

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/



Efficient Hg (II) Ions Sorption from their Aqueous Solutions by Using

Microwave-assisted Grafted Psyllium Husk

A. M. Yousif^a and E. S. Gad^{a,b*}

^a Chemistry Department, College of Science and Arts, Jouf University, Alqurayyat, Saudi Arabia ^b Department of Chemistry, Faculty of Science (Men's Campus), Al-Azhar University, Nasr City 11884, Cairo,

Egypt.

Abstract

To utilize the psyllium husk, an anionic polysaccharide, for developing it to Hg (II) removal from aqueous solutions, we have prepared psyllium based polymeric networks by grafting glycidyl methacrylate (GMA) polymeric chain and by using N,N⁰-methylene bis-acrylamide (N,N-MBAAm) as a cross-linker. It was synthesized under microwave irradiation without adding any radical or catalyst with 140 % grafting efficiency using 850 W MW power in 70 second at 2 M GMA, and 10g/L psyllium husk concentrations as optimum conditions. The synthesized sorbent was characterized by FT-IR, SEM, and thermal techniques. The effect of various parameters such as pH, time, and temperature towards Hg (II) adsorption by the sorbent was analyzed. The optimum conditions of Hg (II) ions sorption were pH (6), 30 min contact time, and 5 x 10^{3-} M initial concentration of mercury. The kinetic data followed the second-order kinetics and reached the maximum uptake capacity after 20 min. Regeneration efficiency was found to be 96% over 5 cycles using acidified thiourea. Recorded high removal efficiencies (up to 97.6 %) of heavy metal ions from real industrial wastewater sample make the investigated sorbent promising in the field of wastewater treatment.

Keywords: Psyllium, Graft, copolymer, HG(II), sorption, Kinetic studies

1. Introduction

During the last decades, Water pollution has received increasing attention due to the increased discharge of heavy metal pollutants in the aquatic systems as an undesirable product of the industrial revolution [1]. Heavy metal ions create a significant risk for animals, plants and the ecosystem. Mercury is a common heavy metal that has high toxicity and is found in many industrial wastes, such as electroplating industries, mine tailing, fertilizers, pulp plastic, paper, battery manufacturing, paint, and oil refining [2, 3]. Mercury spreads in the environment through the wastewater lines of these chemical industries mainly in the form of organic mercury (CH₃Hg) inorganic mercury (HgCl₂) and elemental mercury [Hg] [4, 5]. Humans absorb mercury and its compounds through the gastrointestinal tract, skin, and lungs. Mercury is then stored in the liver, kidneys, spleen, brain, and bones, leading to mutagenic and carcinogenic problems. The minor concentration of Hg (II) ions in water is toxic as the maximum permissible limit is 0.002 ppm in aquatic systems according to the World Health Organization (WHO) recommendations [6]. As a result of the foregoing facts, mercury removal from water has been a challenge for the global scientific community for decades. Many chemical treatment processes have been developed to remove heavy metal ions (including mercury) from industrial effluents. These include reverse osmosis, ion exchange, flocculation, electrodialysis, evaporation, chemical precipitation, membrane separation, and chelation [7]. Most often, these methods are of high cost and may generate secondary pollutants. Sorption from solutions using low-cost sorbents may be considered as an economical and effective method for the removal of different pollutants [8-17]. Psyllium husk, as a biosorbet, is a naturally occurring and renewable polymer and has been used as sorbent in many

*Corresponding author e-mail: <u>e_said56@yahoo.com</u>.; (E. S. Gad).

Receive Date: 21 December 2021, Revise Date: 03 February 2022, Accept Date: 13 February 2022

DOI: 10.21608/EJCHEM.2022.112471.5098

©2022 National Information and Documentation Center (NIDOC)

research works. It is a natural polysaccharide obtained from Plantago ovate plant seeds and consists of arabinoxylan (arabinose 22.6%, xylose 74.6%). It is a fibrous white material possesses hydrophilic nature and it forms a clear colorless gel by water sorption [18]. Psyllium husk, by itself, could not be satisfactorily applied in chelating or sorbing heavy metal ions as it has a low sorption capacity as well as limited durability against acidic media. Therefore, modification of psyllium husk can be carried out to achieve adequate structural and textural properties for efficient sorption. Two main modification methods (through grafting copolymerization in the presence of functional cross-linker) are free radical polymerization method [19] using an external initiator and microwave irradiation method [20]. In fact, the increasing interest in green and clean eco-friendly chemistry has nominated the use of microwave over free radical polymerization method in the grafting modification as it reduced the use of poisonous solvents as well as reducing the reaction period, leading to clean and high yield product formations [21].

