Novel NS Modified Cellulose: Synthesis, Spectroscopic Characterization and Adsorption Studies of Cu2+, Hg2+ and Pb2+ From Environmental Water Samples

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Novel NS modified cellulose: synthesis, spectroscopic characterization and adsorption studies of Cu^{2+}, Hg^{2+} and Pb^{2+} from environmental water samples

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Abstract

In this work, an attempt was made to modify natural cellulose powder via three steps process; oxidation by potassium periodate followed by condensation with aminoguanidine and eventually reaction with phenyl isothiocyanate. The modified cellulose (PhGu-MC) was characterized by several techniques including Fourier transform infrared spectra (FTIR), scanning electron microscope (SEM), and elemental analysis (EA), Brunauer–Emmett–Teller analysis (BET) and thermogravimetric analysis (TGA). The modified cellulose (PhGu-MC) was used as an adsorbent for Cu^{2+}, Hg^{2+} and Pb^{2+} from aqueous solution and environmental water samples. Effects of various factors on the adsorption efficiency were investigated including pH, initial metal concentration, contact time, adsorbent dose, temperature and interfering ions on adsorption was investigated to estimate the optimum adsorption conditions. At optimum adsorption conditions, the adsorption capacities of Cu^{2+}, Hg^{2+} and Pb^{2+} were found to be 50, 94 and 55 mg.g^{-1}, respectively. The adsorption process was, well described by the Langmuir model, and it was found to follow the pseudo-second-order kinetic model. The synthesized (PhGu-MC) has revealed significant potential towards heavy metal removal from environmental water samples.

Key words: NS ligands, cellulose, aminoguanidine , phenyl isothiocyanate **, adsorption ,** Cu^{2+}, Hg^{2+} and Pb^{2+}

1. Introduction

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Clean and safe water is an everlasting need for every individual. In the last few decades, Fresh water resources have been directly threatened by the rapidly growing industrialization all over the world [1]. Discharged industrial waste has significantly contaminated water streams by releasing several pollutants including organic substances and heavy metals [2]. Unlike organic pollutants, heavy metals such as Hg, Pb, Cu, Cd, and Zn are not biodegradable and tend to accumulate and persist for long times [3]. These heavy metals can cause several diseases and disorders even at trace concentrations [4, 5]. For instance, Lead has several health effects including anemia, blood pressure elevation and gastrointestinal disorders [6, 7], while high levels of copper can cause abdominal stress and kidney failure [8, 9], mercury is believed to have poisoning effects on the nervous system leading to severe disorders such as brain damage, memory loss, behavioral abnormalities and autism [10-15].

To avoid their extreme impacts on environment and public health, several techniques have been developed to eliminate heavy metals from water including ion exchange, chemical precipitation, membrane filtration, and adsorption [16-32]. However, adsorption is more extensively preferred over the other conventional techniques due to its affordable cost, simplicity, high efficiency and environmentally friendly nature [33-37].

Cellulose is one of the most commonly used biosorpent, which revealed a great potential for adsorption of heavy metals, especially when chemically modified by binding to new groups via complexation or chelation which greatly enhances its adsorption capacity [38, 44].

Introduction of aminoguanidine to cellulose after its oxidation by the selective oxidizing agent potassium periodate has shown to enhance its adsorption capacity and achieve satisfying removal results for Cu, Hg, Pb, Cd and Zn ions from aqueous solutions [45].

In this research, an attempt is made to modify cellulose by adding an extra procedure to the aforementioned method which is addition of phenyl isothiocyante to the guanyl-modified cellulose and investigate its efficiency in adsorption of three heavy metals (i.e. Cu, Hg, and Pb) from aqueous solutions and real samples. This modification resulted in the formation of a novel adsorbent (PhGu-MC) that contains NS atoms capable of donating electrons. The presence of NS atoms provides a more powerful mode of chelation with metal ions. To the best of our knowledge the modification of cellulose using the N containing ligand (aminoguanidine) and the S containing phenyl isothiocyante is scarcely reported in the literature. Again , no data could be found regarding the use of the modified cellulose (PhGu-MC) as an efficient adsorbent for Cu^{+2}, Hg^{+2} and Pb^{+2} from real contaminated water samples

2. Experimental and methods

2.1. Materials

Aminoguanidine monohydrochloride, Cellulose powder, Phenyl Isothiocyanate, potassium metaperiodate (KIO_4), $CuSO_4$, $HgCl_2$, $Pb(NO_3)_2$, and triethylamine. All chemicals were purchased from Sigma Aldrich and directly used.

2.2 Adsorbent Preparation

Guanyl modified cellulose was prepared by the same procedure followed in the mentioned study [45] except for raising the oxidation time for 6 hrs. Then, 5 ml of phenyl isothiocyanate was added to 0.5g of the guanyl modified cellulose and immersed in 100 ml of ethanol in the presence of triethylamine. The obtained mixture was allowed to reflux for 3 hrs at 80 °C. Yellow powder of the modified cellulose was obtained at the end.

2.3. Instrumentation

Fourier transform-infrared (FT-IR) spectroscopy was carried out to investigate the functional groups present in the modified cellulose. Elemental analysis was done to determine the content of elements in cellulose before and after modification using a Perkin-Elmer 2400 analyzer. Brunauer–Emmett–Teller (BET) analysis was conducted to evaluate the surface area of the modified cellulose. Thermal gravimetric analysis (TGA) was conducted to monitor the mass change of the modified cellulose before and after adsorption of metal ions over temperature range of 30-800 °C by thermo analyzer Shimatzu DT40 (Japan). In addition, Scanning electron microscope (SEM) was used to study the morphological changes between the oxidized cellulose and the final product of cellulose modifications. The concentrations of Cu^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} in mixed solutions were estimated using Agilent's 5100 ICP-AES.

2.4. Metal ion adsorption experiments:

Batch adsorption of Cu, Pb and Hg was carried out in 100 ml reagent bottles containing 50 ml of known initial concentrations of the studied metals (50, 100, 150, 200) ppm and known weights of the modified cellulose (0.01, 0.03, 0.05) g at pH of (3, 4, 5, 6) adjusted by addition of 0.1 M NaOH and/or 0.1 M HCL and temperature of (25, 35, 45) °C for time intervals of (1-24) hrs. The bottles containing the samples were shaken on a mechanical shaker. Concentrations of Cu^{2+}, Hg^{2+} and Pb^{2+} ions in each experiment were measured by atomic absorption at wavelengths 324.8, 283.306 and 253.6 nm, respectively.

Then, adsorption efficiency was evaluated by equations (1) and (2).

$q_e = (C_i\text{-}C_e)v/w$ Eq.(1)

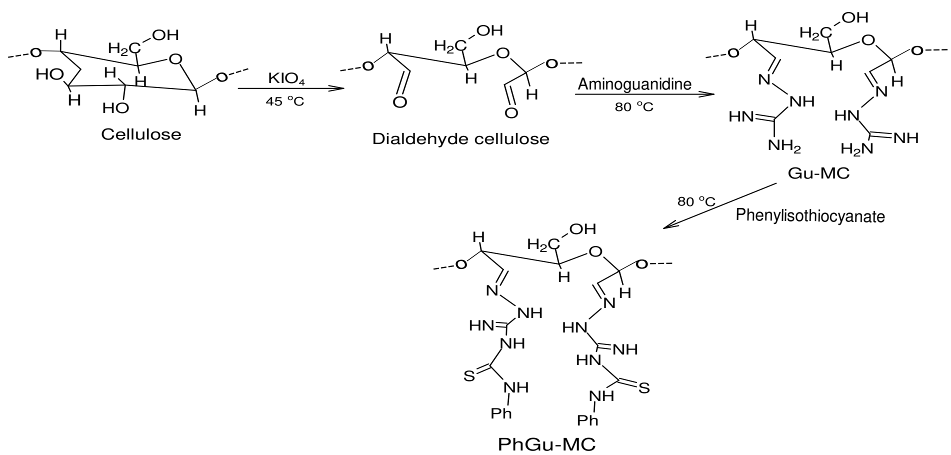
$\text{Removal (\%)} = \frac{(\mathbf{Ci} - \mathbf{Ce})}{\mathbf{Ci}} \times 100$ Eq.(2)

Where q_e is the adsorption capacity in mg.g^{-1}, C_i is the initial concentration of metal ion under study in (mg.L^{-1}), C_e is the equilibrium concentration of metal ions in (mg.L^{-1}), V volume of solution in (litre) and W is adsorbent mass in (g).

