

Removal of Heavy Metals from Wastewater by Adsorption on Polyamidoaminodendrimers Immobilized over Titania

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Abstract: Generation 4 polyamidoamine (PAMAM) dendrimers with ethylenediamine cores (G4-OH) were immobilized on titania (TiO₂) and examined as novel metal chelation materials. Characterization results indicate both the effective immobilization of dendrimers onto titania and retention of the dendrimer on titania following remediation. The effective remediation of Cu(II), Ni(II) and Cr(III), which is model pollutants commonly found in industrial electroplating wastewater, is demonstrated in this work. Important parameters that influence the efficiency of metal ion removal were investigated; e.g. solution pH, retention time, metal ion concentration and composite material dosage. Removal was achieved over a wide metal concentration range within a 1 hr equilibration time. Maximum metal ion removal was achieved at pH ≥ 7 for both Cu(II) and Cr(III) and pH ≥ 9 for Ni(II). Further, the dendrimer/titania composite materials were even more effective when metal ion mixtures were tested. Specifically, a dramatic increase was observed for Ni(II) chelation when in a mixture was compared to a pure nickel solution. These findings suggest new strategies for improving metal ion removal from industrial wastewater.

Key words: Heavy metals • Pollution • Wastewater • Remediation • Organic-Inorganic Composite

INTRODUCTION

Dendrimers, hyperbranched molecules composed of monomers that radiate from a central core, are emerging as an important class of polymers. The structure of these materials has a great impact on their physical and chemical properties. As a result of their unique behavior, dendrimers are suitable for a wide range of applications including environmental remediation, nanoparticle synthesis and nanomedicine [1-3]. Perhaps the most studied are polyamidoamine (PAMAM) dendrimers, which are among the least toxic and are made from inexpensive, readily available materials [4, 5].

Initial efforts in the application of PAMAM dendrimers focused on early generations [1-3], which have flat ellipsoidal shapes. However, higher generation

dendrimers (4 and up) are starburst shaped and are particularly appealing for modern applications. PAMAM dendrimers' key property is their ability to chelate metal ions from solutions. This attribute has primarily been exploited in the synthesis of metal nanoparticles [6-9], however recently dendrimer-based chelation has gained interest. For example, metal-intoxication is a serious environmental concern as they are both toxic and carcinogenic, even at relatively low concentrations [10-13].

A major source of heavy metal introduction into the environment is attributed to industrial processes including automobile emissions, mining activities, battery manufacturing, fossil fuels [14], metal plating and electronic industries [15]. Various removal methods such as membrane processes (dialysis, electrodialysis, reverse

osmosis, etc.), neutralization-precipitation, extraction and ion exchange are useful [16, 17]. However, development of more economical alternatives remains a major goal, which is achieved in the present study through the synthesis of composite materials. Chelation is therefore well placed as a low cost and environmentally friendly technique that has the potential to overcome limitations seen other removal strategies [18-22].

Polymers, activated carbon, metal oxides, silica and ion exchange resins have been used in chelation process [20, 23-28]. High surface area materials, including those just discussed are appealing for separation applications [29]. Hydroxyl and amine-terminated PAMAM dendrimers are, perhaps, the most appropriate for metal complexation applications [30, 31]. PAMAM with OH terminal groups are both cost effective and nontoxic due to a lack of surface amines [32]. Encapsulation of metal ions by generation 4 hydroxyl-terminated PAMAM (G4-OH) involves coordinating each metal ion with one of the dendrimer's 62 tertiary amine sites [33].

In the current study, G4-OH PAMAM dendrimers were immobilized over titania to study the chelation and removal of Cu(II), Ni(II) and Cr(III) from synthetic solutions as models for wastewater produced by the electroplating industry. Titania was selected for the initial effort of making organic-inorganic hybrid materials for several reasons including its mechanical strength and its use already in wastewater treatment as photocatalysts for organics. Since it is already used in other wastewater treatment procedures, titania does not increase the danger by accidental release and the integration of multiple remediation processes in a single unit may be made easier. An extension of the current work would be to evaluate the role of titania as compared to other carriers such as silica and zirconia (in a separate work). The immobilization and retention of the dendrimer to the titania will be demonstrated. Critical parameters that influence metal ion removal including pH, batch retention time, metal ion concentration and material dosage have been examined.