The present work deals with the preparation and characterization of psyllium-based binary grafted polymer via grafting glycidyl methacrylate (GMA) with psyllium husk using N,N⁰-methylene bisacrylamide (NN-MBAAm) as a cross-linker for mercury sorption. The grafting was made under microwave irradiation without adding any radical or catalyst, various reaction parameters were varied and the results were recorded. The graft copolymer was characterized via FTIR, SEM, and thermal analysis. Hg (II) sorption capacity of the produced sorbent [Psy-g-Poly (GMA)] through the batch method experiments has also been investigated.

2. Materials and Methods

2.1. Chemicals and instruments

Plantago psyllium husk (psy), Glycidyl methacrylate (GMA), N,N⁰-methylene bisacrylamide (NN-MBAAm) were Sigma Aldrich products. Mercuric chloride (HgCl₂) and all other chemicals were Prolabo products and were used as received. Double-distilled water was used for synthesis and sorption analysis.

Chemical structures of newly synthesized psyllium husk and grafted psyllium [Psy-g-Poly (GMA)] were examined by Fourier transform infrared (FTIR) (Nicole - 6700) spectrophotometer with wavenumber range of 4000 to 500 cm⁻¹. The surface morphology of pure psyllium husk and grafted psyllium were studied by scanning electron microscope (JSM, 6490). The solution pH was measured using a digital pH meter (Globe instrument auto pH meter). Hg (II) and other heavy metal ions sorption capacities of Psy-g-Poly (GMA) were measured by using inductively coupled plasma optical emission spectrometer (ICP-OES, Model SPS-1500R; SEIKO Instruments Inc.).

2.2. Synthesis of Psy-g-Poly (GMA)

Grafted psyllium [Psy-g-Poly (GMA)] was synthesized via graft copolymerization of GMA onto psyllium husk by irradiating the reaction mixture in a domestic microwave oven in a flask containing NN-MBAAm as a cross-linker. The microwave radiation was periodically paused (at the desired temperature) and resumed (after cooling) at frequent intervals to minimize the competing homopolymer formation and also to prevent formation of unwanted vapors [22].

The grafting reaction was repeated using different values of monomer concentration, microwave power, exposure time, psyllium husk concentration, temperature, and pH. Preferably with methanol, the reaction product was precipitated and then washed with double-distilled water for the removal of unreacted monomer. The polymer was dried in a hot air oven (55 °C) then washed again with acetone (many times) followed by washing with double-distilled water to remove the attached homopolymer from the grafted copolymer. The grafted copolymer was then dried in a hot air oven at 55 °C until a constant weight is obtained. The grafting percentage (%G) of the Psy-g-Poly (GMA) was calculated using the equation [21]:

$$%G = \frac{\text{wt.of grafted psyllium}}{\text{wt.of pure psylliumhusk}} \times 100\%$$
(1)

2.3. Hg (II) sorption method and sorption conditions optimization

A stock solution of 5×10^{-2} M of Hg (II) was obtained by dissolving an appropriate weight of HgCl₂ in 1 L of double-distilled water. All sorption experiments were studied by batch sorption method.

Hg (II) sorption by Psy-g-Poly (GMA) was investigated by varying only one parameter while the others held fixed [23]. Various sorption parameters and their ranges [pH (from 4 to 10), temperature (from 25 °C to 55 °C), 30 min contact time, and 100 ml contact volume at 5×10^{-3} M concentration of Hg (II)] were studied.

2.3.1. Effect of pH

Uptake experiments using different initial pH values were performed by placing 0.1 g of Psy-g-Poly (GMA) sample in a series of flasks containing 100 ml of 5×10^{-3} M concentration of Hg (II) ions solution at equilibrium time of 30 min and at 25°C. Desired pH value was controlled by using 0.1 M HCl or 0.1 M NaOH. The contents of the flask were agitated with a vibromatic shaker at 300 rpm. At the end of the experiment, five milliliters of the solution were taken where the residual concentration of metal ion was determined. the sorption capacity, q_e (mmol/g) was calculated according to the following formula [2].

$$q_{e} = \frac{\left(C_{i} - C_{f}\right)}{W} \times V$$
(2)

where C_i and C_f (mmol/g) are the initial and final Hg (II) concentrations, respectively. V (mL) is the volume of metal solution, and W (g) is the weight of sorbent.

2.3.2. Effect of contact time and kinetic studies

Kinetic studies were completed by using the optimum conditions of 5×10^{-3} M concentration of Hg (II), 0.1 g of sorbent dose at pH 6, and a temperature of 25 °C. 5 mL portions of the solution of the desired batch experiment were taken at different time intervals (from 0 to 25 min) and centrifuged. The residual concentrations of Hg (II) ions were determined at the studied time intervals from which the sorption capacities were calculated.

