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Comparative Study for The Removal of Hg(II) From Aqueous Solutions by Adsorption on The Gum Arabic and Modified Gum Arabic

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In the present investigation, gum arabic (GA) and glycidyl methacrylate modified gum arabic (GMA-GA) were assessed as biosorbents for the removal of Hg(II) from aqueous solutions. For chemical modification of gum arabic with glycidyl methacrylate, an appropriate mixture of water and DMSO was used to dissolve gum arabic and glycidyl methacrylate. The approving of chemical modification and the presence of glycidyl methacrylate groups in the modified structure of gum arabic (GMA-GA) was confirmed by diffuse reflectance spectroscopy (DRS). The equilibrium studies are systematically carried out in a batch process, covering various process parameters that include agitation time, adsorbent dosage and pH of the aqueous solution. It was observed in adsorption and desorption tests that GMA-GA showed significant pH dependence, which affected the removal efficiency, robustly. Adsorption behaviour is found to follow Freundlich and Langmuir isotherms. The adsorption mechanism is described by a pseudo second order kinetics. A regeneration study was also carried out.

Key Words: Adsorption, Heavy metal, Wastewater treatment, Biosorbents, Gum arabic, Modification.

INTRODUCTION

Water pollution due to toxic metals and organic compounds remains serious environmental and public problem. Moreover, faced with more stringent regulations, water pollution has also become a major source of concern and a priority for most industrial sectors. Heavy metal ions are often found in the environment as a result of their wide industrial uses. They are common contaminants in wastewater and many of them are known to be toxic or carcinogenic[1,2]. In addition, heavy metals

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are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. Therefore, their presence in the environment, in particular in water, should be controlled[3,4]. Strict legislation on the discharge of these toxic products makes it then necessary to develop various efficient technologies for the removal of pollutants from wastewater. Biological treatments[5-7], membrane processes[8], advanced oxidation processes[9-12], chemical and electrochemical techniques[13-15] and adsorption procedures[16-18] are the most widely used for removing metals and organic compounds from industrial effluents. Amongst all the treatments proposed, adsorption using sorbents is one of the most popular methods since proper design of the adsorption process will produce high-quality treated effluents. In fact, adsorption is now recognized as an effective, efficient and economic method for water decontamination applications and for separation analytical purposes. The adsorbents may be of mineral, organic, biological origin, activated carbons, zeolites, clays, silica beads, low-cost adsorbents (industrial by-products, agricultural wastes, biomass) and polymeric materials are significant examples[19,20].

In spite of prolific use of activated carbon, it remains an expensive material since higher the quality of activated carbon, the greater its cost. Activated carbon also requires complexing agents to improve its removal performance for inorganic materials. Therefore, this situation makes it no longer attractive to be widely used in small-scale industries because of cost inefficiency.

Due to the problems mentioned previously, research interest into the production of alternative adsorbents to replace the costly activated carbon has intensified in recent years. Among these, polysaccharides such as gum arabic, chitin and starch and their derivatives (chitosan, cyclodextrin) deserve particular attention. These biopolymers represent an interesting and attractive alternative as adsorbents because of their physico-chemical characteristics, chemical stability, high reactivity and excellent selectivity towards aromatic compounds and metals, resulting from the presence of chemical reactive groups (hydroxyl, acetamido or amino functions) in polymer chains. Moreover, polysaccharides have a capacity to associate by physical and chemical interactions with a wide variety of species[19,20]. Hence, adsorption on polysaccharide derivatives can be a low-cost procedure of choice in water decontamination for extraction and separation of compounds and a useful tool for protecting the environment.

The modification of polysaccharides by the insertion of glycidyl methacrylate (GMA) by using DMSO as a solvent has become a common procedure[21-25]. This method consists in coupling GMA double bonds to a polysaccharide structure, which allows cross-linking (or gelation)[26]. However, that procedure cannot be used to modify polysaccharides insoluble in DMSO like the gum arabic (GA), which has interesting properties to be used as a biomaterial[27,28].

