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Glutathione@Fe3O4 Nanoparticles as Efficient Material for the Adsorption of Mercury(II)from Water at Low Concentrations

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Strictly as per the compliance and regulations of:

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Wilfredo Marimón-Bolívar α & Edgar E. González σ

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I. INTRODUCTION

The contamination by heavy metals in bodies of water is animportant environmental problem since there is a facility of dispersion in great distances due to its biogeochemical cycle, which leads to affect the integrity of the organisms of several ecosystems [1]. Many countries in the world have been highly affected by one of them: Mercury. Contamination due to this metal is a problem that compromises at a global level the food safety and the quality of water for human consumption.[2–4].

Although mercury is released into the environment from natural sources, coal-fired power plants and gold mining have been identified as the largest source of mercury[5,6].For example, 2493.8 tons of mercury were released into the environment from coal combustion between 1978 and 1995. On the other hand, mercury is used in open-pit mining by 15 million miners in over 70 countries in artisanal and small-scale gold mining[7], as it happens in Peru where gold production in Madre de Dios mine was 1583 kilograms of gold in 2016 but that process released an estimated 30–40 tonnes of mercury each year into water[8].

This situation is alarming because mercury does not need to be present in large quantities to generate health risks since it proved to be carcinogenic to mammals due to theirA capacity of accumulation in organisms, biomagnification through the trophic chains and their resistance to biodegradation [9,10]. Methylmercury effects in humans include severe damage to the nervous system, congenital malformations, and even death.These affectations take place becausethe multiple Hg chemical species have hydrophobic properties and a strong affinity for the biological compounds in the sulfhydryl groups as well as DNA binding[11]. Moreover, conventional techniques for the remediation of heavy metals in water such as chemical precipitation, adsorption, ion exchange, membrane filtration, reverse osmosis, coagulation and flocculation, electrochemical treatment techniques, advanced oxidation processes, and adsorption processes have some disadvantages. Problems such as high energy demand, a large amount of chemical compounds required, production of large volumes of waste, lead to the search for optimization or development of these processes with new materials.[12].

Within a large numbers of new materials developed, Iron Oxide Nanoparticles, especially Magnetite (Fe_3O_4), are shown as a promising alternative for the application in environmental remediation since they have a superparamagnetic behavior. This behavior allows controlling the material in such a way that it minimizes its dispersion to bodies of water and therefore possible contamination[13,14]. However, it is necessary to consider that the production of this material could generate a high environmental impact to ensure responsible application.

For this purpose, the green synthesis of magnetic nanoparticles has been studied where plant extracts, marine algae and biomolecules are used as reducing, and stabilizing agents.Around the optimization of magnetic properties necessary for the correct implementation of these materials on a

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large scale, biomolecules have shown better results. However, these green materials have not been applied for metal removal at levels of concentrations like the levels found in the effluents to establish real adsorption potentials.

For these reasons, the adsorption of mercury (II) on magnetic nanoparticles modified with Glutathione (*Glutathione@MNPs*) was studied under different pH values, low concentrations, temperature, and ionic strength conditions. Although there are previous studies[15–17] where glutathione is used as an agent modifier of magnetic nanoparticles, these studies synthesize the magnetic material through the traditional coprecipitation route and then perform a process of functionality. This way to obtain the magnetic material leads to little feasibility in large scale application due to the environmental impact generated, so that this work allows to use glutathione as a synthesis agent and modifier in a single step which would allow the implementation of this process in environmental remediation tasks.

II. EXPERIMENTAL

a) Materials

Iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), sodium hydroxide (NaOH) and $HgCl_2$ standard solution (1000 mg/L) were purchased from Merck. Reduced L-Glutathione ($C_{10}H_{17}N_3O_6S$) was purchased from Sigma-Aldrich. All chemicals were analytically pure and used as received without further purification, and all solutions were prepared with double-distilled water.

b) Synthesis of Fe_3O_4 nanoparticles by a green method using glutathione

Fe_3O_4 NPs obtained through the green method (*Glutathione@MNPs*) were synthesized using a methodology described in a previous work[18]. Briefly, 10 mL of a $FeCl_3$ (0.1 mol/L) solution was added to a 100-mL beaker under vigorous mechanical stirring at 75°C. On reaching this temperature, 20 mL of an aqueous solution of L-Glutathione (0.214mol/L) was added dropwise into the beaker with the pH value of the mixed solution adjusted to 10. A temperature value of 85°C was reached and it remained in agitation for one hour. Then the nanoparticles were separated by magnetic field application, washed several times with deionized water and alcohol and dried in vacuum at 40°C for 12 hours.

c) Adsorption studies

Glutathione@MNPs obtained by a green route were added at 25°C to aqueous solution of mercury with concentration of 1 ppm prepared from Cl_2Hg standard solution at different pH values (2-10) adjusted with solutions of (0. 1M) NaOH or HCl with concentration of nanoparticles of 100 mg/L and a stirring speed of 140 rpm for a standard time of 2 hours. The final concentration of the Hg(II) ions was measured using atomic absorption spectroscopy. The adsorption capacity is calculated on the difference of concentrations at the beginning and the end of the process[19, 20]:

$$q_e\left(\frac{mg}{g}\right) = \frac{V(C_0 - C_f)}{m}$$

Where q_e is the adsorption equilibrium of the capacity (mg/g), Co and C_f are the initial concentrations and the equilibrium (mg/l) of the ion in the solution, V is the volume (L) of solution and m is the mass (g) of used adsorbent. Considering the favorable conditions of adsorption tests, kinetics and adsorption isotherms were studied.

d) Adsorption kinetics and adsorption isotherm

The adsorption capacity of Hg (II) ions was studied as a function of time. Therefore, an optimal contact time of the adsorption of Hg (II) on the nanoparticles was established and under this equilibrium time condition, the adsorption kinetics was studied. To determine an adequate kinetic model, the adsorption was evaluated in four equations (Table 1)[21,22].