2.3.3. Effect of Temperature

Temperature effect on Hg (II) sorption was investigated in the range from 25 to 55 °C under other constant parameters of 5×10^{-3} M concentration of Hg (II), 0.1 g of sorbent dose at pH 6 and 30 min equilibrium time using the above-mentioned batch method.

2.4. Regeneration experiment

Regeneration experiments were carried out by equilibrating 0.1 g of Psy-g-Poly (GMA) with 100 mL of $5 \times 10-3$ M Hg (II) ions solution for 1 hour then the maximum uptake was estimated. The sorbent was then washed repeatedly by double-distilled water. By a solution of 0.6 M thiourea acidified with a few drops of 0.2 M H2SO4, the loaded sorbent was regenerated then carefully washed using double-distilled water for the second run reuse. The regeneration efficiency was calculated according to the following equation [2].

% Efficiency =
$$\frac{\text{Uptakein the second run}}{\text{Uptakein the first run}} \times 100\%$$
 (3)

2.5. Treatment of a real industrial wastewater sample

A 100 ml of a real sample obtained from wastewater effluent from batteries factory was conducted to a batch experiment using 0.1 g of Psy-g-Poly (GMA) under the constant parameters of pH 6 and a temperature of 25 °C. The concentrations of five metal ions (Hg (II), Co (II), Cd (II), Cr (VI), and Mn (II)) were analyzed before and after the treatment using ICP-OES instrument.

3. Results and discussion

Grafting of GMA on psyllium husk structure and polymeric network formation were made by microwave-induced polymerization. Linking sites of NN-MBAAm as a cross-linker were illustrated in Scheme 1. Cross-linking of psyllium husk led to the formation of a three-dimensional network structure shown in Scheme 2. The proposed mechanism of grafting cross-linked psyllium husk with GMA was illustrated in Scheme 3.



Scheme	1:-	Linking	sites	of	'NN-MBAAm
--------	-----	---------	-------	----	-----------

CH2	CH2
- chi	CH
ço	ço
NH	NH
CH2	CH2
ŅН	NH
ço	
CH L	CH.

Scheme 2:- Three-dimensional network structure of cross-linked psyllium (C-Psy-OH)



Scheme 3:- The proposed mechanism of grafting cross-linked psyllium husk with GMA to form Psy-g-Poly (GMA)

3.1. Effect of various parameters variation on grafting percentage

To find out the optimum conditions for the grafting under microwave without adding any radical or catalyst, various reaction parameters were varied as follow:

3.1.1. Monomer concentration

Grafting percentage increased with increasing monomer concentration under the fixed psyllium husk concentration of 10g/L, 850 W microwave power, and 70 second exposure time and 25ml reaction volume (Fig.1). The increase in grafting percentage can be attributed to the availability of more grafting sites as well as the existence of additional monomers for grafting.

3.1.2. Effect of temperature

It is obvious from Figure 2 that grafting yield increases with increasing temperature and reached to maximum value 140 % at 95 $^{\circ}$ C.

3.1.3. Effect of monomer solvent

Methanol recorded the highest grafting efficiency among the other studied higher members of alcohols

689

as it was able to swell the backbone effectively relative to other alcohols. The recorded grafting percentage was 56 % (Figure 3).



Figure 1:- % G change with different concentrations of the monomer at a fixed concentration of psyllium husk concentration of 10g/L, exposure time 70 of seconds, MW power of 850W, and solvent volume of 25ml



Figure 2:- % G change with changing temperature at a fixed GMA concentration of 2M, psyllium husk of 10g/L, exposure time 70 seconds, MW power 850W, and solvent volume of 25ml



Figure 3:- % G change with different alcohols at fixed GMA concentration of 2M, psyllium husk concentration of 10g/L, exposure time of 70 seconds, and solvent volume of 25ml

3.1.4. Effect of exposure time

Grafting increased with increasing exposure time (10: 70 second) under the fixed conditions listed in Fig.4. This is maybe related to the availability of more microwave energy resulting in generating extra radicals for graft copolymerization.

3.1.5. Effect of pH

Figure 5 showed the effect of pH on grafting percentage. Grafting copolymerization was carried out in acidic (0.5N HCl), neutral (Double-distilled water), and basic (0.5N NaOH) media, and a maximum grafting percentage of 140 % was found in neutral medium. On the other hand, low grafting percentages of 14 % (for acidic medium) and 82% (for basic medium) were observed. The least grafting efficiency found in acidic medium may be attributed to the fact that H⁺ ion and active OH⁻ groups on the backbone chain were replaced by Na⁺ and Cl⁻ ions, respectively causing a decrease in the number of active sites present on the backbone chains leading to the negligible grafting percentage.