The main objective of this work is to develop and application of gum arabic and chemically modified gum arabic with glycidyl methacrylate (GMA-GA)[29] as potential biosorbents for removal and determination of Hg(II) in polluted solutions. The study also includes the investigation of the effects of pH, equilibrium time and other parameters on the removal efficiency. Adsorption isotherms and the mechanism of adsorption were also investigated.

EXPERIMENTAL

Starting materials were obtained as follows: glycidyl methacrylate (GMA, Acros Organics), N,N,N',N'-tetramethylethylenediamine (TEMED, Sigma), dimethylsulfoxide (DMSO) (Sigma). The following inorganic materials were used: $Hg(NO_3)_2$ (Merck), HCl 37 % (Fluka), NaOH 99.5 % (Merck). The adsorbents used in this project were gum arabic (GA) (purchased from Fluka) and gum arabic chemically modified with glycidyl methacrylate (GMA-GA). All solutions for experiments were prepared with distillated water.

Preparation of modified gum arabic (GMA-GA): Gum arabic was first purified by precipitation in an aqueous solution by the addition of ethanol. The aqueous-DMSO solution was prepared by mixing 51 mL distilled-deionized water and 129 mL of DMSO. After homogenization, 20 g of purified gum arabic were added to the DMSO/H_2O solution. Afterwards, 0.127 mmol TEMED and 75.2 mmol GMA were added. The resulting mixture was stirred for 72 h at 50 °C. The modified polysaccharide, labeled GMA-GA, was purified by precipitation in ethanol and re-mixed in water. This cycle was repeated at least three times. GMA-GA samples were dissolved in Milli-Q® water and dialyzed for 5 days at 4 °C. After that, the purified GMA-GA was lyophilized.

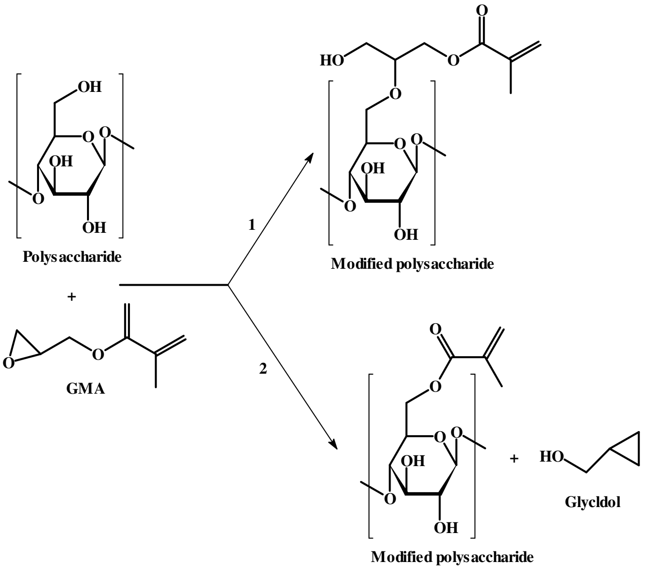
Adsorption experiments: Adsorption experiments were conducted at constant temperature (298 K) on a three dimensional shaker during certain time. The solid-liquid system consisted of 20 mL aqueous solution containing Hg(II) 50 mg L^{-1} and different dose of adsorbent. After sufficient contact time, the solution was filtered and filtrate was analyzed by atomic absorption spectrometer. Standard solutions containing 1, 20, 50, 100 and 500 mg L^{-1} Hg(II) were used for calibration.

DRS Analyses: Solid samples of GA and GMA-GA were ground in an agate mortar. An aliquot of 400 mg of these materials were taken for recording of spectra. Diffuse reflectance spectra of the ground powders are taken on a Shimadzu UV-2100 spectrophotometer equipped with an integrating sphere assembly. All the spectra were taken against barium sulfate in the ultraviolet region at room temperature and plotted in terms of absorbance.

