Research article

Mercury (II) removal from aqueous solutions by iron nanoparticles synthesized from extract of Eucalyptus grandis

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ABSTRACT

Artisanal mining is the main source of mercury emissions in South America, which generates a serious environmental impact due to this toxic metal, recent research is directed to minimize the impact, therefore this study focuses on the green synthesis of nanoparticles for the absorption of mercury in water. For the synthesis of iron nanoparticles, an extract of Eucalyptus grandis was used with iron chloride salts using water as solvent. The synthesized nanoparticles showed a specific surface area of 131.90 m²/g, determined by Brunauer-Emmett-Teller isotherm (BET). Nanoparticles were characterized by Fourier transformed infrared spectroscopy (FTIR) and transmission electron microscopy (MET). The behavior of nanoparticles synthesized during Hg (II) retention was evaluated measuring pH, temperature, nanoparticle dosing, presence of other ions and comparing with other adsorbents. All analyses measured by atomic absorption spectroscopy by the cold vapor technique (CVAAS), presenting a retention percentage for Hg (II) between 75.05 and 79.59% with pH between 4 and 7. The adsorption isothermal was adjusted to the Freundlich model and the percentage of retention of Hg by the synthesized nanoparticle was 79.26%. This work shows a method for obtaining an environmentally friendly mercury adsorbent from iron and E. grandis with a mercury retention capacity comparable to commercial adsorbents.

1. Introduction

Currently, various processes for water decontamination are investigated daily [1, 2, 3, 4], among which are the precipitation of metals by the formation of hydroxides and the adsorption of metals, which are widely used due to their speed and effectiveness. However, numerous drawbacks inclusive of excessive cost, using poisonous solvents and the discharge of environmentally unacceptable chemicals, are related to those extraction strategies for heavy metals [3, 5, 6]. Many of the studies are focusing on replacing common adsorbents with biomaterials, because these are lower cost and in addition to being friendly to the environment, they can be modified more easily; [7, 8, 9, 6]. Some biomaterials have even come to have better adsorbent capacities than the usual materials [10, 11, 12, 6]. In retention processes, more attention has been focused on metal ion recovery and reuse methods. Adsorption is an effective method and is also widely used to capture metal ions such as mercury from different aqueous solutions, obtaining percentages of up to 90% [13, 14, 15]. Mercury is considered a global pollutant due to its high toxicity, bioaccumulation, and persistence in the environment. China in the last 30 years emitted some 2151 tons of Hg, likewise in Colombia, the emission of Hg reached 1470 tons due to its different anthropogenic activities where mercury is used abundantly [16, 17, 18]. Thanks to its excessive use in recent decades in different activities where the mining industry has had extensive management of it, pressure has increased on governments to reduce or eliminate the presence of this metal in industrial processes, especially trying to eliminate the use of mercury on living beings through the manufacture of amalgams, lamps, fungicides, and others. The inclusion of this pollutant in terrestrial ecosystems is given by the activity of some bacteria and microorganisms that transform the metal into its organic forms known as methylmercury (MeHg). Therefore, is necessary to control the levels of mercury in the zones and more severe regulations [18, 19, 20, 21]. Due to the need to reduce mercury contamination in mining areas, one of the strategies proposed worldwide is the use of environmentally friendly adsorbents derived from biomass for mercury recovery [2, 22, 6]. Mining activity in Colombia has increased in recent years, increasing the levels of mercury present in...
water and sediments. Concentrations found in bodies of water have exceeded the established benchmark of 2.00 μg/L [19, 22]. Gold mining affects the environment, polluting and degrading ecosystems, generating health problems for living beings that inhabit these areas [16, 17]. Mining extraction has been generating solid waste, greenhouse gases and mercury emissions from amalgamation [23, 24]. An alternative to solve this contamination problem is presented using mercury ion retention systems based on iron oxide, which through adsorption processes have a good capacity for the retention of mercury ions, especially in systems at the nanometric scale where they are capable of retaining high percentages of these ions [25, 26]. Obtaining smaller size adsorbents has become highly attractive due to improved characteristics of these adsorbent materials as they present much superior properties over their larger counterparts, such as better optical and magnetic properties, as well as greater surface area, which is translates into a greater interaction with the analyte of interest [27, 1, 28]. Using the eucalyptus as a component of synthesis permit reduce the contamination from others compounds used for synthesis of adsorbents habitually used due to its ecofriendly, representing a good advantage plus this biomass is really important in the complexing system due to is part of the stabilizing effect of the nucleus, many of these nanoparticles tend to be considerably unstable in air and the lack of a stabilizer leads to the modification of the material and loss of their properties [27, 29, 21]. However, it is necessary to work with the maximum performance points during synthesis process, to achieve the maximum obtaining of the material, thus reducing the manufacturing cost for large quantities, to nanoparticles, the synthesis with biomass does not require many reagents, which reduces the optimization processes to three parameters, generally established in working temperature, volume of a biomass extract and adding an alkaline solution to end process [28, 30]. In particular, in Colombia, foliage of Eucalyptus grandis is an abundant ecological residue that can be used in order to develop an adsorbent, particularly due to its high content of phenols, an ideal compound when synthesizing materials such as nanoparticles due to that serve both as a complexing agent with metal ions, as well as a stabilizing agent and even as a reducing agent if one were to be needed during the synthesis process [27, 29, 31]. Therefore, in this research, optimization of nanoparticle synthesis of iron oxide nanoparticles was carried out using an aqueous extract obtained from the foliage of E. grandis and its use as an very good adsorbent material for mercury retention in water was explored from establishments where gold is obtained by hand, in the villages of Maravelez and El Tamboral, which are sectors for gold mining, assets of the municipality of Suarez, Cauca, Colombia.