3.1.6. Psyllium husk concentration

% G change with change in psyllium husk concentration in the range of 5 to 15 gram/ L at the fixed GMA concentration of 2M at 850W microwave power, 70 sec exposure time at 95 °C, and reaction volume of 25 ml was investigated. Maximum % G of 140 % was recorded at 10g/L concentration of psyllium husk (Fig. 6). After that, by increasing psyllium husk concentration, % G decreased. This finding may be related to the increase in the reaction medium viscosity that hinders the normal reaction and also may be related to the decrease in GMA: psyllium husk ratio.



Figure 4:- % G change with different exposure time of microwave at fixed GMA concentration of 2M, Psyllium husk concentration of 10 g/L, and solvent volume of 25ml.



Figure 5:- % G change with Acidic, basic and neutral medium at fixed GMA concentration of 2M, Psyllium husk concentration of 10g/L, exposure time of 70 seconds, and solvent volume of 25ml.



husk concentration at fixed GMA concentration of 2M, exposure time 70 seconds, and solvent volume of 25ml.

3.1.7. Effect of microwave power

On increasing microwave power from 200-850 W (Fig. 7), grafting percentage increased at the fixed concentration of GMA of 2 M, 10 g/L concentration of psyllium husk, and exposure time of 70 seconds). This may be attributed to the formation of more radicals for graft copolymerization during high microwave power [21].

From the previously reported findings, we can conclude that the maximum grafting percentage of 140 % was obtained at the optimized exposure time of 70 seconds, MW power of 850W, GMA concentration of 2 M, psyllium husk concentration of 10g/L, and temperature of 95 °C.

3.2. Characterization

3.2.1. FTIR spectra

Spectral analysis was used to confirm the graft copolymerization reaction. FTIR of pure psyllium husk (Figure 8(a)) showed a peak at 3367 cm⁻¹ due to OH stretching vibration, a band at 2930 cm⁻¹ due to - OH and/or -CH stretching vibration [23]. Peak at 1043 cm⁻¹ is due to C-O-C starching vibration. Peaks at 535

Egypt. J. Chem. 65, No. 9 (2022)

cm⁻¹ and 858 cm⁻¹ are due to pyranose ring. The FTIR spectrum of Psy-g-Poly (GMA) Figure 8(b) showed an additional band (apart from usual peaks in psyllium husk) at 1655 cm⁻¹ due to C=O stretching of amide, a peak at 1466 cm⁻¹ due to the NH and CN in plane bending, a peak at 897 cm⁻¹ due to NH and CH out of plane bending of amide. An additional peak is observed at 1753 cm⁻¹ due to the (C=O) group in GMA [24]. These findings obviously confirm the grafting process of psyllium husk.



Figure 7:- % G with changing microwave power at fixed GMA concentration of 2M, psyllium husk concentration of 10 g/L, exposure time 70 seconds, and solvent volume of 25ml



Figure 8:- (a) FT-IR spectra of the Psyllium husk and (b) Psy-g-Poly (GMA).

3.2.2. Scanning electron microscopy

The surface morphologies of pure psyllium husk and Psy-g-Poly (GMA) were studied by SEM and shown in Fig. 9. It is observed from the SEM images that the psyllium husk has smooth and homogeneous surface morphology. On the other hand, the modified psyllium has a rough and heterogeneous surface morphology elucidating the success of the grafting process.

3.2.3. Thermal analysis

Thermal degradation of psyllium husk and grafted psyllium were studied using TGA as shown in Fig. 10. The TGA curve of psyllium husk was divided into three stages (Fig. 10 a). The first weight-loss stage of 14% ranges between 30:250 °C may be related to the loss of surface sorbed moisture and/or softening of the amorphous structure of psyllium husk. The second stage of weight-loss 46% was in the range of 250:300 °C due to the dehydration of saccharide rings and psyllium husk depolymerization. The third stage of weight-loss 37% between 300:440 °C clearly indicates the complete degradation of psyllium husk. TGA curve of Psy-g-Poly (GMA) was also divided into three stages (Fig. 10 b). The first weight-loss stage of 11% occurred in the temperature range of 25:250 °C may be attributed to the loss of water. The second step involves the weight-loss of 39% in the temperature range of 250:300 °C. The third stage between 300:500 °C corresponds to a weight-loss of about 44%. This indicates the complete decomposition of the grafted psyllium chain, elucidating better thermal stability of Psy-g-Poly (GMA) if compared with pure psyllium husk. The increase in thermal stability was due to the presence of NN-MBAAm and GMA moieties which were successfully grafted on psyllium husk leading to the strengthening of its composition through grafting as well as three-dimensional networks structure formation.