A Perkin atomic absorption spectrometer (Perkin-Analyst 100) equipped with a deuterium-arc lamp background corrector was used for absorbance measurements at appropriate wavelengths. The operating conditions were those recommended by the manufacturer, unless specified otherwise. The sample and the acetylene flow rates and the burner height were adjusted in order to obtain the maximum absorbance signal.

RESULTS AND DISCUSSION

Characterization of modified sorbent: It has been assumed that modification of polysaccharides with GMA occur through two different pathway reaction (1-in a protic solvent, 2-in aprotic solvent)[30]. A schematic drawing of these reaction routes is shown in **Scheme-I**. When treated with a protic solvent, the polysaccharide reacts with GMA by opening the epoxy ring. It is considered that the whole GMA molecules are coupled to the polysaccharide structure. The other modification route of the polysaccharide with GMA is transesterification reaction, which occurs in an aprotic solvent. In this case, glycidol is formed as a byproduct and only then, the methacrylate molecule is coupled to the polysaccharide structure. However, the epoxy ring opening reaction route with GMA as a chemical modifier of polysaccharides has been little discussed in the literature[31]. Furthermore, those investigations have hardly addressed branched acidic hetero-polysaccharides of complex structure like gum arabic. The complex structure of gum arabic generates large signals in ^{1}H NMR spectra and therefore it is not possible to determine the degree of modification from these signals. Consequently, the extent of the vinyl groups incorporated into gum arabic cannot be evaluated by NMR analysis. According to the literature[22,23], this parameter has already been determined by ^{1}H NMR analyses. However, the studied polysaccharides, *e.g.* dextran and inulin, have macromolecular structures less complex than that of gum arabic. Therefore, the purpose of this work was to incorporate GMA vinyl groups into the gum arabic structure and to perform their characterization and not to verify whether transesterification and/or epoxy ring opening occur.



Scheme-I: Schematic representation of feasible modification routes of polysaccharides with glycidyl methacrylate[31]

On the other hand, solid samples of gum arabic and GMA-GA were characterized by diffuse reflectance spectroscopy for approving of chemical modification. Fig. 1 shows the DRS spectra of gum arabic and GMA-GA. As can be seen, the presence of new peak for carbonyl group, -C=O in 282 nm is indicative of the chemical reaction.

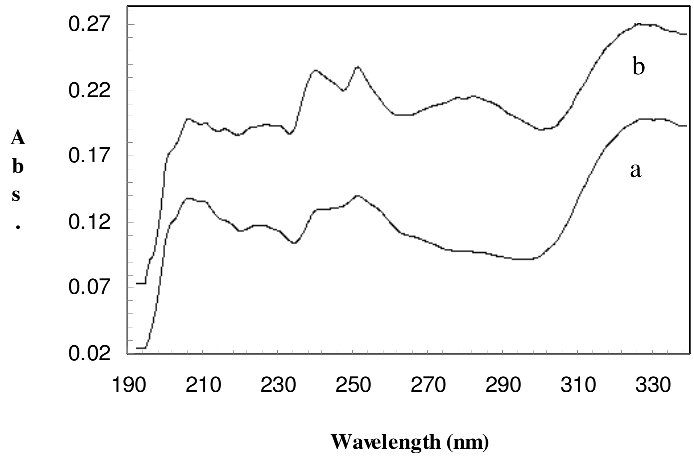


Fig. 1. DRS spectra of (a) GA and (b) GMA-GA

Effect of pH: pH is an important parameter for adsorption of Hg(II) from aqueous solution because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction[32]. To examine the effect of pH on the Hg(II) removal efficiency, the pH of initial solution was adjusted to the corresponding pH value (1.0-8.0) using 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH. As shown in Fig. 2, the uptake of Hg(II) depends on pH, where optimum metal removal efficiency occurs at pH 5 and then declining at higher pH. From Fig. 2, almost no adsorption of mercury ions took place on gum arabic and GA-GMA when pH < 2, probably due to the significant competitive adsorption of hydrogen ions. At pH 2-5, the adsorption capacities increased with the increase in pH for both gum arabic and GMA-GA. The adsorption studies at pH > 8 were not conducted because of the precipitation of $Hg(OH)_2$ from the solution[33].