2. Methodology

2.1. Reagents and materials

Salts of iron (II) chloride tetrahydrate and iron (III) chloride hexahydrate, sodium hydroxide, potassium permanganate, chloride hydroxyamine, borohydride sodium and solution pattern Hg standardized 1000 mg/L used were brand Merk, ACS, Darmstadt, Germany. Honeywell brand concentrated nitric acid, ACS. Seele, Germany, Baker brand concentrated hydrochloric acid, ACS. Xalostoc, Mexico and sulfuric acid concentrate mark PANREAC, ACS. Barcelona, pain.

2.2. Obtaining and preparing the sample

E. grandis foliage sample was obtained from the tree nursery Agro-forestal Cooperative Cauca (COOTRAFORC), located in Gonzales Path of Popayán, Cauca with coordinates 2° 28’34.9”N 76° 34’03.2” W. Since only the leaves were used, foliage samples were sorted and cleaned manually to remove dust, branches or seeds that could later interfere with cross contamination. The wet sample was dried for 2 weeks at room temperature and in shade, turning the leaves frequently until the dry biomass was obtained. Subsequently, the sample was ground in a conventional mill and sieved on a No. 18 mesh sieve, until obtaining a pulverized sample and homogenized in size, after which the sample is stored in previously sterilized glass jars, covered, sealed, and labeled to be used later in the preparation of aqueous extract.

2.3. Obtaining the aqueous extract of E. grandis foliage

For the preparation of aqueous plant extract, a ratio between the plant material and the solvent of 1: 5 weight/volume respectively was used [28], for which the extract was prepared starting with 100.0000 g of E. grandis foliage in 500 mL of deionized water, heating at a temperature of 80 °C for 5 min, later it was filtered under vacuum and centrifuged at 1250 rpm for 5 min, it was used deionized water in order to complete the total volume, the extract was stored at room temperature for later use [30].

2.4. Synthesis of nanoparticle

Coprecipitation method was used, for the synthesis of nanoparticles, two iron salts, iron (II) chloride tetrahydrate (FeCl2 ⋅ 4H2O) and iron (III) chloride hexahydrate (FeCl3 ⋅ 6H2O) were used considering quantities of 0.2650 g and 0.5550 g respectively in 100 mL of deionized water. It was heated to 87 °C for 10 min with constant stirring, then, a volume of 0.8 mL of the previously prepared E. grandis leaf extract was added, 5 min later, 20 mL of a solution of 1.7 M sodium hydroxide (NaOH), was added. The nanoparticles obtained was allowed to precipitate, filtered, and dried in oven at 50 °C for 24 h. Finally dry nanoparticles were macederated and stored for later use in the adsorption tests [28, 30].