Table 1: Kinetic and isothermal models used

Kinetic model	Mathematical expression
Pseudo-First Order	$q_t = q_e(1-e^{-k.t})$
Pseudo-Second Order	$q_t = \dfrac{t}{\left(\dfrac{1}{(k_2 \cdot q_e^2)}\right)+(t/q_e)}$
Elovich	$q_t = \dfrac{1}{\beta}\log(\alpha\beta)+\dfrac{1}{\beta}\log(t)$
Intraparticular diffusion	$q_t = k\sqrt{t}+C$

Isotherm	Mathematical expression
Langmuir	$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$
Freundlich	$q_e = K_F C_e^{1/n}$
Temkin	$q_e = Bln(A) + Bln(C_e)$
Sips	$q_e = \frac{q_m (K_F C_e)^{1/n}}{1 + (K_F C_e)^{1/n}}$

Where k_1 is the constant of Pseudo-First Order (min^{-1}), k_2 is the kinetic constant of Pseudo-second order (g/(mmol·min)), α constant of Elovich's equation (mmol/(g·min)); (g/mmol), k diffusion constant, q_e adsorption capacity at equilibrium (mmol/g), q_t adsorption capacity at the measured time (mmol/g)[19, 23], C equilibrium concentration (mmol/L), q_m amount of metal or contaminant needed to form a surface monolayer (mmol/g), K_L is the equilibrium constant of Langmuir, and K_F is the equilibrium constant of Freundlich. N is the exponent of each characteristic equation [24–27].

Alternatively,adsorption isotherms were carried out by changing the initial concentration of nanoparticles, while the initial metal concentration was 1 mg/L and a constant temperature value was 20°C. The experimental isotherms used for the study of the elimination of metal ions are shown in Table 1.

e) Adsorption thermodynamics

To establish parameters for process scaling studies, the enthalpy change (ΔH^o), free energy of Gibbs (ΔG^o) and entropy (ΔS^o) were established by the measurement of the adsorption capacity at different temperatures and the subsequent application of the following equations[28]:

$$\Delta G^0 = -RT \cdot lnk_L$$

$$lnk_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

$$\Delta S^0 = (\Delta H^0 - \Delta G^0)/T$$

f) Competitive study with ions

To determine the involvement of ions in the adsorption of mercury on the nanoparticles, lots of tests were carried out with concentrations (0-30 mg/L) of 4 ionic species that are frequently found in bodies of water (magnesium, calcium, zinc).The addition of the ions was carried out with sulfate salts because the sulfate ions are frequent in wastewater. The experiments were carried out in triplicate, and the favorable conditions found in the previous sections were kept constant (pH, time and dose of the material).

g) Study of adsorption capacity in real water

For the application in real water, samples from strategic sites in Colombia were selected, specifically in the department of Bolívar and Cundinamarca. The samples were filtered with a 450 mm filter to simulate the water pre-treatment processes that eliminate the suspended material.

h) Adsorption cycles

Desorption of heavy metals was studied with acid and saline eluents (Hydrochloric Acid HCl, Sodium Chloride NaCl, potassium iodide KI) as a function of its concentration according to the *Lehningerprinciple* for the precipitation of proteins using high ionic strength. The nanoparticles used for the adsorption of the mercury ions are diluted in a volume equal to that of the adsorption batches at a stirring speed of 130 rpm and for a time of 1 hour. The degree of desorption was calculated from the following expression:

$$\%Desorption = \frac{Adsorbed\ Metal}{Recovered\ Metal} \times 100\%$$

III. Results & Discussion

a) Characterization of the nanomaterial

The nanoparticles obtained by a green synthesis using Glutathione were characterized to establish the magnetic properties, size, surface chemistry, crystallographic properties, and elemental composition. FTIR analysis showed characteristic peaks of magnetite. The peaks assigned to the iron oxide core can be observed at 580 cm^{-1} (FeO). Moreover, a low-intensity band was evidenced at 3477 cm^{-1}, which is attributed to amine groups (NH and NH$_2$), and the peak recognised to the SH group was detected at ~2500 cm^{-1} which is typically very weak. Furthermore, bands were perceived at 2920 cm^{-1}, which is associated to CH sp3 bonds[29,30]. Instead, it is important to note that the CO stretch band of the carboxyl group, which is representative of the Glutathione spectrum at 1710 cm^{-1}, is absent. This result can be explained by the bonding pattern of the carboxylic acids on the surface of the nanoparticles. Strong adsorption at 1000 cm^{-1} arises from the stretching of the CO single bond. These results revealed that glutathione was attached to the Fe$_3$O$_4$ nanoparticles as a carboxylate [31].