3. Results and discussion

3.1. Synthesis and Characterization of the prepared adsorbent (PhGu-MC)

Natural cellulose powder was subjected to selective oxidation by potassium periodate (KIO_4) prior to its reaction with aminoguanidine at 80 ºC to obtain a dialdehyde form which then reacts with aminoguanidine at 80 ºC. The product was further reacted with phenyl isothiocyanate for the formation of a modified form of cellulose with additional functional groups. Scheme 1 represents the proposed steps of the synthesis reaction.



Scheme 1 **Synthesis of PhGu-MC**

3.2. Digital photographs of native , oxidized, modified and metal laden cellulose

The digital photographs of native cellulose, oxidized (DAC), NS modified (Ph.Gu.MC) and metal laden modified cellulose Cu-PhGu-MC, Hg-PhGu-MC and Pb-PhGu-MC are shown in Fig. 1.(a-f), respectively. The photographs showed obvious colour changes of the modified cellulose before metal uptake (pale yellow) compared to modified cellulose after metal uptake.

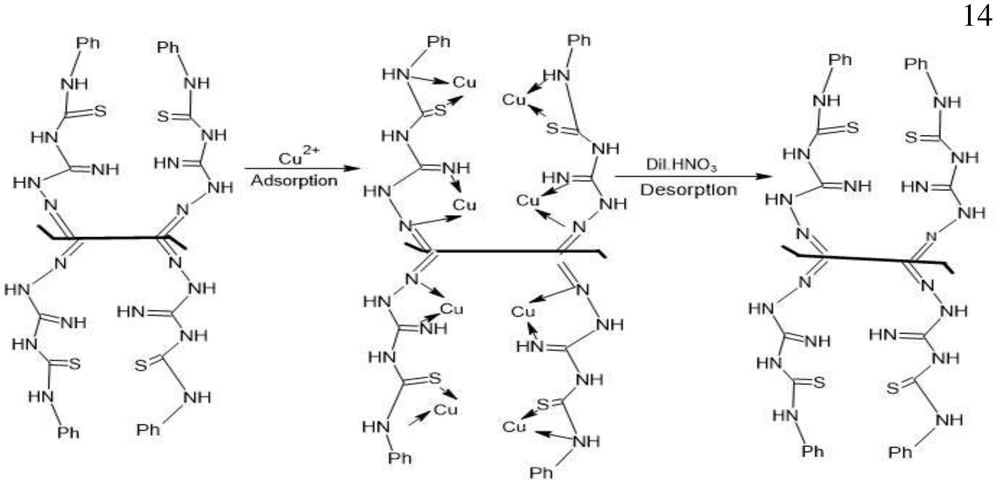
These results indicated that the tendency of the modified cellulose towards the adsorption of the studied metal ions.

3.3. Spectroscopic characterization

3.3.1. Infrared spectroscopy

The obtained IR spectra for native, oxidized and Ph.Gu-MC and Ph.Gu-MC -Cu are presented in Fig. 2(a-e).The IR spectrum of the native unmodified cellulose Fig. 2.a represents some characteristic peaks in the range of 1000–1200 cm^{-1} that correspond to C-O stretching. While the peaks present at 1260–1410 cm^{-1} are attributed to O-H bending vibrations, and those present in the range of 3600–3200 cm^{-1} are corresponding to O-H stretching vibrations [46]. Other peaks present at 2700–3000 cm^{-1} are due to C–H stretching. After oxidation of cellulose by potassium periodate, the spectrum of the oxidized cellulose in Fig.2.b showed an extra moderately sharp peak at approximately 1650 cm^{-1}, which is due to stretching vibration of carbonyl groups (C=O) formed upon oxidation [45]. Modification of cellulose by reaction with aminoguanidine lead to some changes in IR spectrum including mainly the sharp peak at about 1720 cm^{-1}, which could be due to the formation of C=N between the aldehyde groups present in the oxidized cellulose and the amino groups of the added aminoguanidine [45] as represented in Fig.1.c.

While Fig.2.d shows the IR spectrum after further modification by addition of phenylisothiocyanate, the presence of some new peaks at the range of 1120cm^{-1} and 960 cm^{-1} could be related to the C=S group [47] present in the newly added phenylisothiocyanate. In addition, the broad peak at approximately 2900 cm^{-1} could be due to the introduction of phenyl group. Also, the overlapping peaks appearing at the range of 1520 cm^{-1} and 1650 cm^{-1} could be assigned to C-N-H, N=CH- and C=C unsaturated bonds in the aromatic rings of phenyl group [47]. Differences observed in IR spectra support the modification of natural cellulose and introduction of new functional groups. For better evaluation of the mechanism by which the investigated metal ions can coordinate with the active phenylisothiocyanate- aminoguanidine moieties inserted onto the chelating fibers, the FTIR spectra of the Cu^{2+} loaded on PhGu-MC was carried out as a representative example and compared to the free fibers as shown in Fig.2.e. As expected, the main diagnostic peaks of phenylisothiocyanate- aminoguanidine moieties showed some changes resulting including the decrease in bands intensity at the range of 1610 to 1670 cm^{-1} where the main diagnostic peaks of the adsorbent (PhGu-MC) are represented including C=N and C=O groups. Also, the appearance of new stretching vibration of the Cu-N bonds at about 460 Cm^{-1} could confirm the occurrence of Cu^{2+} adsorption on PhGu-MC. Scheme 2 describes an imaginary mechanism of adsorption and desorption betweenPh.Gu-MC and Cu ions as a representative example.



Scheme.2 Mechanism of adsorptionand desorption between Cu^{2+} and active sites of (PhGu-MC).

3.3.2. Elemental analysis

The results of elemental analysis for native cellulose and modified cellulose are summarized in Table 1. The results revealed an addition of nitrogen to the elemental composition of cellulose which indicates the successful modification of cellulose by introduction of new functional groups.

3.3.3. Scanning electron microscopy

The surface morphology of the oxidized cellulose and the further modified cellulose (PhGu-MC) were investigated by scanning electron microscope at magnifications of 5,000X, 15,000X and 27,000X. Fig.3. shows the obtained SEM images at the three magnifications. It can be straightly noticed that the surface of cellulose has become rougher after being modified which indicates the insertion of new moieties to the initial structure. Also, the surfaces of the modified cellulose are shown to involve large cavities and pores that might help in trapping the metal ions in adsorption process.

3.3.4. Brunauer–Emmett–Teller analysis (BET):

The results obtained from Brunauer–Emmett–Teller analysis for the modified cellulose showed that surface area of PhGu-MC is 3.038 $m^2.g^{-1}$ as shown in Table 2. This very low surface area indicates that the adsorption of heavy metals is mainly attributed to complexation with the active functional groups added to the cellulose natural fibers.

3.3.5. Thermal gravimetric analysis (TGA):

Thermal gravimetric analysis (TGA) was conducted to investigate the thermal decomposition of PhGu-MC before and after adsorption of heavy metal ions. As shown in Fig.4, over temperature range of (0-200) ^oC there was very slight weight loss that actually starts after 100 ^oC mainly due to the evaporation of water moieties. Weight loss starts to increase approximately from temperature 250 ^oC to about 450 ^oC due to pyrolysis of the samples. Similar decomposition behavior was observed before and after adsorption. Thermograms of natural cellulose reveal two thermal decomposition steps that usually yield levoglucosan and anhydrocellulose [48]. Whereas, the obtained thermogram of PhGu-MC in Fig. 4a shows four thermal decomposition stages which in turn confirms the occurrence of compositional modification of natural cellulose. At 750 ^{o}C the final remaining weight of PhGu-MC was 0.96% indicating the significant thermal stability of PhGu-MC at very high temperatures. After adsorption of metal ions, the final remaining weights of metal-PhGu-MC complexes at 750 ^{o}C were 41.3%, 40.2% and 56.1% for Cu-PhGu-MC, Hg-PhGu-MC and Pb-PhGu-MC, respectively. The increased value of the remaining after adsorption of metals compared to PhGu-MC indicates their greater thermal stability.