2.5. Nanoparticle Characterization

Characterization of the particle was carried out by instrumental analysis using Transmission Electron Microscopy (TEM) techniques with a JEOLJEM 1200-EX equipment. Spectra were taken by and spectroscopy infrared Fourier transform (FTIR) with tablet KBr using equipment Thermo ® IR Nicolet iS10. Surface area analysis was performed with the isotherm Brunauer–Emmett–Teller (BET) using a computer Nova 1000e Quantachrome.

2.6. Atomic absorption spectroscopy

Mercury measurements were made using the cold vapor atomic absorption technique (EAA-VF). They use a computer Thermo ® ASS S series with accessory steam cold VP100, the analysis method was standardized and validated to equipment conditions to a wavelength and in lamp of 253.7 nm, measured time 4 s size, slit 0.5 nm, 70 s measurement expected, the gas flow 90 mL/min, pump speed 40 revolutions per minute (rpm), low linear least squares fit and working curve 1–12 μg/L (1, 2, 4, 6, 8, 10 and 12 μg/L), with an acceptable fit of 0.995 [32].

2.7. Sample digestion

25 mL of liquid sample were taken and 1.25 mL of concentrated H2 SO4, 0.6 mL of HNO3 and 3.75 mL of 5% potassium permanganate (KMnO4) were added, waiting for 15 min, and subjected to a water bath at 95 °C heating for approximately 2 h. Once the heating process was finished, it was allowed to cool to room temperature and 1.75 mL of 5% hydroxylamine chloride (NH2OH·HCl) solution was added to eliminate excess of potassium permanganate and guarantee the reduction of mercury from Hg2+ to Hg0, then with the borohydride sodium reduce mercury to Hg (0) and obtain as a cold vapor [32, 33].

2.8. Viability of the particle as a retainer OF Hg IN water

To study the retention capacity of mercury, a certified mercury (II) standard of 1000 mg/L was used, from which a standard solution of 1.0
mg/L was prepared with which solutions were prepared for different essays. These solutions were put in contact with the magnetite particle and after reaching the equilibrium time, they were filtered, acid digested and the mercury concentration was determined by atomic absorption spectrometry by the cold vapor technique to determine the percentage of mercury adsorption by nanoparticles [1, 34].

2.8.1. Balance time

To determine the equilibrium time of synthesized nanoparticle, 5.5 mg of particle were weighed, and 200 mL of a 50 μg/L mercury solution was added, it was stirred in ultrasound for 10 s and the mixture was continued with intermittent mechanical stirring for 96 h at a constant temperature of 25 °C. During the process, aliquots of 0.5 mL of the liquid phase were taken in time intervals of 30 min for the first 12 h and then every 12 h, each aliquot was titrated to 25 mL, then digestion was carried out and the mercury concentration was determined by CVAAS to control the basis of testing conducted by Mohmood et al [1] for determining mercury retention by the particle iron oxide.

2.8.2. Nanoparticle dosing

The amount of particle used for the retention of mercury was determined by weighing between 2.5, 3.0, 5.5, 8.0, 12.0 and 15.0 mg of adsorbent and they were added individually to a fixed volume of 10 mL with a concentration of 50 μg/L of Hg, at a temperature of 25 °C. The mixture was stirred until equilibrium was reached, then an aliquot of 0.5 mL was taken, it was added to 25.0 mL, then digestion was carried out and the mercury concentration was determined by CVAAS.

2.8.3. Effect of pH on retention

Solutions were prepared with different pH values (1.0, 2.0, 4.0, 6.0 and 7.0) with a concentration of 50 mg/L of mercury, then was added a volume 10 mL of each solution to different particle samples and stirred until equilibrium was reached. After that time, an aliquot of 0.5 mL was taken, it was added to 25 mL, then digestion was carried out and the mercury concentration was determined by CVAAS.

2.8.4. Influence of temperature

The effect of temperature was evaluated with values between 25, 30 and 50 °C, for this, the conditions used in 2.8.3 were used, which were a dosage of 5.5 mg of nanoparticle, time to equilibrium of 12 h, concentration, and Hg solution volume of 50 μg/L and 10 mL, respectively. Once equilibrium was reached, aliquots of 0.5 mL were taken, it was added to 25 mL, then digestion was performed, and the mercury concentration was determined by CVAAS.