MATERIALS AND METHODS

PAMAM-OH dendrimer, generation 4 solution (G4-OH) were purchased from Sigma-Aldrich (through Dendritech®, Inc. in Midland, MI) as a 10% (mass) solution with methanol as the solvent and used without further purification. This dendrimer is 4.5 nm in diameter and has an ethylenediamine core (2-carbon core) with

64 external hydroxyl functional groups. Its overall formula is given by $C_{622}H_{1184}N_{186}O_{188}$, which results in a molecular weight of 14277.19 g/mol.

Titanium (IV) dioxide or titania (rutile, 99.5% purity, 1 to 2 micron particle size) was purchased from Alfa-Aesar. Standard metal solutions of Cu(II), Ni(II) and Cr(III) with metal concentration of 1000 mg/L were used as metal precursors from nitrate salts. All other reagents were of analytical grade and supplied by Sigma-Aldrich or Merck.

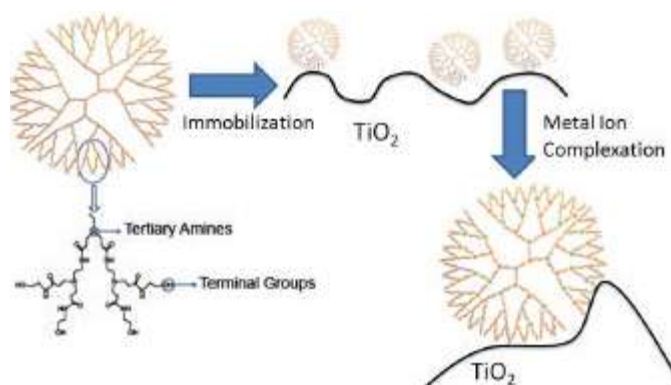
Synthesis and Characterization of TiO₂ Immobilized Dendrimers: The as-received G4-OH dendrimer-methanol solution (1 g) was diluted in a large excess of deionized water. Titania oxide was slowly added to the dendrimer containing aqueous solution to arrive at a slurry mixture. Once all of the titania was added, the dendrimer solution to titania ratio by mass was 1:99. After sonication (VWR ultrasonic cleaner, 135 W, 42 kHz) for 2 hours, the composite material was dried with heating on a hot plate (T = 60°C) to remove the solvent and then in a drying oven (T = 90°C) to remove all excess moisture.

Infrared (FTIR) spectra were acquired with a Perkin Elmer Spectrum 100 FTIR Spectrometer. Air was used for background subtraction. Nitrogen physisorption was performed on a Quantachrome Autosorb I. The specific surface area determined using the standard BET analysis of the adsorption isotherm. Samples were characterized using a Philips PANalytical X-Pert Pro X-ray diffractometer equipped with a Cu K alpha source.

Batch Remediation experiments: Removal of heavy metal ions, Cu(II), Ni(II) and Cr(III), was carried out in 500 mL conical flask with magnetic stirrer by combining an appropriate amount of metal ions and the dendrimer/titania adsorbent. The pH of the aqueous solutions was monitored from 3 to 11 using an Orion pH meter (model 801A) and adjusted as needed with 1 M HCl or 1 M NaOH. Experiments were carried out for 120 minutes. Solutions were filtered after the experiments and metal ion concentrations were analyzed with an Inductive Coupled Plasma (ICP) instrument. The remediated amount was monitored as a function of time by removing 10 ml aliquot of solution for the ICP measurements. Efficiency of metal ion removal was calculated with the following equation:

$$\% \text{ Efficiency of metal removal} = (C_0 - C) / C_0 \times 100 \quad (1)$$

where C_0 is the initial metal ion concentration and C is the retained metal ion concentration.



Scheme 1: The synthesis strategy to immobilize G4-OH dendrimers on titania to achieve dendrimer/titania composites and their use for metal ion separations.