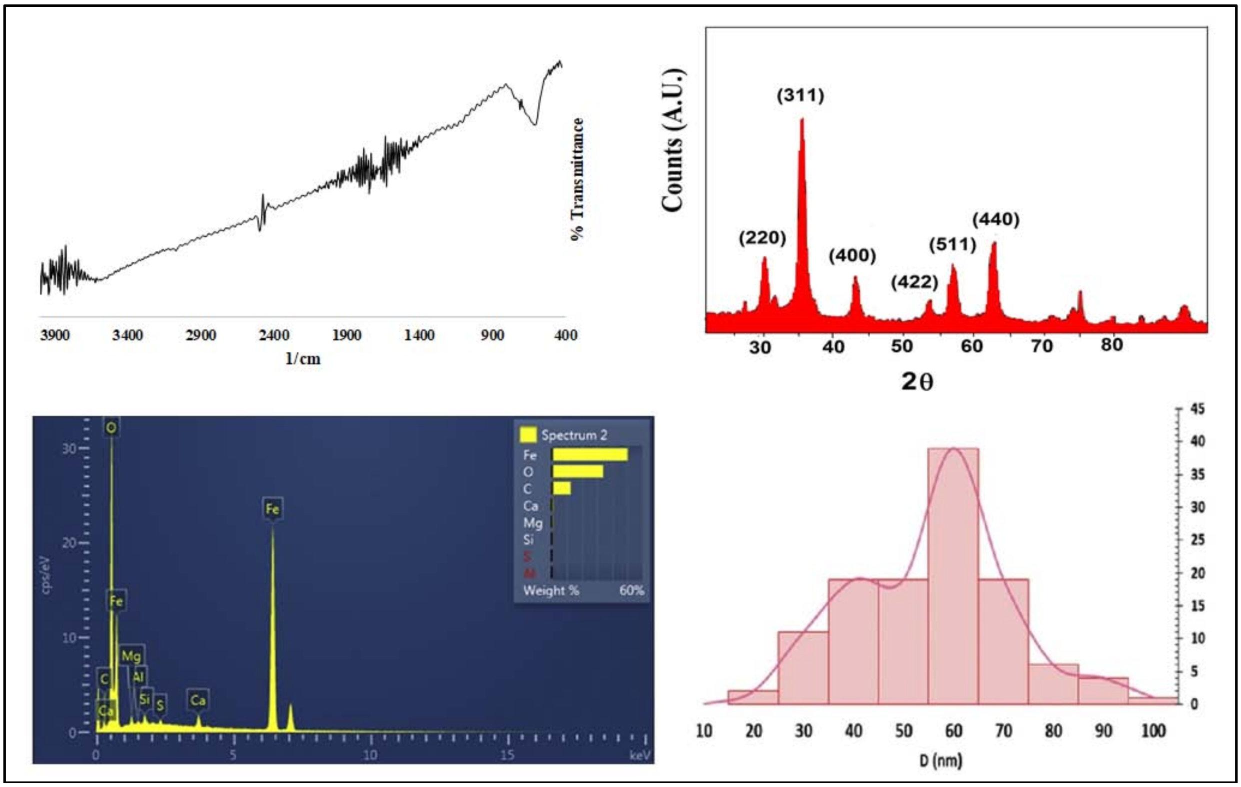

Figure 1: Characterization (FTIR, XRD, EDS, DLS) of Glutathione@MNPs.

XRD characterizations were carried out with CrKα and Cu radiation (1.5406 Å). The angular range was set between 20 and 80° with a scanning speed of 0.04°/s and a step size of 0.04°/s. Fig. 4a and b show the diffractogram of the Glutathione@MNPs. This diffractogram shows indexed peaks as (220), (311), (400), (422), (511) and (440). These peaks correspond to a cubic spinel structure. The crests of XRD were indexed using data from the International Centre for Diffraction Data (ICDD) database. The calculation of the lattice constant yields a value of 8. 30 Å which is close to the value for magnetite: 8. 39 Å. Furthermore, this structure is recognized for having the peak (311) with the highest intensity.

The EDS spectrum is shown evidence the presence of sulfur, which is part of the thiol groups active on the surface according to the FTIR spectrum. The hydrodynamic size was~ 60 nm, while it can be deduced that a greater dispersion in the size of nanoparticles is obtained through green synthesis in comparison to chemical co-precipitation method. Also, this material did not show a reduction in its magnetic properties (Saturation magnetization of 84.5 emu/g) as is usually seen in magnetic nanoparticles obtained by green synthesis, which would make it possible to be used in scale processes [32].

b) Effect of pH

pH is asignificant variable in the behavior of the compounds in the aqueous medium and therefore for the adsorption process since it affects both the protonation of the functional groups of the surface of the adsorbent nanomaterial and the predominance of the chemical species present in aqueous solution. For this reason, adsorption batch studies were performed in a pH range of 3 to 10 (Figure 2).