The change in the adsorption characteristics with solution pH (Fig. 2) may be more clearly explained by the following equations, which depict the major characteristic reactions that can take place at the solid-solution interface of GMA-GA:

$$\text{-NH}_2 + \text{H}^+ \rightarrow \text{-NH}_3^+ \quad (1)$$

$$\text{-NH}_2 + \text{Hg}^{2+} \rightarrow \text{-NH}_2\text{Hg}^{2+} \quad (2)$$

$$\text{-NH}_2 + \text{OH}^- \rightarrow \text{-NH}_2\text{OH}^- \quad (3)$$

$$\text{-NH}_2\text{OH}^- + \text{Hg}^{2+} \text{ (or HgOH}^+\text{)} \rightarrow \text{-NH}_2\text{OH}^- \cdots \text{Hg}^{2+} \text{ (or -NH}_2\text{OH}^- \cdots \text{HgOH}^+\text{)} \quad (4)$$

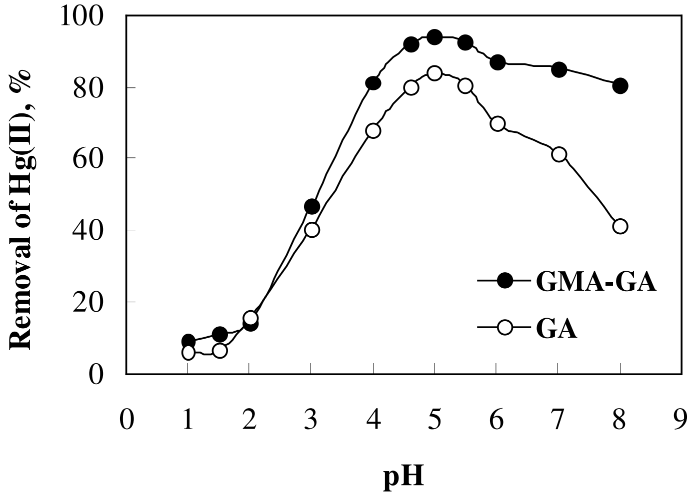


Fig. 2. Effect of solution pH on Hg(II) percentage removal using GA and GMA-GA

The protonation and deprotonation reactions of the amine groups of GMA-GA in the solution was indicated by eqn. 1 and 2 shows the formation of surface complexes of mercury ions with the amine groups and eqn. 3 describes the adsorption of OH^- ions from the solution through hydrogen bond at high pH values[34]. The reaction in eqn. 1 favoured the protonation of the amine groups to form $-NH_3^+$ at lower pH values. With the conversion of more $-NH_2$ groups to $-NH_3^+$, there were only fewer $-NH_2$ sites available on the GMA-GA surface for Hg^{2+} adsorption through eqn. 2. Moreover, the electrostatic repulsion between the Hg^{2+} and the surfaces of the GMA-GA increased with the formation of more $-NH^{3+}$ sites on the surface. All these effects would result in the reduction of Hg^{2+} adsorption on the GMA-GA with decreasing solution pH values. On the other hand, with the increase of solution pH, the reaction in eqn. 1 proceeded to the left, resulting in an increase of the number of $-NH_2$ sites on the surface of GMA-GA for mercury ion adsorption through eqn. 2, thus increasing the adsorption capacity. At higher solution pH, the reaction in eqn. 3 might proceed. This reaction on one hand could reduce the adsorption of mercury ions through surface complexation in eqn. 2, but on the other hand might increase the adsorption of mercury ions through the electrostatic attraction as indicated in eqn. 4.

