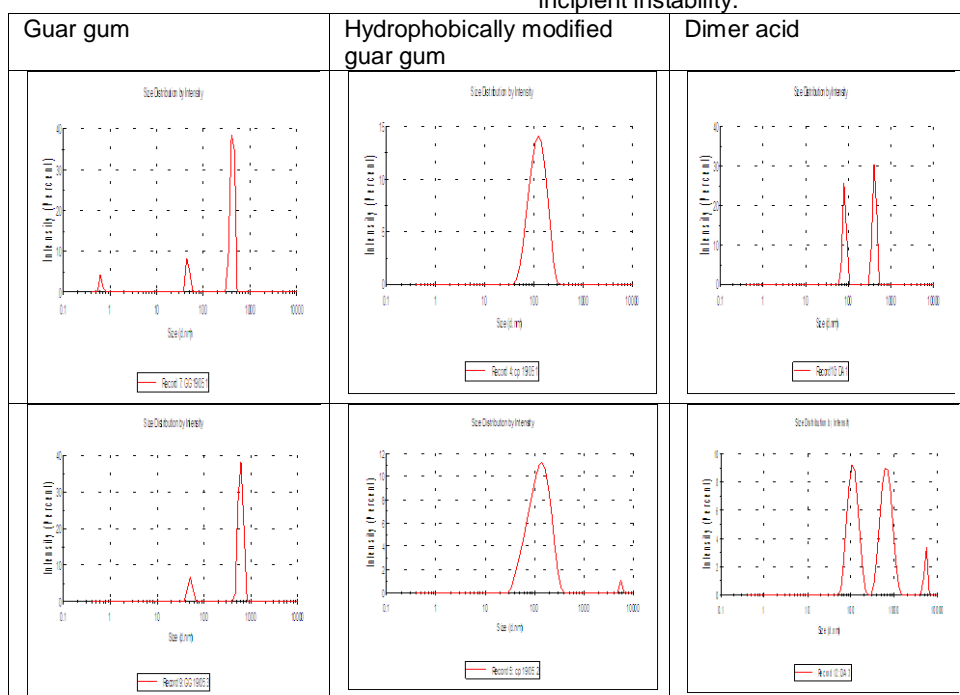


Fig.3. Particle Size Distribution Measurement

Powder X-ray diffraction (PXRD) studies

Wide-angle X-ray powder diffraction data were collected using a Rigaku Miniflex X-ray

diffractometer equipped with Cu K α radiation at 30 kV and 15 mA. Scattered radiation was detected in the range $2\theta = 3-80^\circ$, at a rate of $3^\circ/\text{min}$.