The adsorption process is favored when the pH values are close to 7 and 8 (neutral) while in very acidic and basic conditions it was reduced. This occurs because an interaction with protonated mercury ions (Hg^{2+}) takes place when the surface charge of the material is negative (-35mV), as in this case when the pH is close to 7.5[18]. Likewise, in these pH values the functional groups SH-, NH-, NH_2, and COOH- are negatively charged, which favors the electrostatic interactions. Otherwise, in acid pH values, amino and carboxyl groups tend to acquire a neutral or positive charge that gives rise to repulsive forces. For high pH values, the adsorption potential decreases due to the abundance of OH- ions that react with the Hg^{2+} ions to form precipitable compounds, which is not conducive to the adsorption process[33–35].

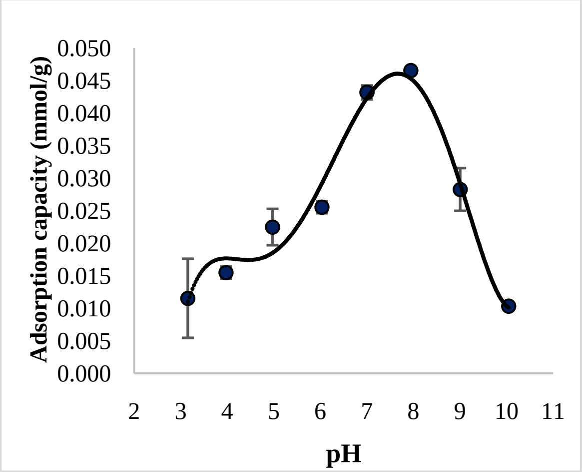

Figure 2: Effect of pH on Hg (II) ions adsorption with *Glutathione@MNPs* (Initial concentration of Hg (II) 1 mg/L; dosage *Glutathione@MNPs* 100 mg/L; T= 25°C; time 60 minutes).

c) Adsorption kinetics

Equilibrium time and adsorption kinetic of Hg(II)on *Glutathione@MNPs* were determined. Figure 3 shows how equilibrium time for the adsorption of Hg(II) was reached in 30 minutes approximately since there is no significant difference with adsorption times after 5 hours.This equilibrium time shown is greater than somereported studies [36,37], which would imply a lower adsorption rate.

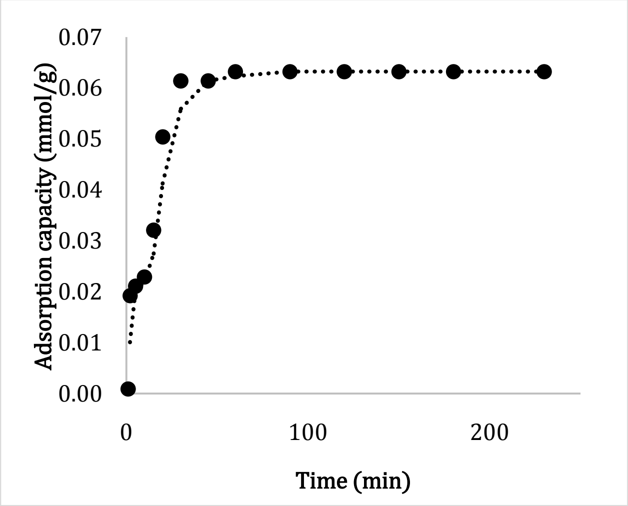

Figure 3: Effect of contact time on the adsorption efficiency of Hg(II). Experimental conditions (1 mg/L Hg, nanoparticle dose 10 mg/L, pH = 8, 140 RPM, 25 ° C).

However, the experimental conditions are different, since the initial concentrations of the metals used are higher compared to the studies reported, especially in the case of mercury. This difference leads taking more time in the process of reaching the steady state since there is a very high amount of metal in the aqueous medium compared to the concentration of the nanomaterial.

To give clarity to the kinetic phenomenon, an experimental data model with kinetic models (Supplementary Figure 1) in its linear form was established. From the linearized adjustment, it can be observed that the kinetic model that best adapts to the experimental data and that can be used to describe the kinetics of adsorption of Hg (II) on *Glutathione@MNPs*is the Pseudo Second Order model (Table two). This means that the speed at which the interaction between the adsorbate and the adsorbent occurs is dominated by the chemical interactions (chemisorption), which prevail over the transport of adsorbate from the liquid phase to the hydrodynamic layer located around the particle, thus as the transport of this hydrodynamic layer to the surface of the adsorbent[38].

Table 2: Kinetic model parameters for adsorption of Hg (II) andCr(VI) by *Glutathione@MNPs*.