Fig. 9:- SEM images of the (a) Psyllium husk (b) Psyg-Poly (GMA)



poly (GMA).

3.3. Effect of various parameters onto the sorption process

3.3.1. Effect of pH

The sorption of Hg (II) as a function of pH was shown in Fig. 11. The uptake studies were carried out in the range of pH from 2 to 6 (prior the precipitation limit of the metal ion). The observed uptake increase during the studied pH range from 40 % to 93 % is because, at low pH values, mercury exists as Hg (II), while at pH 6, mercury exists as a singular positive ion

Egypt. J. Chem. 65, No. 9 (2022)

[Hg (OH)]⁺ which reacts with only one site on the carboxylate moieties in GMA sites [24]. A schematic representation of [Hg (OH)]⁺ sorption on Psy-g-Poly (GMA) was illustrated in Scheme



Scheme 4:- A schematic representation of [Hg (OH)]⁺ sorption on Psy-g-Poly (GMA)



Fig.11:- Effect of pH variation on Hg (II) sorption using the optimum conditions of contact time of 30 minutes, Hg (II) solution volume of 100 ml (5 x 10^{-3} M), and temperature of 25 °C

3.3.2. Effect of contact time and kinetic studies

Fig. 12 showed the uptake of Hg(II) from its aqueous solution on Psy-g-Poly (GMA) at pH = 6. Up to 20 minutes, the increase in the uptake capacities may be attributed to the increase in the metal-binding time with vacant sorption sites. Further increase of time after 20 minutes (equilibrium time) did not lead to a significant increase in the sorption capacity as all available active sites were occupied.

The obtained sorption/time data were applied to two kinetic models, including pseudo-second and pseudo-first-order models [25, 26]. The pseudosecond-order model is formulated as

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$
 (4)

where qe and qt refer to the amount of metal ions sorbed (mmol/g) at equilibrium and at time t, respectively, and k_2 is the pseudo-second-order equilibrium rate constant (g mmol⁻¹ min⁻¹). The pseudo-first order model is formulated as

 $log (q_e - q_t) = log q_e - (k_1/2.303) t$ (5) where k₁ is the pseudo-first-order equilibrium rate constant (min⁻¹). The kinetic parameters are determined from the linear plotting of (t/q_t) versus t for pseudo-secondorder or from plotting log (q_e-q_t) versus t for pseudofirst-order. The data fitted well the pseudo-second order formula as shown in Table 1. Meanwhile, the data did not fit the pseudo-first order model as observed from R^2 value and calculated q_e value if compared to that obtained experimentally (Table 1).



Fig.12:- Effect of contact time on Hg ions sorption using the optimum conditions of pH value of 6, Hg (II) solution volume of 100 ml (5 x 10^{-3} M), and temperature of 25 °C.

3.3.3. Effect of temperature

Temperature effect on Hg (II) sorption was investigated in the range of 25-55 °C under other constant parameters and the results were shown in Table 2. The slight increase in Hg (II) ions sorption with increasing temperature from 25 to 30 °C may be due to the increase in the exposed active sites due to the sorbent swelling. Further increase in the temperature decreased the sorption extent because of some desorption phenomenon due to the exothermic nature of Hg (II)/sorbent interaction.

3.4. Regeneration Experiments

Regeneration efficiency was found to be 96% over five cycles. Then, the efficiency gradually decreased to about 89% after 9 cycles with a standard deviation of $\pm 1\%$. These findings reveal the stability of the resins for repeated use.

3.5. Application of Psy-g-Poly (GMA) for real industrial wastewater sample treatment

Data of the studied sample were recorded in Table 3. The high-observed removal ratios indicate the high efficiency of Psy-g-Poly (GMA) towards the sorption of the studied metal ions even at their low concentrations. These results indicate that the studied sorbent is promising in the field of different wastewater treatments.

3.6. Comparison Study

Comparative sorption capacities of various sorbents toswards Hg (II) ions at different initial concentrations were summarized in Table 4. As illustrated in the table, when the initial concentration of Hg (II) ion varied between 100 and 3369 mg/L, our sorbent equilibrium uptake is quite high if compared with the other works. Besides, our sorbent achieved a satisfactory uptake and selectivity towards Hg (II) ion at very low initial concentrations below 100 mg/L.