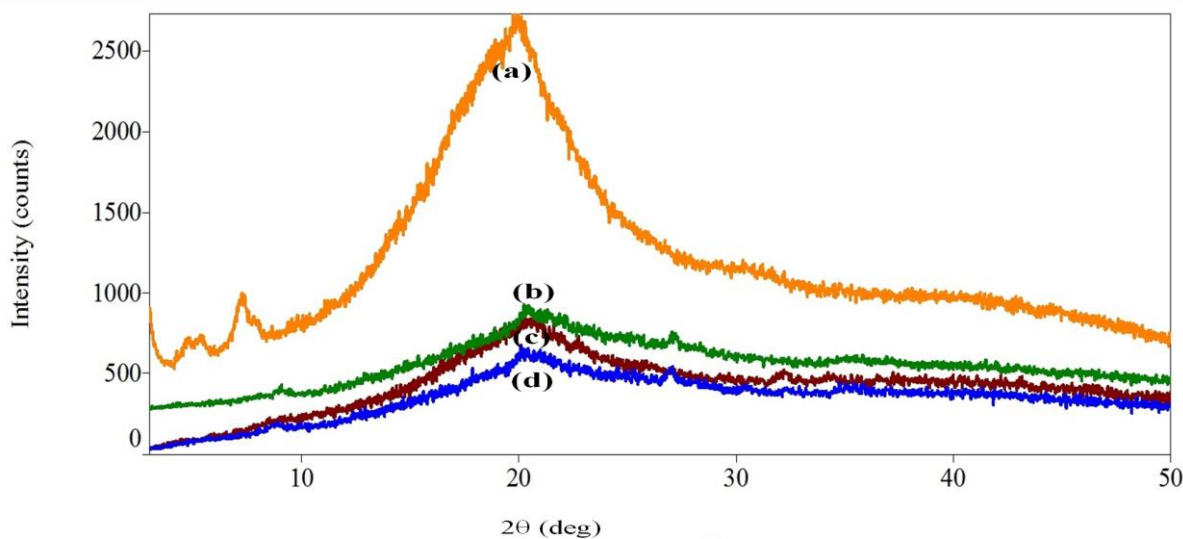


Fig.4. XRD Patterns of (a) HMG (b) HMGNC (c) HMG Cu (d) HMGNC Cu

Table – 1 Calculations of IC value

Sample code	2 theta	d(angle)	FWHM	FWHM (in radian)	0.9 λ	2 Θ/2	Θ in radian	dhkl
HMG	5.21	16.9	1.34	0.023316	0.1386	2.605	0.04548	2.27404
2	7.23	12.22	0.52	0.009048	0.1386	3.615	0.06312	4.22279
3	7.7	11.4	0.56	0.009744	0.1386	3.85	0.06722	3.68182
4	42.4	2.13	6.9	0.12006	0.1386	21.2	0.37016	0.05427
HMG Cu	44.53	2.033	18	0.3132	0.1386	22.265	0.38875	0.01981
HMGNC	44.2	2.047	15.6	0.27144	0.1386	22.1	0.38587	0.02302
HMGNC Cu	42.9	2.11	9	0.1566	0.1386	21.45	0.37452	0.04112

Table 2

Sample code	2 Theta (Crystalline)	Height	2 Theta (amorphous)	Height	Ic	Ic %
HMG	4.7678	725	5.0368	670	0.07586207	7.58621
2	5.3827	745	6.1128	620	0.16778523	16.7785
3	7.2657	1005	7.6885	815	0.18905473	18.9055
4	19.9092	2714	30.1316	1165	0.57074429	57.0744
HMGNC Cu	8.8724	192	9.2919	166	0.13541667	13.5417
2	20.5241	645	26.3966	440	0.31782946	31.7829
3	27.0025	538	27.7016	435	0.19144981	19.145
HMGNC	9.0123	166	9.758	123	0.25903614	25.9036
2	20.4309	663	26.35	423	0.36199095	36.1991
3	27.1423	497	28.1676	404	0.18712274	18.7123
HMGCu	20.5707	838	28.8667	464	0.44630072	44.6301
2	32.1758	511	32.7351	449	0.12133072	12.1331

The XRD graphs of the metal ion loaded samples (Fig.4) showed the Amorphous and crystalline peaks showing strong interaction with the adsorbent matrix.

The XRD pattern of nanocomposite is indicated the amorphous structure; few crystalline peaks corresponding to fullers' earth (FE) are appeared with decreased intensity, It was clearly seen in the XRD patterns of metal ion adsorbed nanocomposite that crystallinity is slightly increased specially with that of Cu(II). The distinct and complex peaks in XRD pattern of the metal loaded HMGNC indicated the deposition of crystallized metal ion which may correspond to metal hydroxides and metal carbonates

The calculated values of D_{hkl} , % Ic and d (nm) are shown in Table1 From the calculated d values it is clearly understood that the gallery spacing of clay platelets has been increased. It indicates the coordination of metal ion with functional groups on nanocomposite after entering the interior of the polymer matrix, destroys the regular arrangement of biopolymer chains.

Scanning Electron Microscopy (Sem)

The surface morphology of various samples was examined using Scanning electron microscopy (SEM) by Field Emission Gun Scanning Electron Microscope (FEGSEM) Make: FEI Ltd., Model: Nova Nano SEM 450) with an accelerating voltage of 20V to 30kV. The samples were coated with gold using

sputtering technique. The images were captured at various magnifications. SEM images revealed the morphological changes after metal sorption. Some distortions present on the surface offered the favourable conditions for metal ions retention between the interstices. After metal binding, the material exhibited flocculation of the swollen HMGNC. micro precipitation of metal ions on the adsorbent is apparent.