		Value
Pseudo-first order	q_e (mmol/g)	0.075
	K_1 (min^{-1})	0.036
	R^2	0.9271
Pseudo- Second order	q_e (mm/g)	0.066
	K_2 (mmol $g^{-1}min^{-1}$)	1.828
	R^2	0.995
Elovich	α (mmol/(g.min))	1.4e-5
	β (g/mmol)	2.9274
	R^2	0.980
Intraparticular Diffusion	K_i ($mmol\cdot g^{-1}\cdot min^{-1/2}$)	2.554
	C (mmol/g)	12.63
	R^2	0.872

It should be noticed that the diffusion limiting effects (mass transfer) could also be minimized by the agitation applied to the system so that transport of ions from the liquid to the surface of the material was facilitated. Similarly, Pseudo-second order model describes how adsorption occurs only at localized sites and does not imply an interaction between the adsorbed ions and that the adsorption energy does not depend on the surface coverage, as well as the absorption of metallic ions in the coals activated is governed by a second order rate equation [39]. From the above, it can be established interaction of Hg ions with the (-SH) groups on the surface of the nanomaterial are the dominant ones in the process, which would serve as an ideal adsorbent for removal contamination in waters by mercury ions.

d) Isothermal studies of the adsorption

Adsorption isotherms describe the equilibrium of the adsorption of a material on a surface at a constant temperature. At high proportions of metal concentration relative to the nanomaterial, the concentration gradient serves as a driving force to overcome the resistance to mass transfer that promotes a favoring of adsorption[40]. The effect of the nanomaterial dose on the efficiency of heavy metal adsorption was carried out at 20°C with different amounts of *Glutathione@MNPs* (10-100mg/L) using a 50 ml batch with an initial concentration of 1 mg/L of mercury (figure 4). As can be seen, the adsorption capacity of the material decreases with the increase of the adsorbent dose.

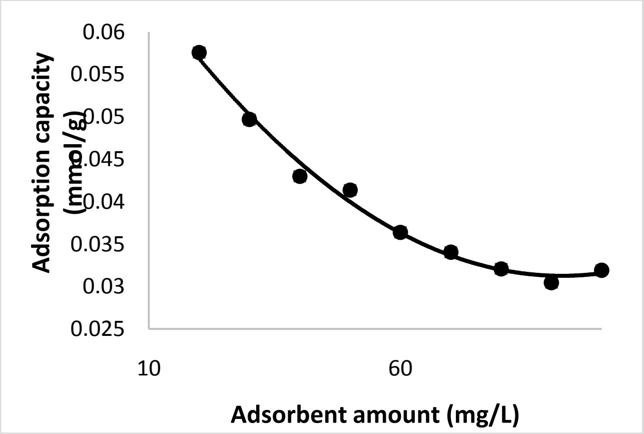

Figure 4: Adsorption isotherm for a) Hg (II)

This phenomenon happens because when the initial concentration of metal used is high, MNPs with the availability of active functional groups decreases concerning the mercury ions. Conversely, when there is a large amount of MNPs, and the final concentration of the metal is lower, the saturation of the active sites is not reached and, therefore, a poorer capacity of adsorption is expressed. For example, a 50% decrease in the dose of nanomaterials (from 100 to 50 mg/L) only leads to an increase in the final mercury concentration from 1.8 to 2.9 mmol/L, but the adsorption capacity of 33 increases at 43 mmol/L.

To determine the adsorption mechanism and the maximum adsorption capacity, the linear adjustments of the isothermal models were made (Supplementary Figure 2). It can be seen that for mercury adsorption, Langmuir equation fits better to the experimental data, which suggests monolayer adsorption on a homogeneous surface. This adsorption is associated with thiol groups, and there is negligible interaction between the species adsorbed[41,42]. These results lead to the fact that, due to the adsorbate /adsorbent interaction, the adsorption energy decreases linearly as the deposition of metal ions increases on the active sites [26,27,35]. The parameters resulting from these linear models are shown in Table 3.

Table 3: Parameters of adsorption isotherms

	Parameter	Value
Langmuir	Q_m	34.843
	KL	0.479
	R^2	0.9827
Freundlich	KF	11.648
	N	1.257
	R^2	0.9822
Temkin	A	1.714
	B	10.82
	R^2	0.9775
Sips	q_m	36.135
	KF	0.0007
	N	0.991
	R^2	0.981

Here we can notice that all correlation coefficients were higher than 0.92, so that, to a certain extent, the four adsorption isotherm models could be used to describe the Hg(II) adsorption equilibrium, but results would be found more in line with the experimental with Langmuir. From the parameters obtained, it is detected that the maximum adsorption capacity (q_m) of *Glutathione@MNPs* on Hg (II) is 36,126 with a Freundlich coefficient of *1/n* of 0.795 that is less than 1, which expresses an outstanding affinity between the adsorbent and metal. Compared with other studies (Table 4), the adsorption capacity shown by the material is satisfactory since, although it is not one of the highest, the initial concentration of mercury for the studies is lower and this is reflected in the adsorption capacity[43,44].

In other words, for the application in remediation, where mercury contamination values are around 0.1 ppm, working with concentrations higher than 10 ppm gives an erroneous adsorption capacity so, when repeating the studies for the materials compared with contractions equal to the one used in this study, the reported adsorption capacities will be much lower. A proof of this is the capacity of adsorption shown in [36] is 74.85 mg/g being the MOF (Metal Organic Framework) one of the materials with the largest surface area and hence very high adsorption capacities but with a high environmental impact when this material is obtained.

Table 4: The Maximum adsorption capacity of several adsorbents on Hg(II).