3.4. The influence of variables on adsorption performance of PhGu-MC

The modified cellulose (PhGu-MC) was used as an adsorbent for Cu^{2+}, Hg^{2+} and Pb^{2+} from aqueous solution and environmental water samples. Effects of various factors on the adsorption efficiency were investigated including pH, initial metal concentration, contact time, adsorbent dose, temperature and interfering ions on adsorption was investigated to estimate the optimum adsorption conditions.

3.4.1. Effect of pH on adsorption:

The effect of pH value in the range of 1-6 on the removal of metals by the modified cellulose (PhGu-MC) is represented by Fig.5. Adsorption capacity (q_e) shows an increasing trend with increasing pH values till it reaches its maximum at pH 6 for Cu^{2+}, $Hg^{2+}$and Pb^{2+}. The observed trend can be explained by the pronation process that takes place at acidic medium where protons are attached to the negatively charged groups on the fibers of the adsorbent which in turn competes with metal ions that are meant to be adsorbed.

3.4.2 Effect of adsorbent dose on adsorption:

The dose of adsorbent was varied from 0.01 mg to 0.1 mg and the adsorption capacity was estimated for each dose. Fig.6. describes the relationship between adsorbent dose and adsorption capacity of PhGu-MC. It can be concluded from the figure that adsorption capacity increases as the adsorbent dose increases in a direct relationship this can be simply due to the increased number of active sites present. Then, when saturation by heavy metals is achieved the adsorption capacity turns to remains constant as the adsorbent dose increases. Cu^{2+} and Pb^{2+} have shown saturation values at dose of 0.05 mg of PhGu-MC. While the maximum adsorption capacity for Hg^{+2} was achieved by only 0.03 mg. The obtained results proved that PhGu-MC is highly efficient adsorbent for heavy metals at very low dosages.

3.4.3. Effect of contact time on heavy metal adsorption and related kinetic parameters:

Fig.7. represents the relationship between time of contact and adsorption capacity for PhGu-MC. Hg^{2+} by PhGu-MC was the most rapid followed by Pb^{2+} and Cu^{2+}. Maximum adsorption capacity of PhGu-MC was reached approximately in the first 6 hours then equilibrium was reached. The obtained experimental data were fitted to the two adsorption kinetic models; pseudo-first-order and pseudo-second-order models to predict the adsorption mechanism. The kinetic parameters were calculated using equations (3) and (4).

Pseudo-first-order linear equation:

$$1/q_{t(ads)} = k_1/q_{e(ads)}t + 1/q_{e(ads)} \qquad \text{Eq.(3)}$$

Pseudo-second-order linear equation:

$$t/q_{t(ads)}=1/k_2q_e{}^2{}_{(ads)}+ (1/q_{e(ads)})t \qquad \text{Eq.(4)}$$

Where $q_{e(ads)}$ is the adsorption capacity at equilibrium, $q_{t(ads)}$ is the adsorption capacity at time t, K_1 is the adsorption rate constant of pseudo-first-order model and K_2 is the adsorption rate constant of pseudo-second-order model.

The kinetic parameters estimated from the two models are summarized in Table 3, whereas the plotted curves are shown in Fig.8 and 9. From the parameters derived from pseudo first order curves, it can be noticed that correlation coefficients (R^2) were high, but the theoretical equilibrium adsorption capacity $q_{e(ads)}$ for each metal were not consistent with the experimental records. On the other hand, pseudo-second-order model calculated parameters were in agreement with experimental results as R^2 values were also high as they were approaching 1, and adsorption capacities all agree with the experimental ones. Regarding rate constants ($K_1$and K_2) calculated in each model, it can be straightly observed that rate constants calculated from first order model were high which means a slow adsorption rate which in turn doesn't agree with experimental results. While rate constants derived from the second order model were much smaller which makes more sense and correlate with experimental results. So, it can be deduced that the adsorption of Cu^{2+}, $Hg^{2+}$and Pb^{2+} by PhGu-MC perfectly exhibited the pseudo-second-order kinetic model. It can be also concluded that chemisorption is the main dominant process and it is suggested to be as well the limiting factor.

3.4.4. Effect of initial concentrations and related isotherm models:

The effect of initial concentration of metals on adsorption was studied by varying initial concentration over the range of (50-250) ppm while all the remaining parameters were held constant. Fig. 10 describes the relationship between initial concentration of metal ions and adsorption capacity of PhGu-MC. As shown in the figure, adsorption capacity increases as the initial concentration of metal ions increases till all the active sites of the adsorbent dose are occupied by metal ions then equilibrium is reached and the adsorption capacity remains constant as the initial concentration increases.

For better expression of the effect of initial concentration on adsorption process, Langmuir and Freundlich models of adsorption isotherms were employed using their linearized equations (5) and (6).

$\ln q_e = \ln K_F + 1/n \ln C_e$ Eq.(5)

$C_e/q_e = (1/K_L q_m) + (C_e/q_m)$ Eq.(6)

Where q_e is the adsorption capacity at equilibrium, K_F is Freundlich constant, n is the heterogeneity factor that reflects the energy distribution in bonds, Ce is metal concentration at equilibrium, K_L is the Langmuir constant and q_m is the maximum adsorption capacity of a single layer.

The convenience of the adsorption process was then investigated by calculating (R_L) which is the separation factor constant using equation (7).

$R_L = 1/ (1+C_o K_L)$ Eq. (7)

Where K_L is the Langmuir adsorption constant and C_o is the initial concentration of metal ions. R_L values greater than 1.0 indicate unsuitability of the adsorbent, while R_L values between 0 and 1 indicate suitability of the studied adsorbent.

The derived parameters are listed in Table 4. From the estimated values of the parameters for PhGu-MC, it was found that correlation coefficients were very high in Langmuir model which means that the experimental data significantly fit to Langmuir model. While R^2 coefficients derived from Freundlich isotherm plot were much lower. In addition, the maximum adsorption capacity for a single layer (q_m) obtained from Langmuir plot were all in agreement with experimental records which well confirms that adsorption process would be best described by Langmuir isotherm model. All the calculated values of R_L lie between 0-1 confirming suitability of the two modified cellulose (PhGu-MC) as an adsorbent for the studied metal ions.

3.4.5. Effect of temperature on metal ions adsorption and related thermodynamic parameters:

In order to study the effect of temperature on adsorption of the studied metal ions, some thermodynamic properties were investigated including Gibbs free energy change (ΔG^o), thermodynamic equilibrium constant (K_c), standard entropy change (ΔS°) and standard enthalpy change (ΔH°). The values of the mentioned thermodynamic parameters are calculated after plotting 1/T against LnK_c using equations 8, 9 and 10.

$K_C = C_{ad} / C_e$ (Eq.8)

$\ln K_C = \Delta S^o_{ads} / R - \Delta H^o_{ads} / RT$ (Eq.9)

R is gas constant (8.314 J/mol K).

$\Delta G^o_{ads} = -RT \ln K_C$ (Eq.10)

Fig.11 shows the plotted curves and the obtained values are all listed in Table 5. The investigated temperature range was 298 K to 318 K.

Values of Gibbs free energy ΔG^o_{ads} for all the adsorption process were all indicating the spontaneity of the adsorption process under the investigated temperature range. Values of enthalpy change (ΔH°) were also negative for all the adsorption processes indicating the exothermic behavior of them. Standard entropy change (ΔS°) is a measurement of randomness or energy distribution in the system. ΔS° values were all negative as well indicating the low randomness which reflects the strong affinity between the two modified cellulose (PhGu-MC) and the adsorbed metal ions, which is a very good indication of the adsorption efficiency of the two adsorbents. Thus, it can be concluded that high temperatures are not favorable for adsorption of the studied metal ions by the two studied adsorbents. So, adsorption experiments are more preferred to be conducted at moderately low temperatures such as 298 K which is the normal room temperature.