RESULTS AND DISCUSSION

Synthesis and Characterization of Dendrimer/titania Composites:

As shown in Scheme 1, G4-OH dendrimers were immobilized on titania in a slurry process. The presence of the dendrimer in the freshly prepared composite is verified by FTIR (Figure 1). The spectral features do not significantly change following the application of the composite materials as remediation agents for Cu, Cr and Ni. This finding indicated that the dendrimer does not leak into the water during testing. The bands associated to the various functionalities of the dendrimer were analyzed using identification existing in the literature [34-36]. The bands at 2972, 2921 and 2849 cm^{-1} correspond to asymmetric C-H methyl stretching, asymmetric C-H methylene stretching and symmetric C-H methylene stretching. The bands at 1648, 1546 and 1279 cm^{-1} indicate amide functionality through amide C=O stretching, amide C-N stretching and amide C-N-H bending/closing and amide C-N-H bending/opening respectively. The bands at 1459, 1428 and 1349 cm^{-1} associate, respectively, to H-C-H scissoring, H-C-H asymmetric deformation and H-C-H rocking, wagging and twisting. In addition to the vibrational signatures of the dendrimer, evidence of chemical linking of the organic dendrimer to the titania exists. The bands at 1092 and 1046 cm^{-1} correspond to Ti-O-C bonds [37]. The existence of these bands suggests a chemical interaction between the dendrimer and titania. Moreover, electrostatic interactions and hydrogen bonding may also be possible for dendrimer adsorption onto titania.

First, the isoelectric point (point of zero charge) of titania is near 5 and the loading process is performed in a solution with pH of 7. At this pH, PAMAM

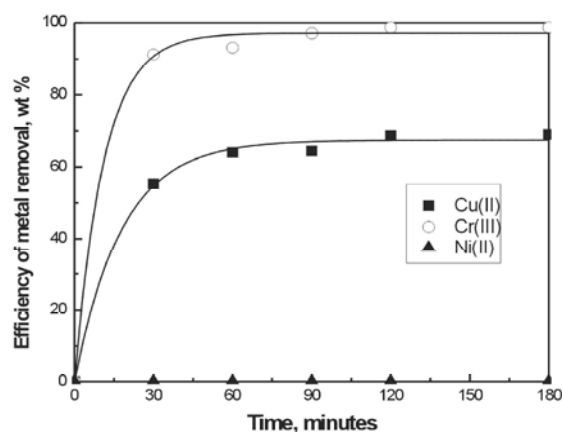


Fig. 2: Precipitation of Cu(II), Cr(III), or Ni (II) ions from aqueous solutions (independently) at pH 7. Conditions: Concentrations (for each metal ion) = 50 mg/L and temperature = 25°C.

dendrimers are positively charged, while the surface of titania is negatively charged. Therefore, strong electrostatic interactions existed between the dendrimer and titania. Second, PAMAM dendrimers are terminated with 64 hydroxyl groups, which could form multiple hydrogen bonds with hydroxyl groups on the surface of titania in water.

The pore properties and specific surface areas of the titania were measured before and after dendrimer immobilization. As expected, the titania and the dendrimer/titania composite yielded similar results. The BET surface areas were 2.7 m^2/g . The pore diameters and volumes were 2.8 nm and $8 \times 10^{-3} \text{cm}^3/\text{g}$, respectively. The structure of titania was also confirmed with a diffraction pattern of the rutile phase obtained. The (110), (101), (200), (111), (211), (220) and (310) Miller indices were observed.

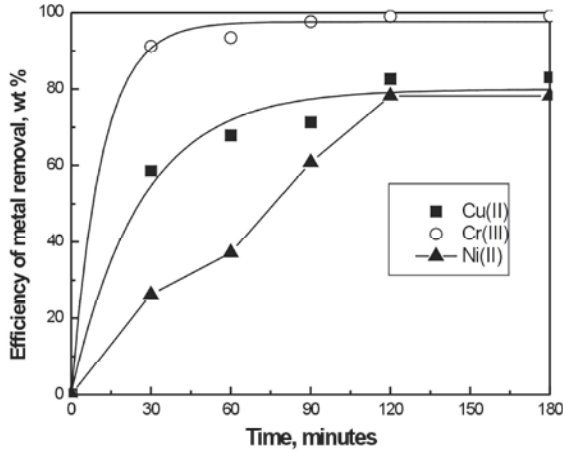


Fig. 3: Precipitation of Cu(II),Cr(III), or Ni (II) ions from aqueous solutions (independently) at pH 9. Conditions: Concentrations (for each metal ion) = 50 mg/L and temperature= 25°C.