Material	q_m/C_0 (L/g)	Ref
Dendrimers of polyamidoamine oxide on magnetic graphene	1.162	[45]
Chelation fiber functionalized with thiourea	0.20	[46]
Modifiedtitaniumdioxidenanotubes	0.05	[34]
Chitosan stabilized magnetic iron sulfide nanoparticles	4.42	[47]
Nano-absorbent PGMA (poly glycidyl methacrylate) magnetic functionalized triethyleneteramin	1.08	[48]
Exhausted coffee waste	6.35	[49]
Alkynyl carbon materials	1.61	[50]
Modified silica gel surface with chelating ligand	1.14	[51]
l-Cysteine functionalized bagasse cellulose nanofibers	0.58	[52]
Synthetic FeS and natural pyrite	7.69	[53]
Aminophosphonic acid functionalized polyacrylonitrilefiber	3.68	[54]
This work	34.88	-

e) Adsorption thermodynamics

The study of adsorption thermodynamics offers more information regarding the viability of the adsorption process and the evaluation of thermodynamic parameters such as the enthalpy energy change (ΔH^0), entropy (ΔS^0), Gibbs free energy (ΔG^0) which are significant parameters for the engineering application of the treatment system [55]. For this, adsorption tests were carried out at different temperatures (20-30 °C) as shown in (Supplementary Figure 3). Adsorption capacity was not favored by the increase in temperature. For the determination of the thermodynamic parameters, the graphs of Ln K were made concerning the inverse of the temperatures, where the enthalpy and entropy changes are obtained from the intersection, and the slope of the straight line acquired. These values are shown in Table 5. The positive values of ΔH^0 reveal the endothermic nature of the adsorption process. Likewise, these enthalpy givesindicative of the adsorption mechanisms since it can be used to determine the source of the interaction force that exists between the adsorbent and the adsorbate, indicatingthe binding strength.

Many studies show a decreasing behavior of the capacity of adsorption when the temperature increases, which leads to ΔH^0 being negative. However, other studies have shown an increase in the ability of adsorption when the temperature increases leading to ΔH^0 being positive [56–60]. This difference in behavior is due to the chemical nature of the species that take place in the adsorption[61].

Values of ΔH^0 between 4 and 40 kJ/mol are characteristic of physical interactions, while values of 40 to 800 kJ/mol correspond to chemical interactions [62].

The negative ΔG^0 for the adsorption of Hg (II) suggest that this process is spontaneous and favorable. The positive ΔS^0 indicated the increase in randomness during the adsorption or disorder in the solid-liquid interface that is a sample of the dynamic phenomena of desorption adsorption even at equilibrium.

Table 5: Thermodynamic parameters of the adsorption of Hg on *Glutathione@MNPs*

T (K)	ΔG^0 (kJ $\cdot$ mol^{-1})	ΔH^0 (KJ $\cdot$ mol^{-1})	ΔS^0 (KJ $\cdot$ mol^{-1} $\cdot$ K^{-1})
293	-11.021	45.702	0.118
298	-10.404		
303	-9.828		

f) Adsorption Mechanisms

Based on the previous results (nanomaterial characteristics and the thermodynamic study), the adsorption mechanism of Hg(II) ions on *Glutathione@MNPs* could be established. The process was carried out mainly by ion exchange on the surface of the nanoparticles due to the resulting loads and chemical formations categories of both the metal and the nanomaterial in their dependence on the pH. This formations happens because sulfur is considered to be an electron donor atom that can present complexes with weak metal acids such as mercury[63,64]. Since, a pH close to the neutral values, the mercury species formed ($Hg(OH)_2$, $HgOH^+$ y Hg^{2+}) interacts with the thiol groups in this way:

$$-SH + Hg^{2+} \rightarrow SH - Hg^{+}$$

$$-SH + HgOH^{+} \rightarrow SH - HgOH$$

$$-SH + Hg(OH)_2 \rightarrow -SH \cdots Hg(OH)_2$$

$$-OH + Hg(OH)_2 \rightarrow -O \cdots Hg(OH)_2^{1-} + H^{+}$$

Because the surface of the nanomaterial is homogeneous (thiols, hydroxyls, amines and carboxyl groups) different adsorption mechanisms take place, giving priority to the route governed by the chemical affinity of the thiols towards mercury ions, but when these are saturated adsorption processes physical in the other ligands take place. The oxygen atoms attached to the hydroxyl groups attached to the iron atoms may also behave as weak bases that interact with the mercury ions. [65]:

$$2(-OH) + Hg^{2+} \rightarrow (-O)_2 \cdots HgOH + H^{+}$$

$$-OH + HgOH^{+} \rightarrow -O \cdots HgOH + H^{+}$$

This proposed mechanism can be supported in the same way by the interpretation of FTIR spectra before and after adsorption (Supplementary Figure 4). There is no remarkable difference in the peaks expressed at~ 1628 cm^{-1} (carboxyl groups) or 3480cm^{-1} (amino groups) before and after adsorption. For this reason, it is proposed that the active adsorption sites active for the adsorption of mercury would be the- SH groups (Figure 5 and Supplementary Figure 5).