3.3.6. Effect of some selected interfering ions:

Effect of the presence of foreign ions on adsorption of heavy metals was investigated under the optimum adsorption conditions. Removal percentages for every metal were estimated in the presence of 50 ppm of some interfering ions. Concentration of the interfering ions was exactly equal to the metal concentration. Results are all summarized in Table 6. It can be concluded from the obtained results that the presence of 50 ppm of cations such as Mg^{2+}, Fe^{2+}, Ca^{2+} and Al^{3+} and anions such as PO_4^{3-} , acetate, oxalate and edetate doesn't significantly affect the removal of heavy metals by PhGu-MC. The results give a promising indication about the selectivity of PhGu-MC which reveals its potential to work efficiently in more complicated media.

3.4. Adsorption from multi-metal solutions as a selectivity indicator:

A mixture of the metals under study was prepared to investigate the adsorption efficiency of the two prepared adsorbents in multi-metal solutions. As shown in Table 7, removal percentages show the same trend of mono-metal solutions with no obvious differences. The results also correlate with the conclusion obtained in interfering ion section that the modified cellulose (PhGu-MC) would act efficiently in complicated multi-component samples.

ICP–AES was used to determine the concentrations of the multiple metal ions in studied solutions.

3.5. Desorption and reusability of PhGu-MC*:*

To test the reusability of PhGu-MC, five cycles of adsorption-desorption have been carried out under the optimum conditions, using 5 ml of 0.1M HNO3, the obtained results are shown in

Table 8. From the results, it was clear that the adsorption efficiency of PhGu-MC was only slightly decreased after cycle five, the adsorbent maintained about 95% of its initial efficiency.

3.6. Applications in natural environmental water samples:

Analysis three real samples of water was carried out to investigate the probability of environmental applications of the proposed method. Tap water and Nile water samples were obtained in Al-Mansoura city, while the sea water sample was from Marsa Matrouh City. The three types of water were subjected to preconcentration procedure for the heavy metals under study. Satisfying removal percentages were achieved in all the samples as shown in Table 9. In addition, the obtained results all agree with the previous results that were obtained throughout the research work. It can be concluded that the two prepared adsorbents are valid to selectively remove heavy metals from natural water samples.

3.7. Comparison between adsorption capacity of PhGu-MC and other adsorbents:

Table 10 summarizes number of published adsorbents and their adsorption capacity towards metal ions. Comparing the adsorption capacities obtained from most of the mentioned studies, Ph.Gu-MC was found to have higher adsorption capacity. Taking Cu^{+2} as an example, Ph.Gu-MC has an adsorption capacity of 50 $mg.g^{-1}$ while all the listed methods revealed adsorption capacities ranged from 1.75 to 36 $mg.g^{-1}$.

4. Conclusions

The NS modified cellulose (Ph.Gu-MC) was successfully synthesized via three chemical reactions and characterized by several characterization techniques including FTIR, SEM and BET. Ph.Gu-MC has proven to be an efficient adsorbent for Cu^{2+}, Hg^{2+} and Pb^{2+} with adsorption capacities of 50, 94 and 55 $mg.g^{-1}$, respectively. Adsorption of metals by Ph.Gu-MC is proposed to perfectly fit pseudo-second order kinetic model and Langmuir isotherm model. In addition, adsorption process was found to be spontaneous and exothermic at different temperatures based on thermodynamic calculations.

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Figures

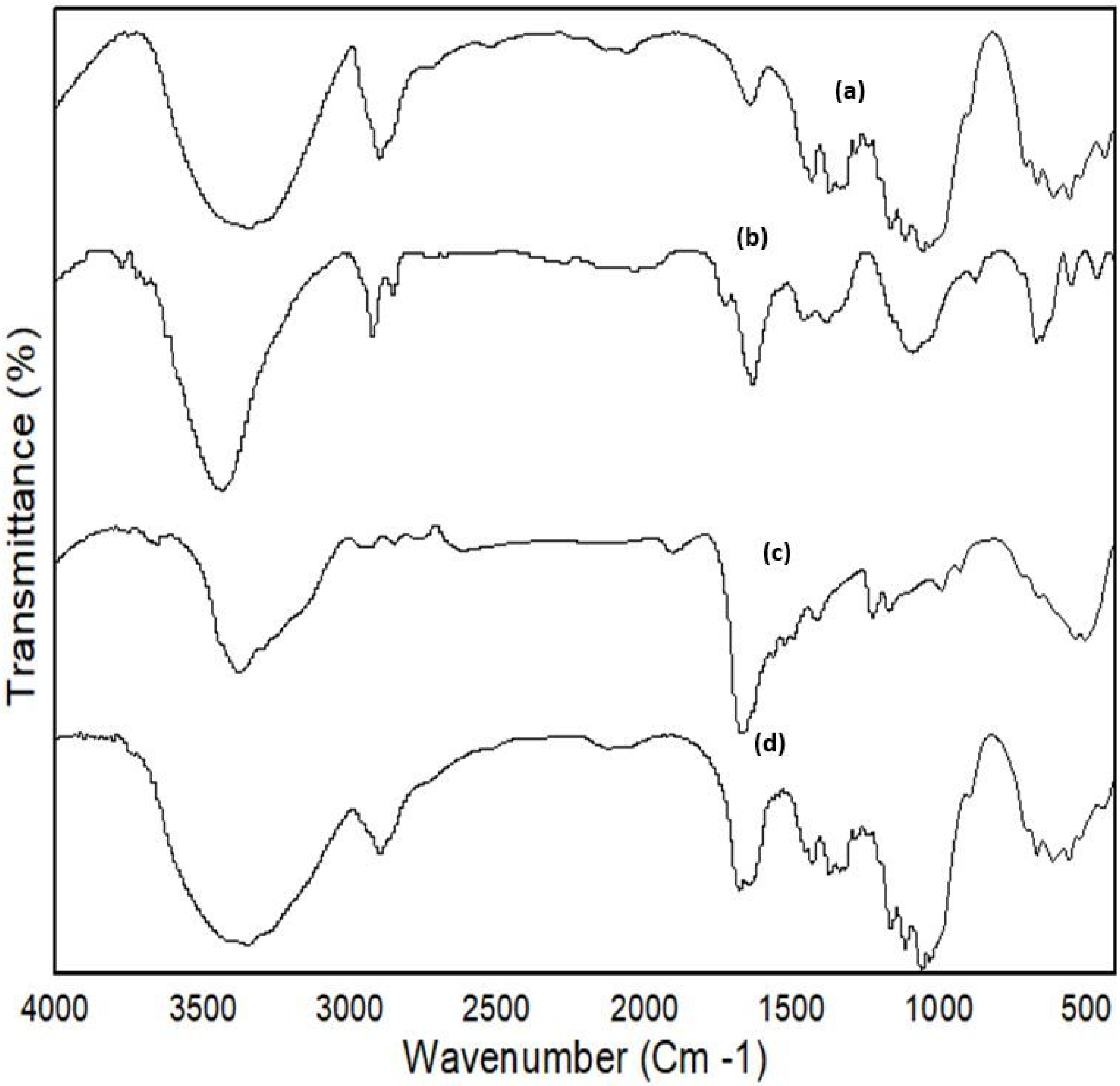

Figure 1

FTIR spectra of (a) native cellulose, (b) oxidized cellulose, (c) Gu-MC, (d) PhGu-MC.