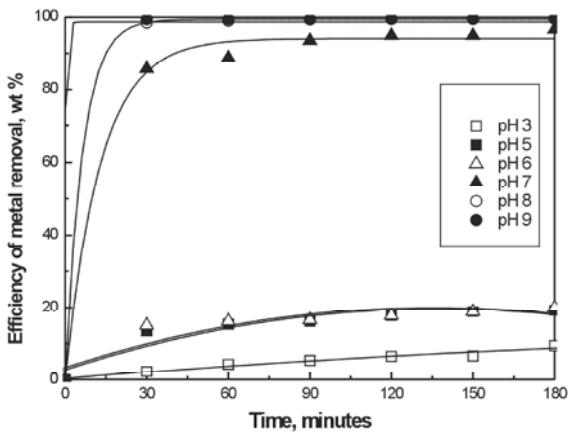


Fig. 4: Effect of pH on the Cu(II) ions removal from aqueous solution by dendrimer/titania composites. Conditions: Concentration of Cu(II) ions= 50 mg/L, dendrimer dosage = 1g/L and temperature=25°C.

Efficiency of Dendrimer/titania Composites for Metal Ion Removal from Wastewater: The effect of pH on the removal of Cu(II), Cr(III) and Ni (II) ions (independently) from aqueous solution by precipitation (in absence of the dendrimers) at pH 7 and 9, respectively, is shown in Figures 2 and 3. Removal of Cr(III) ions by precipitation was very high as indicated by a removal efficiency of 99% after 90 minutes with both pH values of 7 and 9. In contrast, removal of Cu(II) ions by precipitation gradually increased with both increasing time and pH and reached a maximum removal efficiency of 64 and 78% at pH values of 7 and 9, respectively, after 3 hours. Removal of Ni(II) ions by precipitation occurred only

Table 1: Solubility Product Constants (K_{sp}) at T = 25°C

Substance	Formula	K_{sp}
Chromium (III) hydroxide	$Cr(OH)_3$	6.3×10^{-31}
Copper (II) hydroxide	$Cu(OH)_2$	2.2×10^{-20}
Nickel (II) hydroxide	$Ni(OH)_2$	2.0×10^{-15}

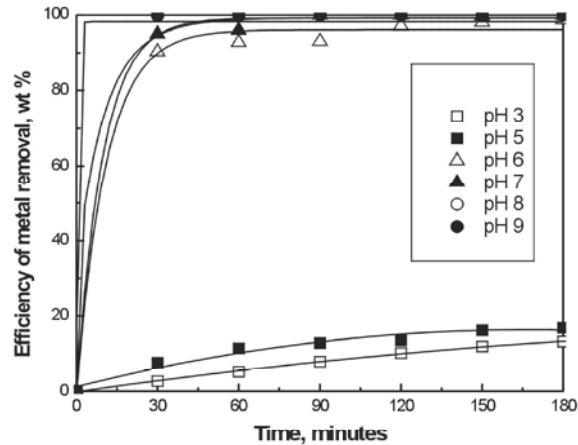


Fig. 5: Effect of pH on Cr(III) ions removal from aqueous solution by dendrimer/titania composites. Conditions: Concentration of Cr (III) ions = 50 mg/L, dendrimer dosage = 1g/L and temperature=25°C.

at pH 9 (no precipitation was observed at pH 7). The precipitation gradually increased with increasing time reaching the maximum removal efficiency of 76% after 3 hours. The different precipitation behavior is attributed to the difference in the solubility product constants (K_{sp}) of their hydroxide in solution in the order $Cr(III) < Cu(II) < Ni(II)$. For example, the precipitation of $Ni(OH)_2$ is relatively difficult, compared to the other two metal hydroxides, due to its higher K_{sp} value [38] (Table 1).