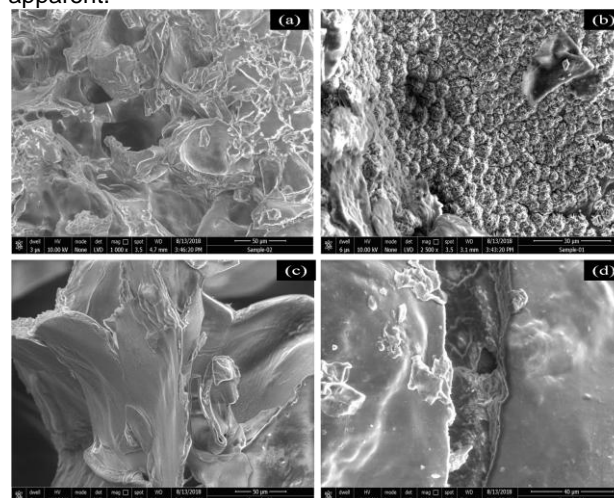


Fig.5. SEM images of HMG, HMGCU, HMGNC and HMGNCu

Isotherm Study

Sorption experiments

Preparation of adsorbate solution

Stock solution of Cu metal ion was prepared by dissolving required quantity of analytical grade salts in the DI water. The salts used are CuSO₄.5H₂O, in preparing stock solution. The stock solution was further diluted with DI water to desired concentration for obtaining the test solutions.

Adsorption of Metal Ion

Batch adsorption method was used in this study. Pre weighed samples of HMGNC were immersed in aqueous solution of metal ion taken in stoppered test tubes and were manually agitated intermittently. The extent of metal ion removal was investigated by changing adsorbent dose and concentration of the adsorbate solution. At appropriate time intervals, 5 mL of supernatant solution was separated by centrifugation and concentration of unadsorbed metal ions was determined by atomic absorption spectroscopy on a Shimadzu atomic absorption spectrophotometer AAS-6300. All the experiments were carried out thrice and the average of three values was used in the analysis of data

Adsorption Isotherms

Adsorption isotherm studies were carried out at temperature 296 K. The effect of the metal ions concentration on the adsorption capacity was also studied. 0.02 g of nanocomposite was contacted with 20 mL of known initial concentration of aqueous metal ion solution and the amount of adsorbed metal ions was calculated by the following equation:

$$q_e = \frac{C_0 - C_e}{W} \times V$$

Where q_e is the amount of metal ion adsorbed onto unit amount of the HMGNC (mg g^{-1}); C_0 and C_e are the concentrations (mg L^{-1}) of metal ion in the initial solution and in the aqueous phase after adsorption, respectively; V (mL) is the volume of the aqueous phase, and W (g) is the weight of HMGNC.

The adsorption isotherms reveal the specific relation between the concentration of the adsorbate and its adsorption degree onto adsorbent surface at a constant temperature. The adsorption capacity of HMGNC for the removal of metal ions from aqueous solution was quantified using the Langmuir, Freundlich, Temkin and Dubinin-Kaganer-Radushkevich (D-K-R) isotherm models.