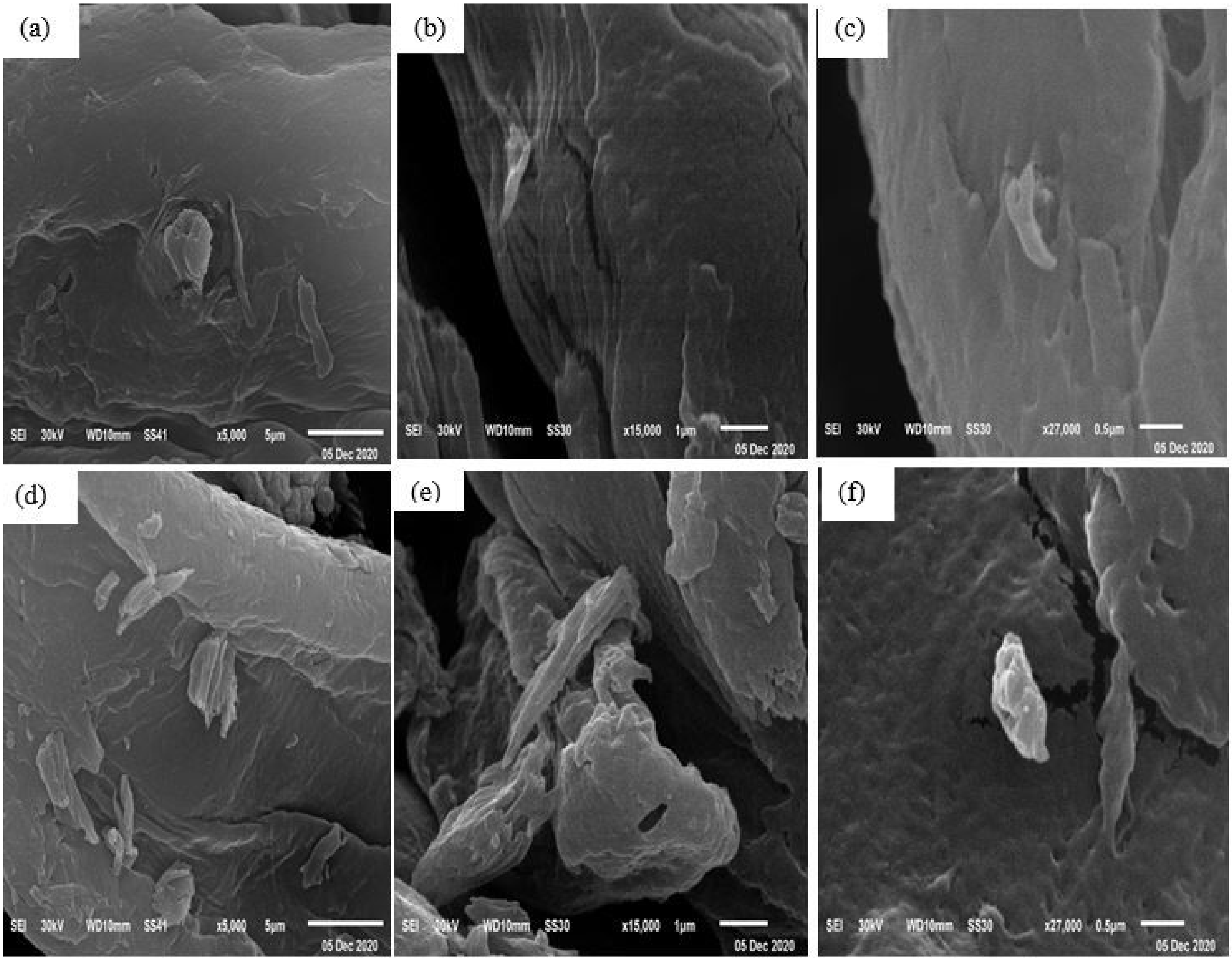

Figure 2

SEM images of oxidized cellulose at (a) 5000x,(b) 15000x, (c) 27000x and PhGu-MC at (d)5000x, (b)15000x and (f)27000x.

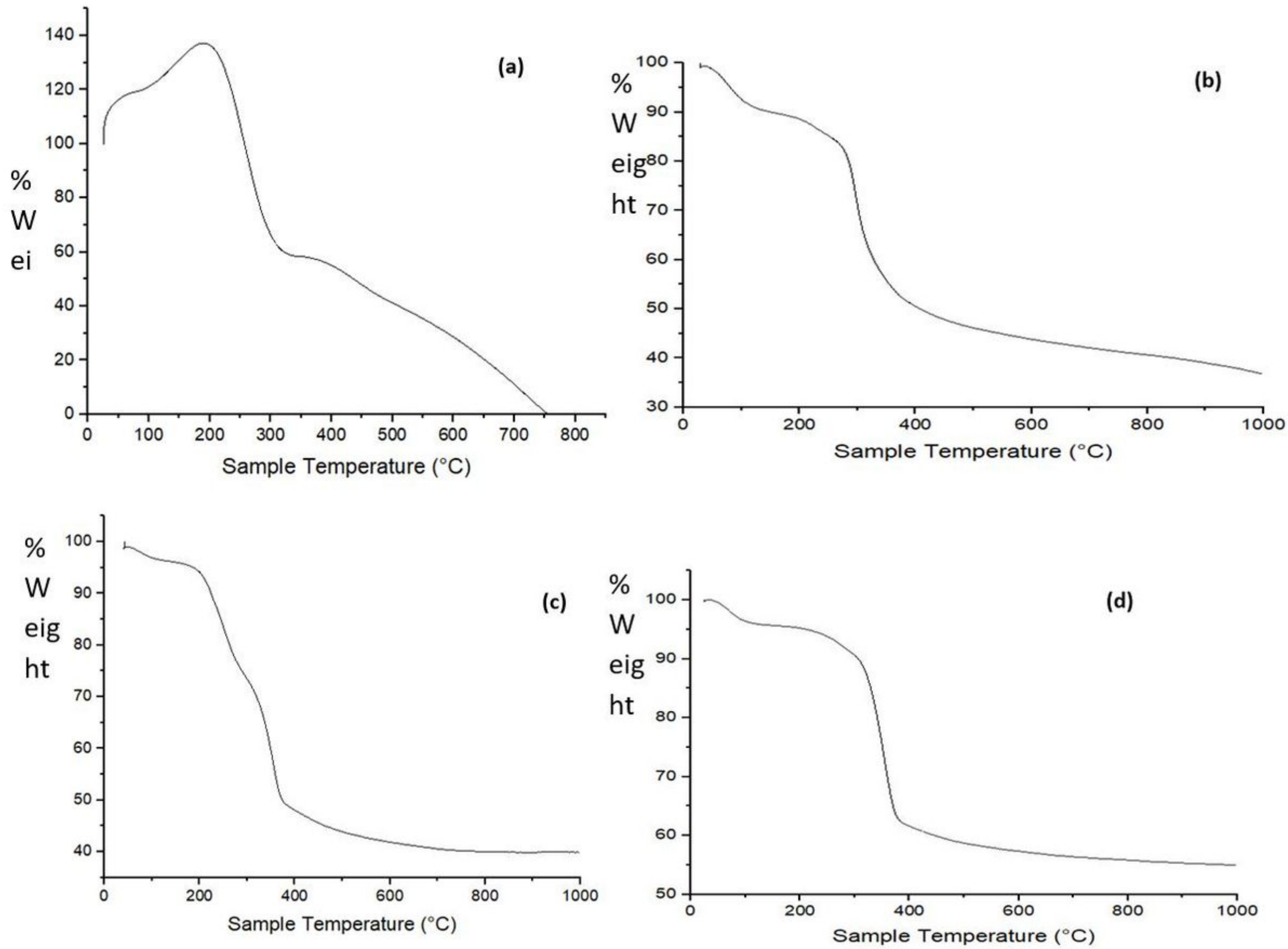

Figure 3

TGA curves of (a) PhGu-MC, (b) Cu-DiGu-MC, (c) Hg-DiGu-MC, (d) Pb-DiGu-MC.