Effect of adsorbent dose: The dependence of Hg(II) sorption on adsorbent dosage was studied by varying the amount of GMA-GA and gum arabic from 0.25 to 3.0 g, while keeping other parameters (pH and contact time) constant. Fig. 3 presents the Hg(II) removal efficiency for two types of adsorbents used. Form Fig. 3, it can be observed that removal efficiency of the GMA-GA and gum arabic improved with increasing dose from 0.25 g to 1 g. This is expected due to the fact that the higher dose of adsorbents in the solution, the greater availability of exchangeable sites. This also suggests that after a certain dose of adsorbent, the saturation of

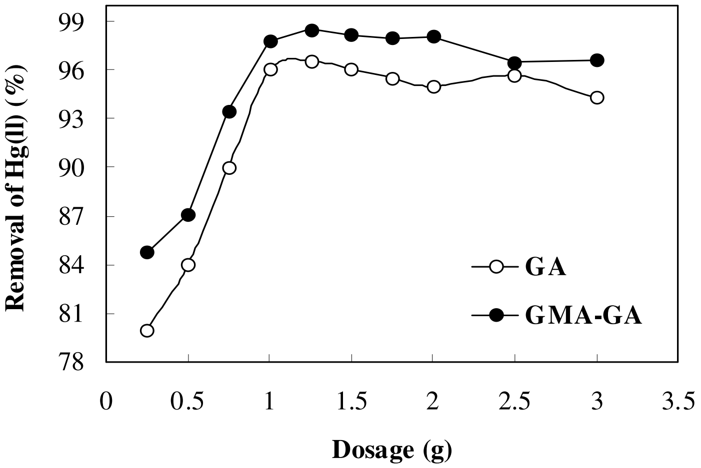


Fig. 3. Effect of sorbent dosage on removal of Hg(II) (%)

available metal binding sites occurs and hence the amount of Hg(II) bound to the adsorbent and the amount of Hg(II) in solution remains constant even with further addition of the dose of adsorbent.

Effect of agitation period: Fig. 4 shows the effects of contact time on percentage Hg(II) removal with the absorbent dose, pH and temperature held constant. The removal efficiencies increased rapidly as contact time increases with optimum removals of 98.0 and 96.0 % obtained around 7 and 10 min for GMA-GA and gum arabic, respectively. The rapid removal is an important consideration in water treatment processes as it controls the volume of liquid that can be treated in a given time and impacts the process selection and design. Moreover, this rapid two-stage kinetics is typical of the physico-chemical uptake of metals to surface binding sites[35].

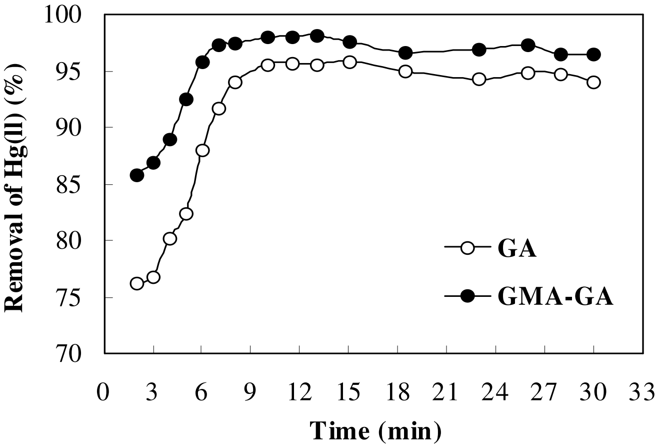


Fig. 4. Effect of contact time on Hg(II) percentage removal using GA and GMA-GA

Adsorption isotherms: The empirical Freundlich relationship does not indicate a finite uptake capacity of the adsorbent. This relationship can be reasonably applied to the low or intermediate concentration ranges. Freundlich isotherm equation is given by:

$$q_e = k_f C_e^{1/n} \quad (5)$$

and is linearized as:

$$\log q_e = \log k_f + 1/n \log C_e \quad (6)$$

where q_e is the equilibrium adsorption capacity of Hg(II) on the adsorbent (mg/g), C_e the equilibrium Hg(II) concentration in solution (mg L^{-1}), k_f Freundlich constant (L mg^{-1}) and n is heterogeneity factor. The present data, plotted in Fig. 5, shows relatively good agreement for Freundlich relationship (correlation coefficient, R^2 = 0.9699 and 0.9858 for gum arabic and GMA-GA, respectively). Linearity of the relationship indicates strong binding of Hg(II) to the adsorbents gum arabic and GMA-GA. The values of k_f and n were determined from the slope and intercept of the linear plot of log q_e *versus* log C_e (Fig. 5) and the data are given in Table-1. From Table-1, the adsorbent GMA-GA seems better with respect to slope than gum arabic.

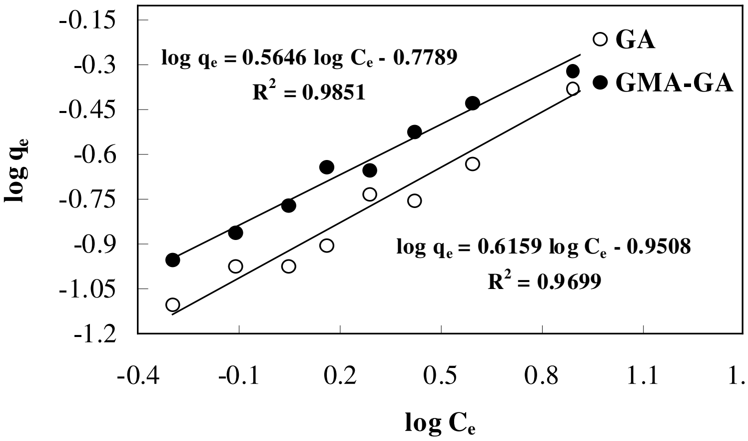


Fig. 5. Freundlich linear isotherm for the adsorption of Hg(II) using GA and GMA-GA

TABLE-1
LANGMUIR AND FREUNDLICH CONSTANTS FOR THE UPTAKE OF MERCURY

Adsorbent type	Freundlich constants		Langmuir constants	
	n	k_f	q_m	b
GA	1.62	0.11	17.1	0.012
GMA-GA	1.77	0.17	34.0	0.007

Langmuir isotherm is the most widely used two-parameter equation. The relationship is of the form:

$$q_e/q_m = bC_e/\,(1+bC_e) \qquad (7)$$

or

$$C_e/q_e = C_e/q_m + 1/bq_m \qquad (8)$$

q_m the maximum capacity of adsorbent (mg g^{-1}) and b is the Langmuir adsorption constant (L mg^{-1}). Langmuir isotherm for the present data is drawn in Fig. 6 between C_e and C_e/q_e. q_m and b are calculated from the slope ($1/q_m$) and intercept ($1/bq_m$) (Table-1). The isotherm lines have good linearity (correlation coefficient, R^2 = 0.9919 and 0.9935 for gum arabic and GMA-GA, respectively) indicating strong binding of Hg(II) to the surface of gum arabic and GMA-GA. On the other hand, the mean qm value in the present investigation for GMA-GA is better than those obtained for gum arabic.