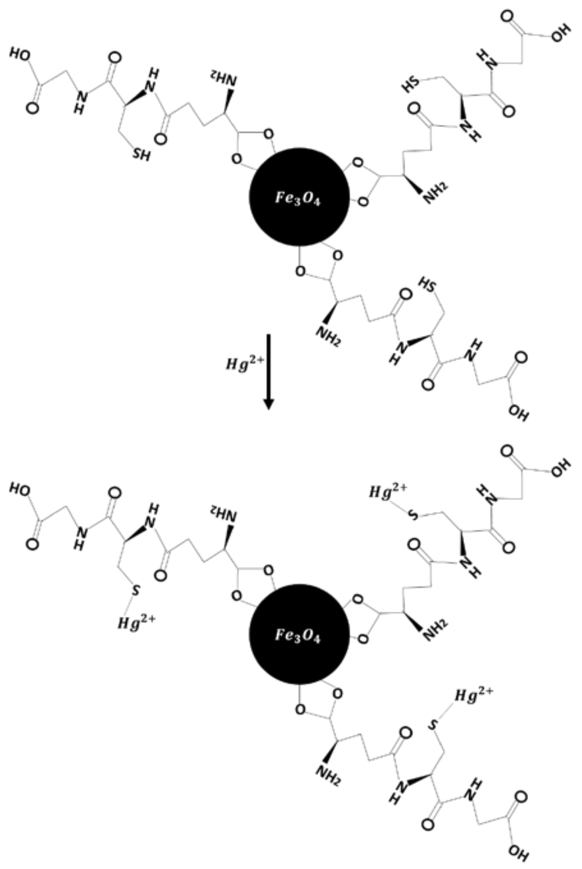

Figure 5: Proposed mechanism adsorption for Hg(II) on *Glutathione@MNPs*.

g) *Ion interference*

The competitive adsorption of ions coexisting to the binding sites is usually a problem when conventional adsorbents are used for the removal of heavy metals. To investigate the effect of coexisting ions, mercury solutions were prepared with cations of an equal or similar charge.In Figure 6, the behavior of nanomaterial is presented in the presence of calcium, magnesium, sodium and zinc ions concerning the adsorption of mercury. As evidenced in [66], the improvement in the capacity of adsorption of mercury ions occurs with the increase of the ionic strength with cations such as Na$^+$, Zn$^+$, Mg^{2+}, Ca^{2+}.

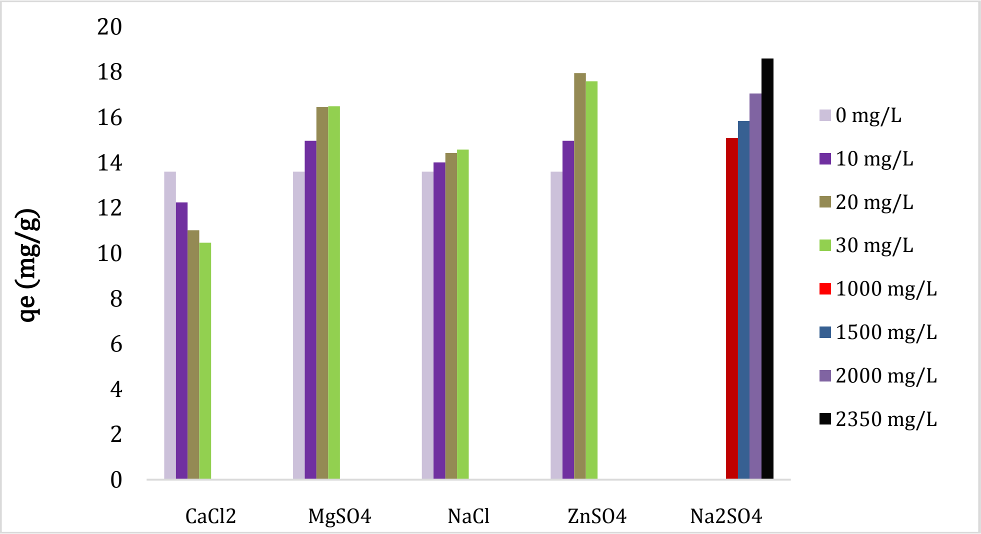

Figure 6: Metal ion interference in Hg (II) adsorption

In this case, the presence of calcium cations interfered in the adsorption process decreasing up to 10%. This could be due to the agglomeration of the nanoparticles which leads to a decrease in the available surface area and the presence of Cl$^-$ anions from the calcium precursor salt used, which form complexes with the mercury ions, thus decreasing the interaction with thiol groups [67]. In the case of the influence of sulfate ions, interference is studied with concentrations around the limit of allowed discharges (~1500 mg/L). It can be seen that when sulfates coexist with mercury ions, the adsorption process is not affected, but on the contrary, there is a favoring of the interactions that can be associated with the fact that sulphate ions could eliminate electrostatic repulsions that mercury could have with the positive charges of the surface of the material, decreasing the entropy of the system and thus optimize the adsorption.

h) Desorption and reusability

To evaluate the possibility of regeneration and reusability of the *Glutathione@MNPs* as an adsorbent, batch desorption experiments were conducted. From Figure 7, it can be observed that for the concentrations studied potassium iodide (KI) is the one that best performs the process. This favourability in the process shown by KI is given that the iodine ions have a high affinity for the Hg(II) atoms that cause the phenomenon of saline displacement in comparison with the dissociation and union of mercury with the Chlorine or hydroxyl ions.