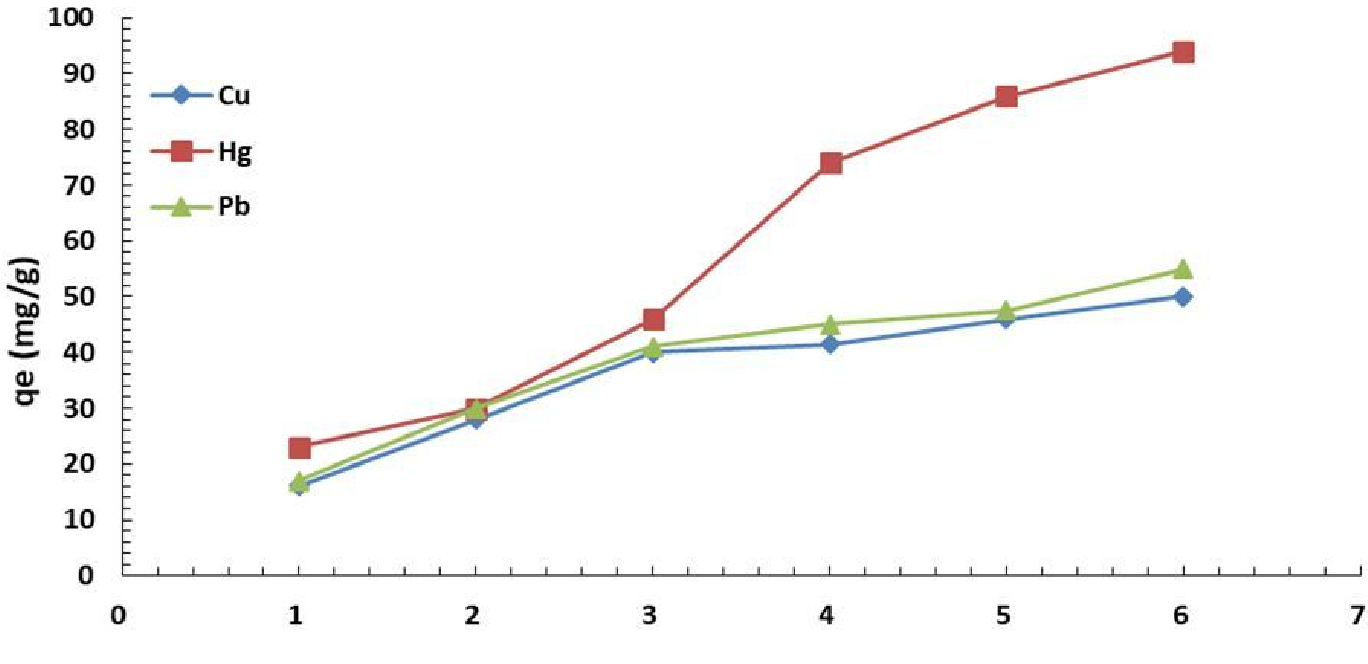

Figure 4

Effect of PH on adsorption of heavy metals by PhGu-MC.

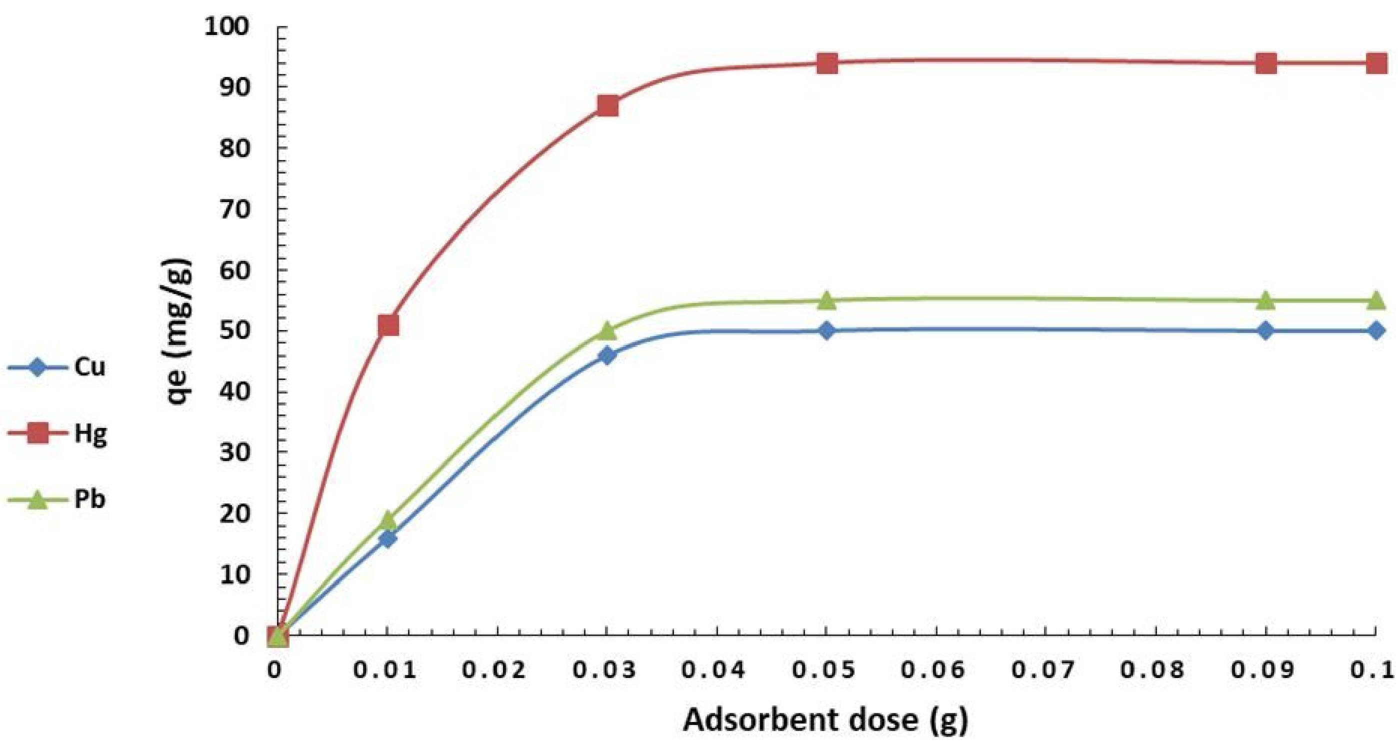

Figure 5

Effect of adsorbent dose on adsorption of heavy metals by PhGu-MC.