As with pure precipitation, the removal of metal ions with dendrimer/titania composites is highly dependent on the pH of the solution. This dependency results because pH can affect the surface charge of the adsorbent and the degree of ionization of the adsorbate [39]. The effect of pH on the removal of Cu(II), Cr(III) and Ni (II) ions on dendrimer/titania composites is illustrated in Figures 4-6, respectively. Metal ion removal increased with increasing pH reaching maximum values after shorter time (1 hour) compared to precipitation. At pH 7, the removal efficiencies were 96.6, 99.9 and 29.7% for Cu(II), Cr(III) and Ni (II), respectively. Raising the pH to 9 resulted in a slight increase in Cu(II) removal to 99.6% and a drastic increase in Ni(II) removal to 99.8%. On comparing these results with that of precipitation (Figures 2 and 3), the dendrimer/titania composites had little effect on Cr(III)

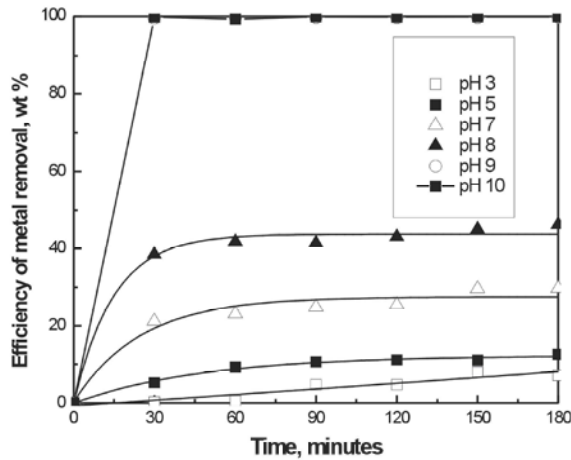


Fig. 6: Effect of pH on the Ni(II) ions removal from aqueous solution by dendrimer/titania composites. Conditions: Concentration of Ni (II) ions = 50 mg/L, dendrimer dosage = 1g/L and temperature=25°C.

removal as it is already precipitated easily due to its low K_{sp} value. On the other hand, the dendrimer/titania composites improved the Cu(II) removal from 64% to 96.6% at pH 7 and from 78% to 99.6% at pH 9. A very significant increase in the removal efficiency of Ni(II) was achieved with the dendrimer/titania composites compared to precipitation (from zero to 29.7% at pH 7 and from 76 to 99.8% at pH 9 with shorter time). The dendrimers aid in removal because tertiary amines are able to efficiently complex metal ions from aqueous solutions [33,40, 41].

The effect of metal ion concentration on their removal from solutions by dendrimer/titania composites is presented in Figure 7. With low initial metal ion concentration (10 mg/L), almost complete removal was achieved for all three metals. Dendrimer/titania composites operated efficiently over a wide concentration range for both Cu(II) and Cr(III) ions. However, with Ni(II), the removal decreased gradually with an increase of Ni (II) ion concentration; removal efficiency was 87.9% with a Ni (II) concentration of 800 mg/L. This observation is due to the differential affinity of dendrimers towards certain metals. According to the Irving–Williams series, which ranks divalent metal ions by their tendency to complex regardless of the nature of the complexing agent, cations were ranked as follows: Cu(II) > Zn(II) > Pb(II) > Ni(II) {Petrov and Nenov (2004)}. Current results correlate with this proposed relationship as Cu (II) was easier to complex than Ni (II).

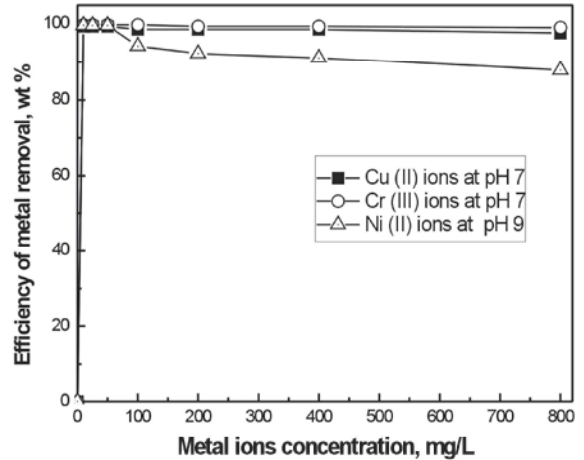


Fig. 7: Effect of metal ion concentration on their removal from solutions by dendrimer/titania composites. Conditions: Dendrimer dosage = 1g/L, time = 1h and temperature=25°C.