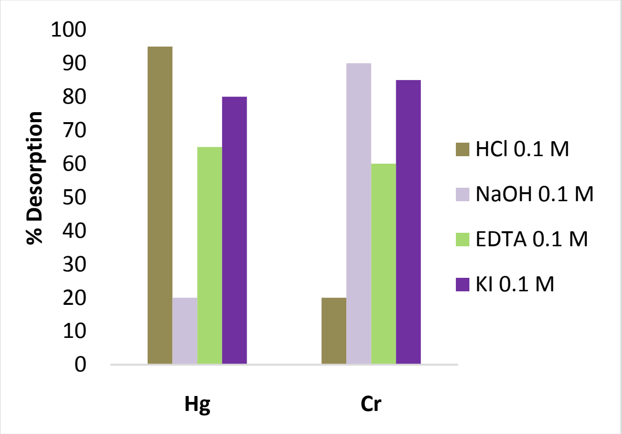

Figure 7: Percentages of recovery of Hg and Cr using different eluents.

Reuse tests showed a decrease in the percentage of adsorption higher than 20% only after the tenth cycle of mercury adsorption (Figure 8). These results could be an indicative for the favorability in the application of this material in process at scale.

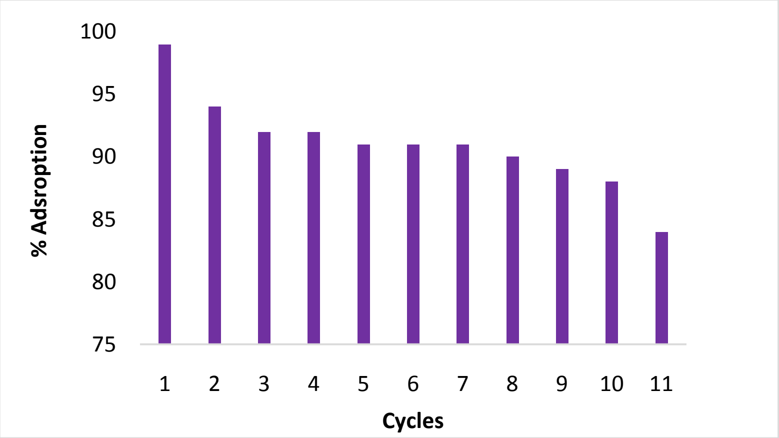

Figure 8: Consecutive adsorption cycles for the adsorption of Hg on *Glutathione@MNPs*.

i) Tests with real water

To survey capability of *Glutathione@MNPs* for removal of Hg (II) from real water, some batch experiments were conducted. Concentrations of the initial physicochemical parameters before adsorption were analyzed, and the results were summarized in Table 6. It should be noticed that the assessment of the presence of mercury and the best evaluation of the adsorption potential of *Glutathione@MNPs* on mercury ions, made an addition of 100 ppb of the metal before treatment, which is a value 10 times higher than the average of the limits of wastewater discharges allowed by resolution 0631 from Colombia for the different economic sectors[68]. The number of nanoparticles added to each treatment was 40 mg/L with an adsorption time of 1 hour at 25°C and a stirring speed of 130rpm.

Table 6: Characteristics of surface and residual water before and after treatment

		Bogotá River	Wetland	San Francisco River	WWTP	San Jorge River
pH		6.30	7.36	5.99	5.32	6.05
Dissolved oxygen (mg/L)		3.4	4.9	6.3	1.5	4.01
DQO (mg/L)		58	45	143	459	50
Conductivity (μS/cm)		272	501	681	747	303
Sulphate (mg/L)		5	11	1	8	6
Nitrates (mg/L)		0.1	0.1	ND	0.3	0.1
Hg (II) (ppb)	Before	1928	1067	1116	984	582
	After	246	153	156	565	78

The results indicated that Hg (II) in real water was removed, and the removal efficiency of Hg(II) reached an average of 78%. It can be observed that in rivers and wetland the percentage of removal is greater than 85% indicating capacity of adsorption. In the case of WWTP, adsorption capacity was not equally favorable (less than 50%), may be due mainly to the physicochemical conditions found, especially the acid character that is lower than the other trials. Likewise, the conductivity value of the sample is higher, which indicates a presence of ions in solution that could interfere in the adsorption process, so an initial pre-treatment of pH adjustment and a decrease of conductivity could increase the efficiency of the process.

These results show that, despite the coexistence of other compounds and non-ideal laboratory characteristics, the function of adsorption of material towards mercury ions is not affected, which would indicate an implementation potential in this type of waters.

IV. CONCLUSIONS

The results obtained confirmed that the material of *Glutathione@MNPs* can eliminate mercury (II) ions from aqueous solutions efficiently. This adsorption depends strongly on parameters such as initial metal concentration, pH, contact time and coexisting ions.

The adsorption process follows an isotherm behavior of Langmuir for mercury ions with maximum adsorption capacity on mercury ions of 34.8 mg/g under conditions of mercury concentration of 1 mg/L.

The adsorption kinetics follows a Pseudo-second order regime for mercury with an equilibrium time of Less than 30min. The coexistence of metals from real waters such as magnesium and zinc does not interfere in the removal of mercury. The thermodynamics of the process shows that the interaction with the mercury ions is of chemical order (especially with the functional groups's thiols and hydroxyls) since it expresses binding energy of 45.7kJ/mol.

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