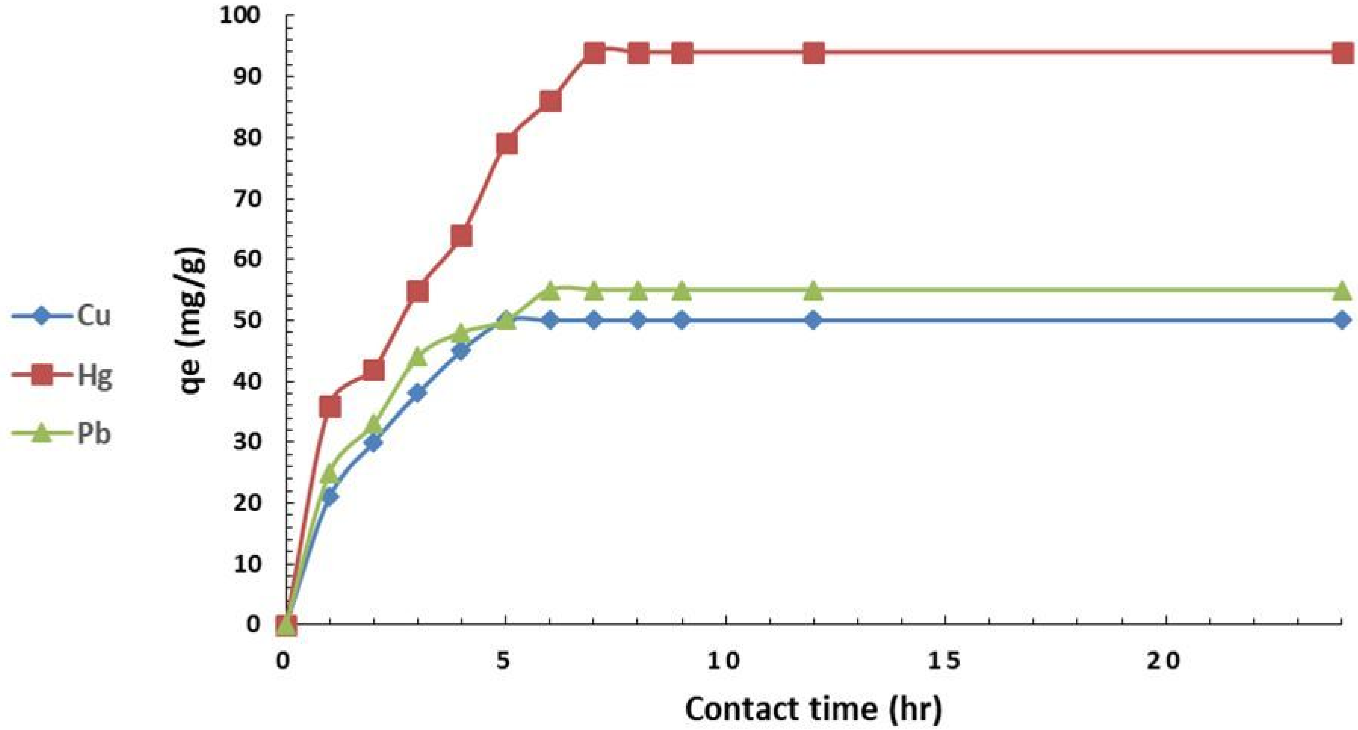

Figure 6

Effect of contact time on adsorption of heavy metals by PhGu-MC.

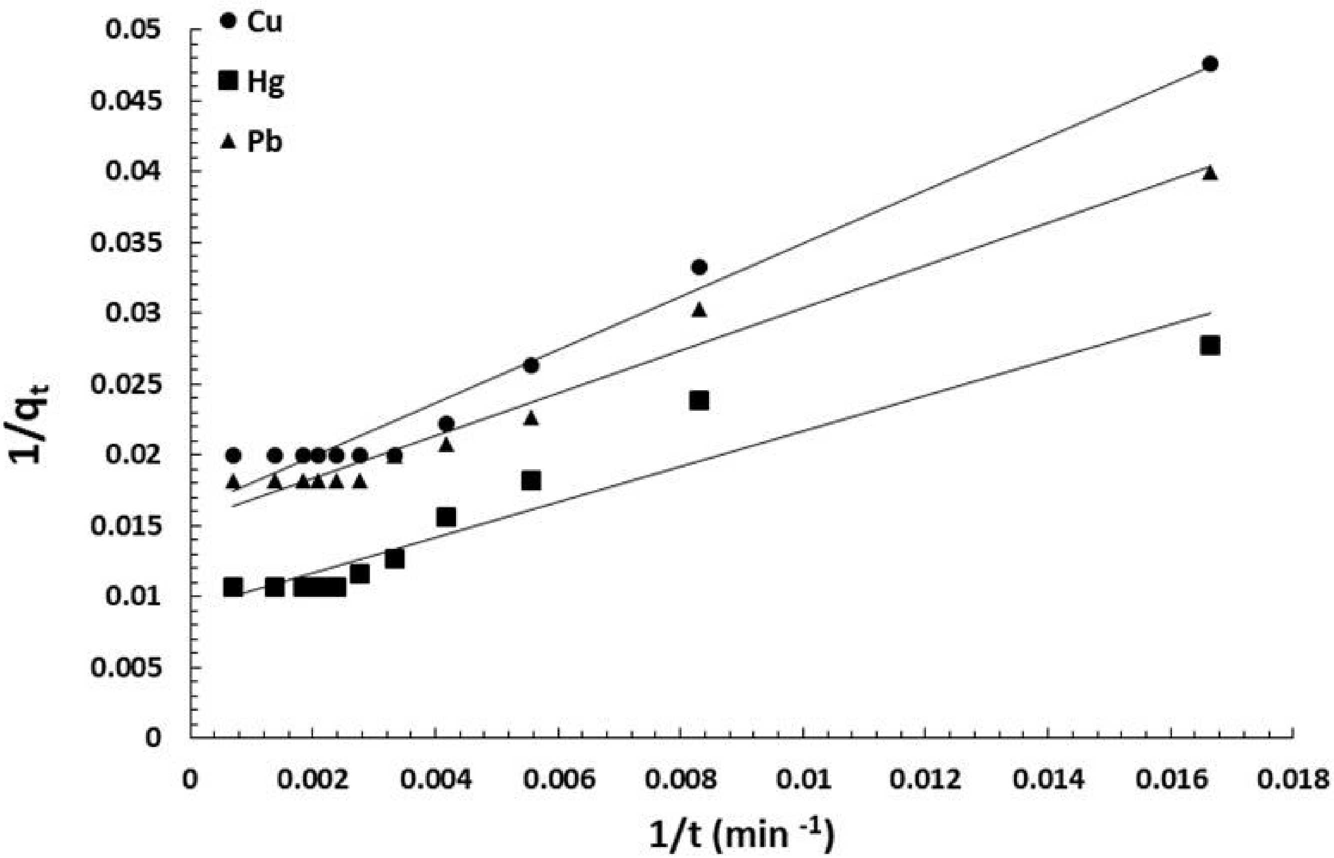

Figure 7

Pseudo-first order plot of metals adsorption by PhGu-MC.

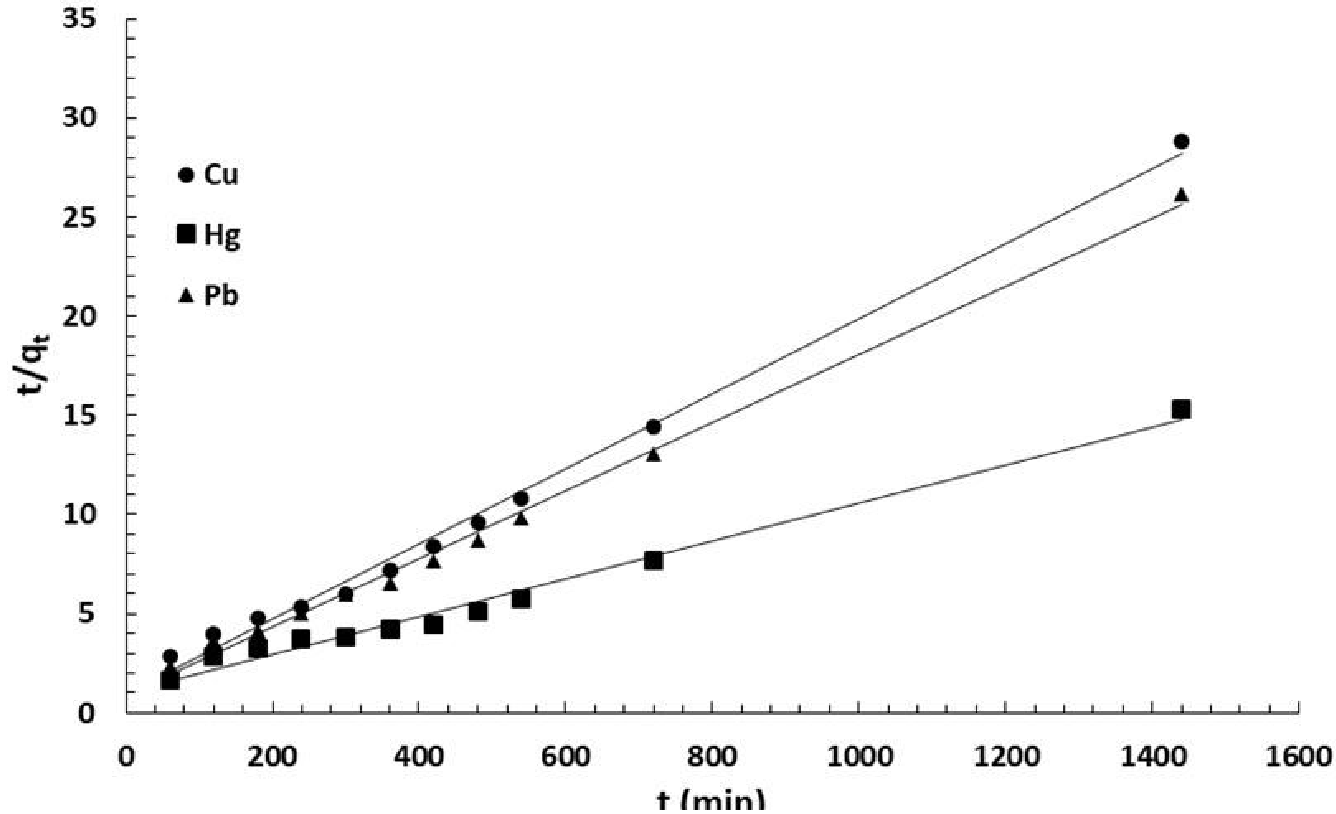

Figure 8

Pseudo-second order plot of metals adsorption by PhGu-MC.