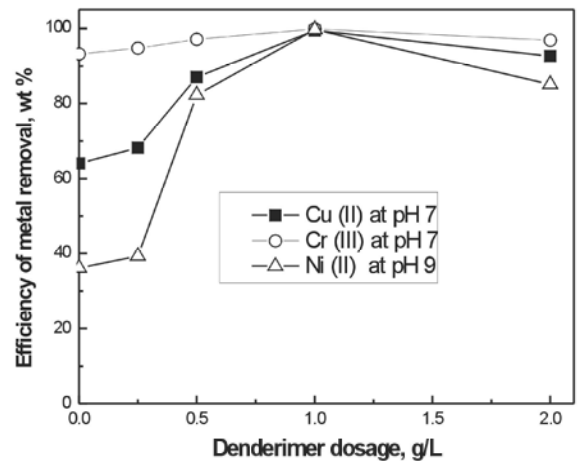


Fig. 8: Effect of dendrimer/titania composite dosage on the metals ion removal. Conditions: Concentration of metal ions = 50 mg/L, time = 1h and temperature=25°C.

The effect of dendrimer/titania dosage on metal ion removal is illustrated in Figure 8. The effect of increased dosage on Cr (III) was negligible as precipitation is a strongly competing process, however, Cu(II) and Ni(II) ion removal efficiency increased with increasing dosage. This trend is expected due to an increase in the number of complexation sites. The removal efficiency reached maximum values of 99.6 and 99.2% for Cu(II) and Ni(II) ions, respectively, after 1 hour with a dosage of 1 g/L.

The simultaneous removal of Cu(II), Cr(III) and Ni (II) ions from solution by dendrimer/titania composites at pH 7 is shown in Figures 9. The existence of the three metal

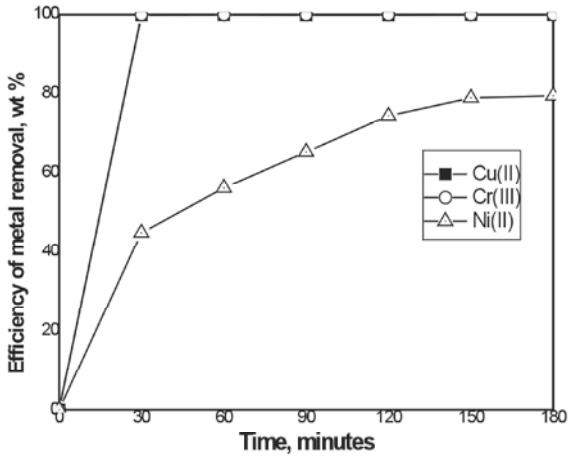


Fig. 9: Removal of Cu(II),Cr(III) and Ni (II) ions mixture simultaneously from aqueous solution by dendrimer/titania composites at pH = 7. Conditions: Concentration of metal ions = 50 mg/L,dendrimer dosage = 1 g/L and temperature=25°C.

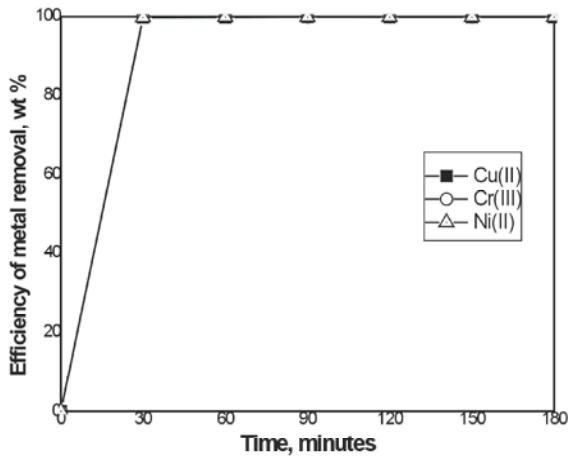


Fig. 10: Removal of Cu(II),Cr(III) and Ni (II) ions mixture simultaneously from aqueous solution by dendrimer/titania composites at pH = 9. Conditions: Concentration of metal ions = 50 mg/L,dendrimer dosage = 1 g/L and temperature=25°C.