Table 1:- Pseudo-second and Pseudo-first-order sorption parameters of the sorption of Hg (II) on cell- Psy-g-Poly (GMA) at initial concentration of $5x10^{-3}$ M and $25^\circ C$

	Pseudo-first order				Pseudo-second order			
q _e (mm	^{exp)} ol/g)	q _{e (calc)} (mmol/g)	$\frac{K_1}{(\min^{-1})}$	\mathbb{R}^2	$q_{e (calc)}$ (mmol/g)	$\begin{array}{c} \text{K}_2 \text{ (g mmol}^{-1} \\ \text{min}^{-1} \text{)} \end{array}$	\mathbb{R}^2	
2.	4	3.4	2.14	0.85	3.1	0.028	0.98	

Table 2:- Effect of temperature on the sorption of Hg (II) on cell- Psy-g-Poly (GMA) at initial concentration of $5x10^{-3}$ M and 30 minutes equilibrium time

Temp. (°C)	25	30	35	40	45	50	55
$q_e (\text{mmol/g})$	2.40	2.52	2.35	2.26	2.19	2.16	2.11

Table 3:-	ICP	results	of wastewater	[.] real sampl	le before a	nd after t	reatment	with	the inv	estigated	resin
										en garrea	

	endeer real sample selere al	a alter di cathitente () ithi the	ar estigated resin
Metal ion	C_i (mg/L)	C _f (mg/L)	Removal efficiency (%)
Hg(II)	1.51	0.08	94.7
Mn (II)	0.071	0.001	98.5
Co (II)	0.65	0.061	90.6
Cd (II)	0.171	0.013	92.4
Cr (VI)	2.67	0.061	97.6

Sorbent name	Ci	$q_e (mg/g)$	Reference
	(mg/L)		
PAN-AA	200	180.4	[13]
St-PEG-PAA	300	158.2	[14]
AgNPs-St-PEG-PAA	300	182.6	[16]
P3HT-CNT/Ti	200	164.1	[16]
PAA-MWCNTs	18	5.6	[27]
PAN-PRGO	150	164.8	[17]
P(AA-co-MA-co-DMTU)	400	198.2	[28]
CTS-g-PAA	3669	798.9	[29]
Cys-C@Fe3O4	100	94.3	[30]
cell- Psy-g-Poly (GMA)	3550	918.8	This work
	1002	481.2	
	20	18.9	
	1.5	1.4	

Table 4. Adsorption capacity of various sorbents for Hg (II) ion at different initial concentrations

Table 4 abbreviations: acrylonitrile (AN); acrylic acid (AA); polyethylene glycol (PEG); silver nanoparticles (AgNPs); 3-Hexylthiophene (P3HT); carbon nanotube (CNT); multiwall carbon nanotubes (MWCNTs); partial reduction graphene oxide (PRGO); partial reduction graphene oxide (MA); dimethylthiourea (DMTU); chitosan (CTS); cysteine (Cys); carbon (C).

4. Conclusion

The synthesis of a binary grafted copolymer of Psyllium [Psy-g-Poly (GMA)] was successfully achieved by using microwave irradiation without adding any radical or catalyst by grafting GMA using N,N-MBAAm as a cross-linker. The grafting copolymerization was carried out using different monomer concentrations, microwave power, exposure time, psyllium husk concentration, time, temperature, and pH to achieve maximum grafting percentage. The synthesized grafted psyllium exhibited high efficiency towards mercury ions sorption. The sorption of Hg (II) ions by Psy-g-Poly (GMA) was found to be pHdependent and pH 6 was found to be suitable for the sorption process. The sorption followed the secondorder kinetic model and reached the maximum uptake capacity after 20 min. The loaded sorbent was easily regenerated at reasonable efficiency using acidified thiourea. The obtained sorbent showed remarkable efficiency in the removal of Hg(II) along with other heavy metal ions from real industrial wastewater samples. The sorption characteristics of Psy-g-Poly (GMA) presented in this paper make it promising in the field of heavy metal ions removal from different aquatic systems.

5. Conflicts of interest

There are no conflicts to declare

References

- [1] Prabhat K. Rai, Heavy metal pollution in aquatic ecosystems and its phytoremediation using wetland plants: an ecosustainable approach, *International Journal of Phytoremediation* 10 (2008) 133–160.
- https://doi.org/10.1080/15226510801913918
- [2] Ahmed M. Donia, Ahmed M. Yousif, Asem A. Atia, Hassnaa M. Abd El-Latif, Preparation and characterization of modified cellulose adsorbents

Egypt. J. Chem. 65, No. 9 (2022)

with high surface area and high adsorption affinity for Hg (II), *Journal of Dispersion Science and Technology*, 35 (2014) 380–389.