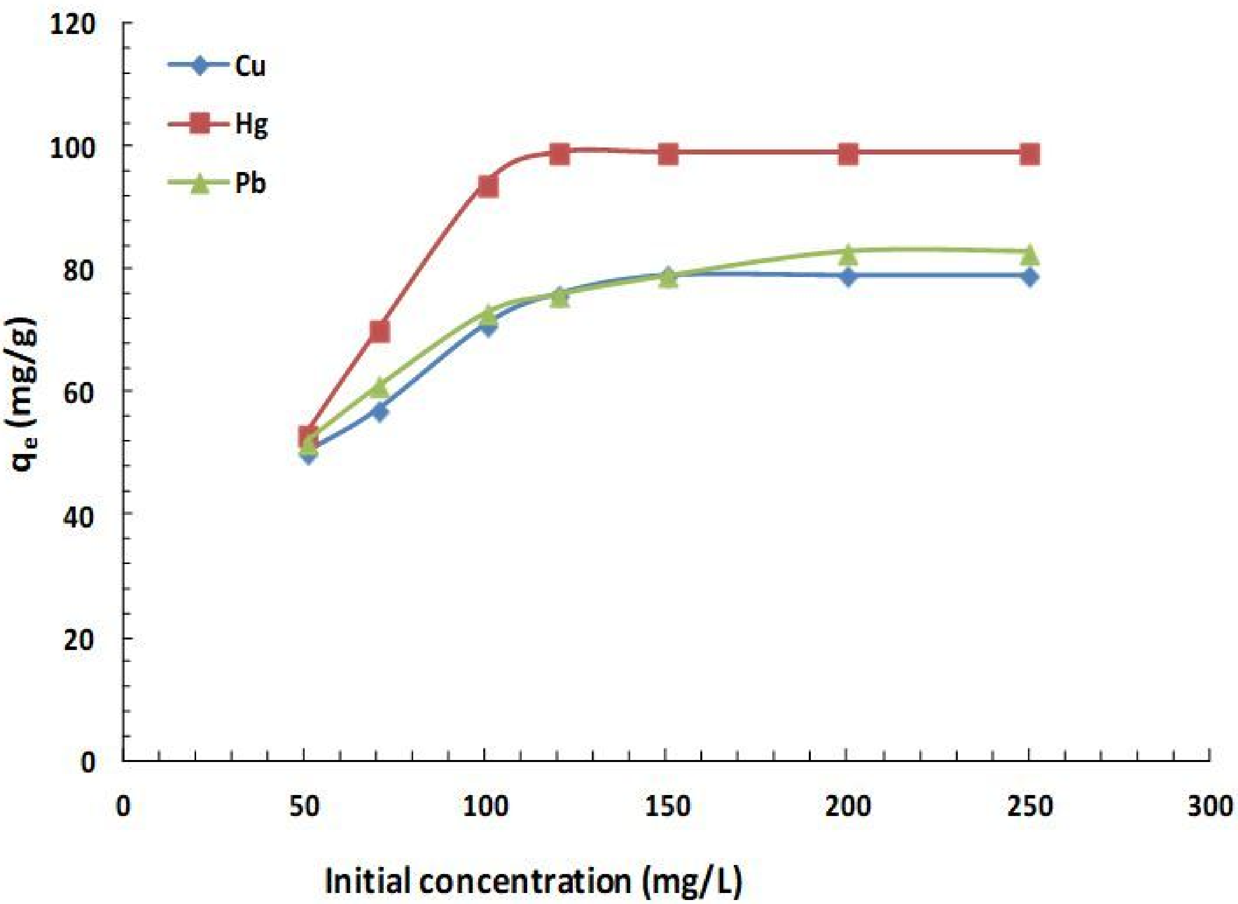

Figure 9

Effect of initial concentration on adsorption of heavy metals by PhGu-MC.

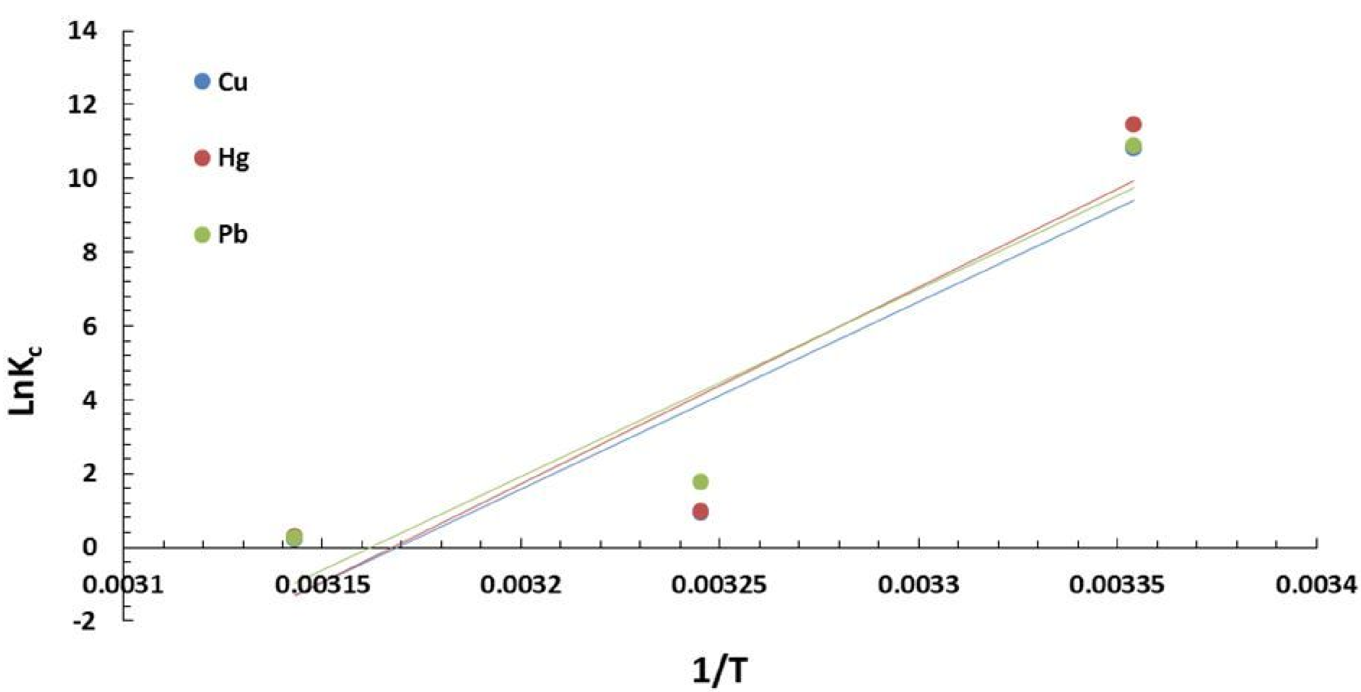

Figure 10

Relationship between LnKc and 1/T for adsorption of Cu^{+2}, Hg^{+2} and $Pb^{+2}$by PhGu-MC.