ions in a mixture greatly enhanced the removal efficiency with shorter time particularly for Ni(II), which reached a removal efficiency of 56% after 1hour (compared to 29.7% in the individual solution of Ni) and a maximum of 79.4% after 3 hours. Complete removal of the three metals ions by the dendrimers, was achieved after 30 minutes at pH = 7 for both for Cu(II) and Cr(III) and pH 9 for Ni (II) ions (Figure 10). The better removal efficiency for Ni(II)

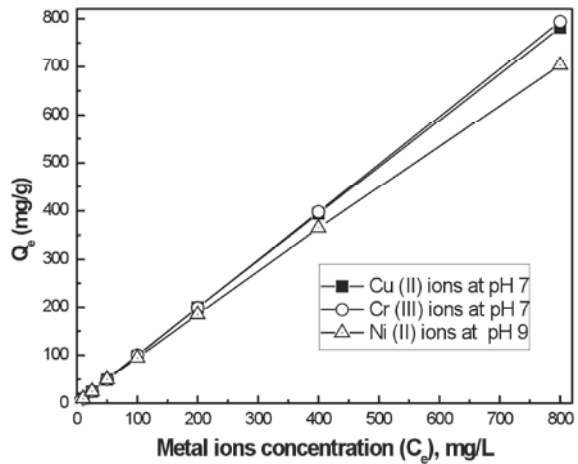


Fig. 11: Langmuir isotherm for removal of Cu(II),Cr(III),Ni (II) ions from solutions bydendrimer/titania composites. Conditions: Dendrimer dosage = 1 g/L, time = 1h and temperature=25°C.

ions in the simultaneous solution may be attributed to the improvement of association and growth of the Ni complexes in the presence of Cu (II) and Cr (III) ions in a single solution [42].

The adsorption isotherm can be used to describe how solutes interact with adsorbent. Langmuir isotherm is one of the most common models to represent the adsorption of components from liquid phase onto solid phase. The Langmuir isotherm is represented as follows;

$$Q = k_{ads} C_e / (1 + K_{ads} C_e) \quad (2)$$

where Q is the amount of metal ions adsorbed per gram of adsorbent (mg/g), C_e is the metal ions concentration at equilibrium (mg/L). Langmuir isotherm for removal of Cu(II),Cr(III),Ni (II) ions from solutions by adsorption on thedendrimer/titania composites had been applied for this study (Figure 11). The sorption of metal ions was carried out at different metal ions concentration ranging from 10 to 800 mg/L on 1g/L dendrimers dosage, with the optimum time (1 hour) and pH value for each metal ion (pH 7 for Cu(II)) and Cr(III) ions and pH 9 for Ni(II) ions). It can be seen that, Langmuir model fits well the experimental data ,the linear plots indicates the high affinity of the dendrimers towards all the three metal ions.

CONCLUSIONS

Remediation of Cu(II), Cr(III) and Ni (II) ions from synthetic wastewater solutions was successfully achieved using Generation 4 polyamidoamine dendrimers (G4-OH) immobilized on titania. Using these composite materials, the metal ion removal rate increased when compared to precipitation and occurred over a wide concentration range (up to 800 mg/L for each of the three metals) within an equilibration time of 1 hr. Whereas Cu (II) and Cr (III) were easily removed, Ni (II) proved difficult, which was expected due to its stability in a basic solutions. When solutions of multiple metal ions were mixed, an increase in removal efficiency and decrease in the time were observed. This interesting synergistic effect suggests new strategies to improve wastewater processing. Langmuir isotherm model fits well the adsorption experimental data. The mechanistic aspects of remediation and material regeneration are currently the focus of ongoing investigations.

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