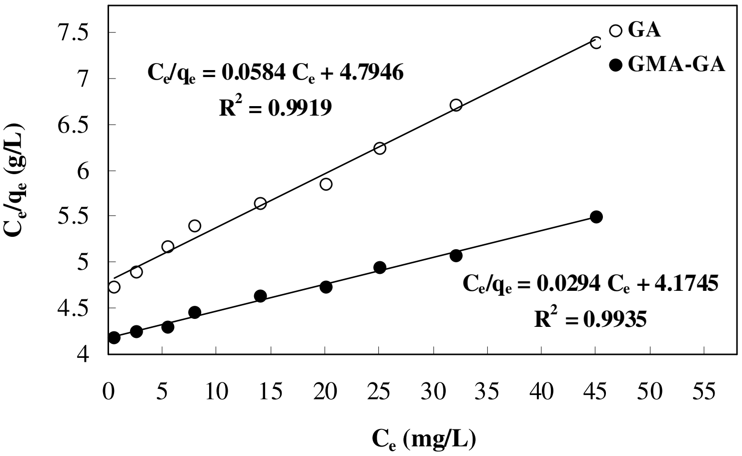


Fig. 6. Langmuir linear isotherm for the adsorption of Hg(II) using GA and GMA-GA

It has been reported that the effect of isotherm shape with a view to predicting if an adsorption system is 'favourable' or 'unfavourable'. The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which is defined by:

$$R_L = 1/(1+bC_0) \qquad (9)$$

where C_0 is the initial Hg(II) concentration (mg L^{-1}) and b is Langmuir adsorption equilibrium constant (mL mg^{-1}). The parameter indicates the isotherm shape according to Table-2.

TABLE-2
EFFECT OF SEPARATION FACTOR ON ISOTHERM SHAPE

R_L value	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

The values of R_L calculated for different initial Hg(II) concentrations for gum arabic and GMA-GA are given in Table-3. The R_L values show that favourable adsorption of Hg(II) on gum arabic and GMA-GA takes place, therefore gum arabic and GMA-GA are favourable adsorbents[36].

TABLE-3
R_L VALUES BASED ON THE LANGMUIR EQUATION

Hg(II) initial concentration (mg L^{-1})	R_L values	
	GA	GMA-GA
2	0.976	0.986
5	0.943	0.966
8	0.912	0.947
10	0.893	0.934

Kinetic studies: The order of adsorbate-adsorbent interactions has been described using various kinetic models[37]. Traditionally, the pseudo first order model derived by Lagergren finds wide application. In the case of adsorption preceded by diffusion through a boundary, the kinetics in most cases follows the pseudo first order rate equation of Lagergren:

$$dq_t/dt = K_{ad} (q_e - q_t) \quad (10)$$

Plot of log $(q_e - q_t)$ *versus* t gives a straight line for first order kinetics and the adsorption rate constant, K_{ad} is computed from the plot. Lagergren plot of log $(q_e - q_t)$ *versus* agitation time t, for the present data is not linear. Hence, pseudo first order kinetics can not describe the mechanism of Hg(II)-GA and GMA-GA interactions. On the other hand, several authors have shown that pseudo second order kinetics can describe these interactions very well in certain specific cases[12,38]. The pseudo second order kinetics is given by:

$$dq_t/d_t = K_{ad} (q_e - q_t)^2 \quad (11)$$

Rearranging the above equation, we get in the linear form

$$t/q_t = 1/(K_{ad}q_e^2) + (1/q_e)\ t \quad (12)$$

If the pseudo second order kinetics is applicable, the plot of (t/q_t) *versus* t gives a linear relationship that allows computation of q_e and K_{ad}. The pseudo second order model which considers the rate-limiting step as the formation of chemisorptive bond involving sharing or exchange of electrons between the adsorbate and the adsorbent is therefore applied. In the present studies the kinetics is investigated with 20 mL of aqueous solution of initial Hg(II) concentration of 50 mg L^{-1} at room temperature with dosages of 1 g in the agitation time interval of 1.5 to 40 min. Fig. 7 indicates the suitability of pseudo second order rate equation. The second order rate constant is in the range of 0.003 to 0.007 g mg^{-1} min^{-1}. The suitability of second order rate equation for the present data indicates chemisorption as the rate controlling step. From the Fig. 7, the following pseudo second order rate equations are obtained.