- https://doi.org/10.1080/01932691.2013.791626
- [3] Mustafa Tuzen, Ahmed Sari, Durali Mendil, Mustafa Soylak, Biosorptive removal of mercury (II) from aqueous solution using lichen (Xanthoparmelia conspersa) biomass: kinetic and equilibrium studies, *Journal of Hazardous Materials* 169 (2009) 263–270.
- https://doi.org/10.1016/j.jhazmat.2009.03.096
- [4] Siddhesh N. Pawar, Kevin J. Edgar, Alginate derivatization: a review of chemistry, properties and applications, *Biomaterials* 33 (2012) 3279– 3305.
- https://doi.org/10.1016/j.biomaterials.2012.01.007
- [5] Lissette Agüero, Dionisio Zaldivar-Silva, Luis Pena, Marcos L. Dias, Alginate microparticles as oral colon drug delivery device: a review, *Carbohydrate Polymers* 168 (2017) 32–43.
- https://doi.org/10.1016/j.carbpol.2017.03.033
- [6] Tawfik A. Saleh, Mustafa Tuzen, Ahmet Sarı, Polyamide magnetic palygorskite for the simultaneous removal of Hg (II) and methyl mercury; with factorial design analysis, *Journal of Environmental Management* 211 (2018) 323–333. https://doi.org/10.1016/j.jenvman.2018.01.050
- [7] L.L. Tavlarides, J.H. Bae, C.K. Lee, Solvent Extraction, Membranes, and Ion Exchange in Hydrometallurgical Dilute Metals Separation, Separation Science and Technology, 22 (1987)
- 581–617. https://doi.org/10.1080/01496398708068970
- [8] Ahmed M. Yousif, Osama F. Zaid, Waleed A. El-Said, Emad A. Elshehy, Ibrahim A. Ibrahim, Silica nanospheres-coated nanofibrillated cellulose for removal and detection of copper(II) ions in

aqueous solutions, *Industrial & Engineering Chemistry Research*, 58 (2019) 4828–4837. <u>https://doi.org/10.1021/acs.iecr.8b06343</u>

- [9] Ahmed M. Yousif, Osama F. Zaid, I.A. Ibrahim, Fast and selective adsorption of As(V) on prepared modified cellulose containing Cu(II) moieties, *Arabian Journal of Chemistry*, 9 (2016) 607–615. https://doi.org/10.1016/j.arabic.2015.02.004
- [10] Sherif A. Labib, Ahmed M. Yousif, Ibrahim A. Ibrahim, Asem A. Atia, Adsorption of rhodium by modified mesoporous cellulose/silica sorbents: equilibrium, kinetic, and thermodynamic studies, *Journal of Porous Materials*, 25 (2018) 383–396. https://doi.org/10.1007/s10934-017-0449-3
- [11] Ahmed M. Yousif, Sherif A. Labib, Ibrahim A. Ibrahim, Asem A. Atia, Recovery of Pt (IV) from aqueous solutions using magnetic functionalized cellulose with quaternary amine, *Separation Science and Technology*, 54 (2019) 1257–1268.

https://doi.org/10.1080/01496395.2018.1534866

- [12] Ahmed M. Yousif, Masateru Nishioka, Yoshito Wakui, Toshishige M. Suzuki, Adsorption of Pd(II), Pt(IV), and Rh(III) on a ligand encapsulated polymer resin assisted by thermal heating or microwave irradiation, *Solvent Extraction and Ion Exchange*, 30 (2012) 77–87.
- https://doi.org/10.1080/07366299.2011.581053
- [13] Adel A. El-Zahhar, Abubakr M. Idris, Mercury(II) decontamination using a newly synthesized poly(acrylonitrile-acrylic acid)/ammonium molybdophosphate composite exchanger, *Toxin Reviews*, 1 (2020) 1–13.
- https://doi.org/10.1080/15569543.2020.1824191
- [14] A. Saberi, M. Sadeghi, E. Alipour, Design of AgNPs-base starch/PEG-Poly (acrylic Acid) hydrogel for removal of mercury (II). *Journal of Polymers and the Environment*, 28 (2020) 906– 917.

https://doi.org/10.1007/s10924-020-01651-9

[15] Ahmed M. Yousif, Rapid and selective adsorption of Rh(III) from its solutions using cellulose-based biosorbent containing iminodiacetate functionality, *Separation Science and Technology*, 46 (2011) 2341–2347.

https://doi.org/10.1080/01496395.2011.595034

[16] C. Long, X. Li, Z. Jiang, P. Zhang, B. Feng, Adsorption-improved MoSe₂ nanosheet by heteroatom doping and its application for simultaneous detection and removal of mercury (II), *Journal of Hazardous Materials*, 413 (2021) 125470–125487.

https://doi.org/10.1016/j.jhazmat.2021.125470

[17] Fathi S. Awad, Khaled M. AbouZied, Ayyob M. Bakry, Wean M. Abou El-Maaty, Ahmed M. El-Wakil, M. EL-Shall, Polyacrylonitrile modified partially reduced graphene oxide composites for the extraction of Hg(II) ions from polluted water, *Journal of Material Science*, 56 (2021) 7982–7999. https://doi.org/10.1007/s10853-021-05797-2