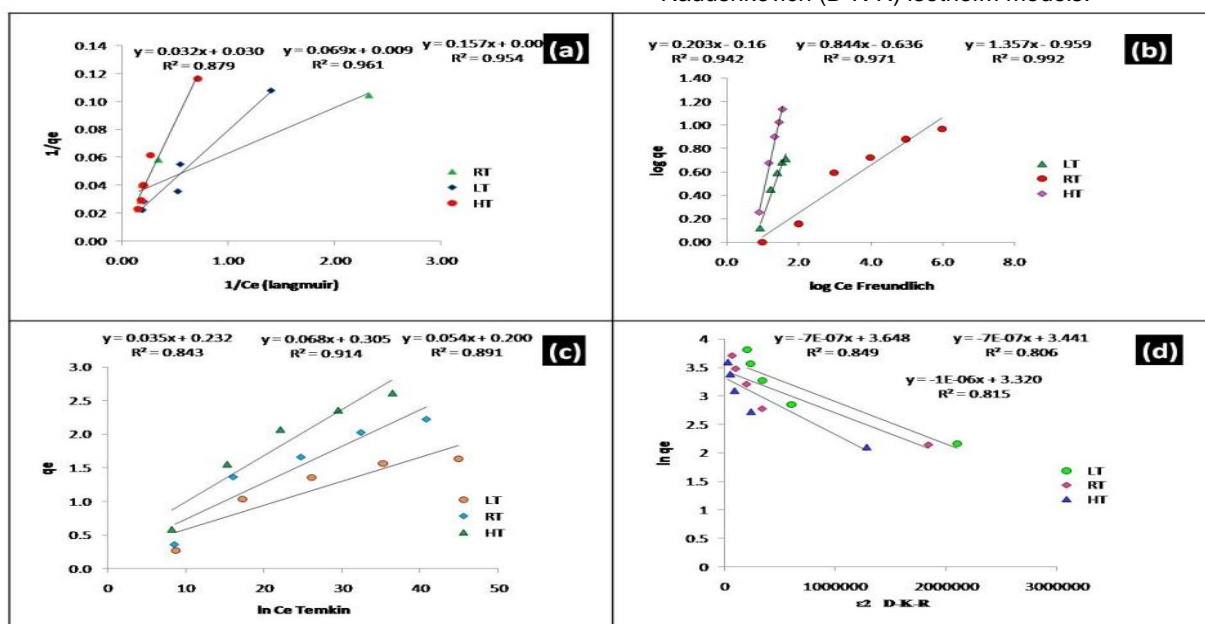


Fig.6. - Adsorption isotherms for Cu metal ion (a) Langmuir (b) Freundlich (c) Temkin (d) Dubinin -Kaganer-Raduskevich

Table 3- % Removal of Cu(II) from guar gum nanocomposite

S.No.	Initial concentration	% Removal of Cu(II)		
		18 °C	28 °C	38 °C
1.	10	86.9	85.7	82.0
2.	20	85.9	80.5	76.4
3.	30	87.0	82.5	73.6
4.	40	88.0	81.1	73.6
5.	50	89.8	81.6	72.8

Langmuir Model

This model assumes that the adsorptions occur at specific homogeneous sites on the adsorbent and is used successfully in many monolayer adsorption processes. Following is the linearized form of Langmuir equation:

$$C_e / q_e = (1 / q_{\max} \cdot K_L) + (C_e / q_{\max})$$

Where, q_e (mg/g) is the adsorption capacity at equilibrium; C_e (mg/L) is the concentration of metal ions at equilibrium and q_m (mg/g) is the monolayer

adsorption capacity of the adsorbent (mg/g). K_L (L/mg) is the Langmuir constant related to the free energy of adsorption or affinity of the binding sites. A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L , also known as the separation factor, given by

$$R_L = 1 / [1 + q_m (C_0)]$$

While $R_L > 1$ represents unfavourable adsorption, and $R_L = 1$ represents linear adsorption while the adsorption process is irreversible if $R_L = 0$. The value of R_L lies between 0 and 1 for favourable adsorption. Values of q_m and K_L were calculated by plotting graph between $1/q_e$ and $1/C_e$ (Fig. 3, the high values of correlation coefficient ($R^2 = 0.954-0.961$) indicate a good agreement between the parameters and confirms the monolayer adsorption of metal ions on to HMGNC surface. The dimensionless parameter R_L is between 0.046 and 0.24 of metal ion consistent with the requirement for a favourable adsorption process. The relevant graphs and values of various parameters are shown in Fig.3 and Table1 respectively.

Freundlich Model

The Freundlich isotherm is based on assumption that adsorption is on a heterogeneous surface by multilayer adsorption and exponential distribution of sites and their energies, which can be expressed by the following equation:

$$q_e = K_F C_e^{1/n}$$

or the logarithmic form of linearized Freundlich equation:

$$\ln q_e = \ln K_F + (1/n) \ln C_e$$

K_F and n are the Freundlich adsorption isotherm constants, being indicative of adsorption capacity and the adsorption intensity (or degree of nonlinearity), respectively. The n value of Freundlich equation gives an indication of the favourability of sorption. It is generally stated that value of n in the range of 2–10 is good, 1–2 as moderately difficult and less than 1 as poor sorption feature. Values of different Freundlich constants i.e. K_F and n were calculated from intercept and slope between $\log q_e$ and $\log C_e$. The values of K_F were calculated 4.32, 1.44 and 9.09 (mg/g) (L/mg)^{1/n} and those of n were calculated to be 1.18, 4.92 and 0.736. Values of n are in the range of moderately difficult which is in agreement with the inference drawn from swelling behaviour that the HMGNC matrix expands slowly to provide space for the solvent molecules. Hence, a heterogeneous surface for multilayer adsorption with exponential distribution of sites becomes available only gradually.

The linear correlation coefficients of the Freundlich model are 0.971, 0.942 and 0.992 which are lesser than those for Langmuir model. This indicated that the adsorption of the nanocomposite for metal ion can be better explained by the Langmuir model than by the Freundlich model.

3.5.7 Temkin Model

This isotherm is based on the assumption that the surface of adsorbent is heterogenous with

active sites having uniform binding energies and heat of adsorption of all the molecules in layer decreases linearly because of the adsorbate-adsorbent interaction.

$$q_e = B \ln A_T + B \ln C_e$$

B is constant related to heat of adsorption ($B = RT/b_T$, where $R =$ universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), $T =$ temperature (K) and $b_T =$ Temkin isotherm constant). A_T is Temkin isotherm equilibrium binding constant (L/g) equilibrium binding constant (L/g) related to maximum binding energy. Value of B and A_T obtained from slope and intercept of the plot of q_e and $\ln C_e$. Value of $R^2 = 0.914$ were showing good agreement between all the parameters which suggested that Temkin adsorption isotherm model is also applicable for the adsorption of metal ion onto adsorbent. B represents the value of initial heat of adsorption, high value of B indicated great affinity of adsorbate for the adsorbent.

Dubinin-Kaganer-Radhuskevich (DKR) model

Dubinin-Kaganer-Radhuskevich (DKR) adsorption isotherm is used to predict the nature of adsorption process, i.e. whether the adsorption process is chemical or physical process. It also gives idea about characteristic porosity of adsorbent and apparent energy of adsorption process. Linearized form of the DKR model is given below:

$$\ln q_e = \ln q_s - \beta \varepsilon^2 \quad \dots (1.6)$$

Where, $q_e =$ amount of adsorbate in the adsorbent at equilibrium (mg/g); $q_s =$ theoretical isotherm saturation capacity (mg/g); $\beta =$ activity coefficient related to mean adsorption energy (mol^2/J^2) and $\varepsilon =$ Polayni potential ($\text{kJ}^2 \text{ mol}^2$), calculated by equation:

$$\varepsilon = RT \times \ln(1 + 1/C_e) \quad \dots (1.7)$$

Slope and intercept of the plot between $\ln q_e$ and ε^2 gives value of q_s and β . The approach was usually applied to distinguish the physical and chemical adsorption of metal ion with its mean free energy, E per molecule of adsorbate (for removing a molecule from its location in the sorption space to the infinity), which can be computed by the relationship

$$E = 1 / \sqrt{-2\beta}$$

The adsorption potential is independent of the temperature, but it depends upon the nature of the adsorbent and adsorbate. E provides information about the nature of adsorption either chemical ion exchange or physical adsorption. The values of E between 8 and 16 kJ/mol indicate the chemical ion exchange as the adsorption process and if $E < 8$ kJ/mol, the adsorption process is of a physical nature. However, R^2 values were lowest for D-K-R model indicating poor correspondence.

Conclusions

Nanocomposite prepared from Guar gum, Natural polymer biodegradable, non toxic. The results of equilibrium adsorption were evaluated by three isotherm adsorption models and experimental data fitted very well to the Langmuir model. Three kinetic models were used to model the kinetics of adsorption. Though, natural materials used in this preparation are susceptible to fungal growth under wet condition

within a week, the nanocomposites did not show such growth even in a month. Langmuir isotherm model described very well the experimental data, with high correlation coefficients. Adsorbed Cu metal ions indicated HMGNC to be a very versatile material for metal ion remediation from the polluted water.

Footnotes

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