$$\text{For GMA-GA} \quad t/q_t = 0.2068\ t + 12.156 \quad (13)$$

$$\text{For GA} \quad t/q_t = 0.2571\ t + 9.0841 \quad (14)$$

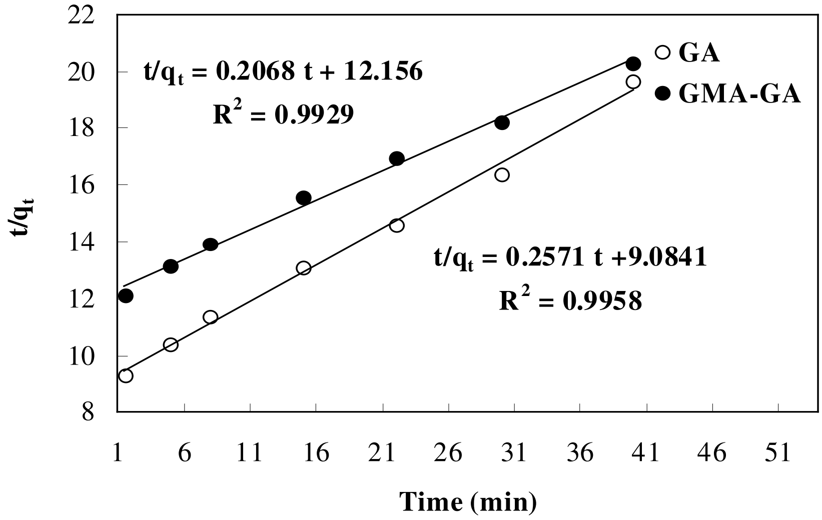


Fig. 7. Pseudo second order kinetics for the adsorption of Hg(II) using GA and GMA-GA

Desorption studies: For practical applications, the regeneration and reuse of an adsorbent are important. From the pH study, it has been found that the adsorption of mercury ions on GMA-GA at pH = 2.0 was negligible. This suggested that desorption of mercury ions from GMA-GA was possible around pH 2.0. Therefore, HCl solutions of different pH (2.5, 2.0 and 1.5) were used to examine the desorption study. It was found that the desorption percentages were 79, 91 and 93 % in the HCl solutions of pH 2.5, 2.0 and 1.5, respectively. The higher desorption efficiency at lower pH value could be referred to the sufficiently high H^+ concentration, which led to the strong competitive adsorption.

The reusability of GMA-GA as an adsorbent was also studied after the desorption process. The reusability was checked by following the adsorption-desorption process for three cycles and the adsorption efficiency in each cycle was analyzed. The adsorption process was followed by shaking 25 mg of GMA-GA in 5 mL of 200 mg L^{-1} mercury ion solution at pH 5.0 for 10 min at 200 rpm. The desorption study was conducted in the HCl solution at pH 1.5 as mentioned above. It was found that the adsorption capacities were 31.24, 32.64 and 32.18 mg/g in the first, second and third adsorption-desorption cycles, respectively. Thus, the GMA-GA adsorbent can be reuse almost without any significant loss in the adsorption performance.

Conclusion

Gum arabic (GA) was chemically modified with glycidyl methacrylate (GMA) with an appropriated mixture of water and DMSO. The presence of GMA groups in the GMA-GA structure was detected by diffuse reflectance spectroscopy. The cross-linking reaction of GMA-GA gave rise to the formation of a GMA-GA solid sample. The GMA-GA sorbent showed significant pH dependence, which had a considerable effect on the mercury removal and adsorption mechanism. The GMA-GA exhibited high performance as an adsorbent for removal of Hg(II) from aqueous solutions. Adsorption of Hg(II) by gum arabic and GMA-GA are depended contact time, pH solution and dosage of adsorbent. The adsorption data fit in both Freundlich and Langmuir isotherms and is well described by pseudo second order kinetics. In addition, acid solutions at pH = 2 was suitable for the desorption of mercury ions and the reusability of GMA-GA was good.

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