[18] Deepak Kumar, Jyoti Pandey, Pramendra Kumar, Vinit Raj, Psyllium mucilage and Its use in pharmaceutical field: an overview, *Current Synthetic and Systems Biology*, 5 (2017) 1–7 POL 10 4172/2222 0727 1000124

DOI: 10.4172/2332-0737.1000134

[19] James W. Anderson, Lisa D. Allgood, Ann Lawrence, Linda A. Altringer, George R. Jerdack, David A. Hengehold, Jorge G. Morel, Cholesterollowering effects of psyllium intake adjunctive to diet therapy in men and women with hypercholesterolemia: meta-analysis of 8 controlled trials, *The American Journal of Clinical Nutrition* 71 (2000) 472–479.

https://doi.org/10.1093/ajcn/71.2.472

- [20] V. Singh, P. Kumar, R. Sanghi, Use of microwave irradiation in the grafting modification of the polysaccharides–A review, <u>Progress in Polymer</u> <u>Science</u>, 37 (2012) 340-64.
- https://doi.org/10.1016/j.progpolymsci.2011.07.005
- [21] P. Jatav, N. Agarwal, A Study: Graft copolymerization of methylmethacrylate onto psyllium, IOSR *Journal of Applied Chemistry*, 8 (2015) 4–12.
- DOI: 10.9790/5736-08520412
- [22] G. Sen, S. Mishra, G. Rani P. Rani R. Prasad, Microwave initiated synthesis of polyacrylamide grafted Psyllium and its application as a flocculant, *International Journal of Biological Macromolecule*, 50 (2012) 369–375.
- https://doi.org/10.1016/j.ijbiomac.2011.12.014
- [23] Ahmed M. Yousif, Ehab S. Gad, H. El-Sharary, Fabrication of a magnetic cellulose sorbent functionalized with amine moieties and studying its selective sorption behaviour towards copper (II) ions from their aqueous solutions, *Egyptian Journal of Chemistry*, 64 (2021) 7195–7201.
- DOI: 10.21608/ejchem.2021.56138.3204
- [24] D. Kumara,b, J. Pandeya, N. Khanb, P. Kumarb, Patit P. Kundu, Synthesize and characterization of binary grafted psyllium for removing toxic mercury (II) ions from aqueous solution, *Materials Science & Engineering C*, 104 (2019) 109900.
- https://doi.org/10.1016/j.msec.2019.109900
- [25] Ehab S. Gad, Medhat Owda, R. Yahia, A Novel Starch Nanoparticle Citrate Based Adsorbent for Removing of Crystal Violet Dye from Aqueous Solution, *Egyptian Journal of Chemistry*, 63 (2020) 2075–2095.

DOI: 10.21608/EJCHEM.2019.16593.2013

[26] Ahmed M. Yousif, Asem A. Atia, Osama F. Zaid, I.A. Ibrahim, Efficient and fast adsorption of phosphates and sulphates on prepared modified cellulose, *Journal of Dispersion Science and Technology*, 36 (2015) 1628–1638.

Egypt. J. Chem. 65, No. 9 (2022)

https://doi.org/10.1080/01932691.2014.988346

- [27] H. Cheng, J. Yu, K. Zeng, G. Hou, Application of Poly(Acrylic Acid)-Multiwalled Carbon Nanotube Composite for Enrichment of Rrace Hg(II), *Plasma Processes and Polymers*, 10 (2013) 931–937. https://doi.org/10.1002/ppap.201300014
- [28] Mi Y. Kim, H. Seo, Tai G. Lee, Removal of
- Hg(II) ions from aqueous solution by poly(allylamine-co-methacrylamidecodimethylthiourea), *Journal of Industrial and Engineering Chemistry*, 84 (2020) 82–86.
- https://doi.org/10.1016/j.jiec.2019.12.023
- [29] M. Zhang, P. Yang, G. Lan, Y. Liu, Q. Cai, J. Xi, High crosslinked sodium carboxyl methylstarch-g -poly (acrylic acid- co-acrylamide) resin for heavy metal adsorption: Its characteristics and mechanisms, *Environmental Science and Pollution Research*, 27 (2020) 38617–38630. https://doi.org/10.1007/s11356-020-09945-0
- [30] X. Xu, A. Schierz, N. Xu, X. Cao, Comparison of the characteristics and mechanisms of Hg(II) sorption by biochars and activated carbon, *Journal* of Colloid and Interface Science, 463 (2016) 55– 60.https://doi.org/10.1016/j.jcis.2015.10.003