2.8.5. Influence of other ions

The tests of the influence of different metal ions on the particle were carried out by preparing 10 mL solutions varying the ion content in each one (Hg^{2+}, Hg^{2+} + Se^{4+}, Hg^{2+} + Cd^{2+} and Hg^{2+} + Se^{4+} + Cd^{2+}) with all the ions at the same concentration of 50 μg/L with 5.5 mg of nanoparticle and the samples were shaken until equilibrium was reached. After adsorption, 0.5 mL aliquots were taken, it was gauged to 25 mL, then digestion was carried out and the mercury concentration was determined by CVAAS.

2.8.6. Adsorption isotherm

To determine the type of interactions of the particle with the analyte, the adsorption isotherm test was performed in which constant volumes of 10 mL of mercury solutions were taken at different concentrations (15–500 μg/L) and is addition or an amount of 5.5 mg of adsorbent, the mixture was stirred until equilibrium is reached. After equilibration, 0.5 mL aliquots were taken, it was gauged to 25 mL, then digestion was carried out and the mercury concentration was determined by CVAAS.

2.9. Holding capacity in water samples

To evaluate the retention capacity of the mercury nanoparticle iron oxide, samples were used of wastewater contaminated with mercury, from the strike up systems gold extraction of the paths Maravellez and the Tamboral of the municipality of Suarez, Cauca-Colombia (South America). In Figure 1 shows the location of the tables where the material is processed to extract gold in an artisanal way with mercury and where the samples were taken. Were 10 taken mL water to which was added 0.5 volume mL of solution pattern mercury of 1.0 mg/L to obtain a sample fortified with a total concentration of 50 μg/L. Also were made 10 mL of seven composite samples of water from the strike up, before, after and at the point of extraction of gold in each engage, which after being filtered contacted with 5.5 mg of the particle each, shaking until equilibrium is reached. After equilibration, 0.5 mL aliquots were taken, it was gauged to 25 mL, then digestion was carried out and the mercury concentration was determined by CVAAS.

2.10. Comparative study between adsorbents

Mercury retention capacity of the nanoparticle synthesized with E. grandis foliage was determined by comparing it with the retention capacity of a modified resin of Pinus palustris tannins [35] and with commercial activated carbon [36], weighing 5.5 mg of each material, to which 10 mL of 50 μg/L of mercury solution was added to each one and stirred until equilibrium was reached. After equilibration, 0.5 mL aliquots were taken, they were gauged to 25 mL, then digestion was performed, and the mercury concentration was determined by CVAAS.

3. Results and discussion

3.1. Synthesis of nanoparticle

In the nanoparticle synthesis process, the effect of NaOH concentration and extract volume on the yield is observed, while temperature did not show an effect on the synthesis yield. The NaOH interacts with the nucleus of the particle information, generating iron hydroxides which, by dehydration, allow the formation of crystals of the iron oxide of interest (Fe_{2}O_{4}), while the volume of extract can affect when it comes into contact with the iron ions, increasing the impedance of the NaOH to interact with the forming particle [30]. Temperature did not show a significant effect on the synthesis if it does not exceed 87 °C to avoid the start of the degradation of the organic compounds present in the natural extract. Optimal conditions allowed to obtain a synthesis yield of 98.99% to iron nanoparticle, results that are similar to those expressed by Galeas et al., 2017 who reported yields of 94% and exceed the results expressed by Robles et al., 2019 whose synthesis yields reached a maximum of 35.03% [10, 37, 38].

3.2. Obtaining aqueous extract from E. grandis

Aqueous extract obtained presented a slightly brown color and its infrared spectrum is shown in Figure 2, finding a band at 3319.61 cm^{-1} that is indicative of the hydroxyl groups (-OH) of the polyphenols found in the extract, a band was also observed at 1634.74 cm^{-1}, this represents the group carbonyl (-CO), which together with the hydroxyl group, expresses the presence of carboxylic groups (-COOH) within the E. grandis extract, a fact that is corroborated by comparing these results with those obtained by Salgado et al 2018, where finds that for the study by Infrared spectroscopy for aqueous extracts of Eucalyptus globulus, for these two bands the values are quite similar [39], so this allows us to recognize that in the prepared extract, largest component found it belongs to the polyphenols, a compound in which eucalyptus is rich and which later became part of the nanoparticles during the process of their synthesis.

3.3. Nanoparticle Characterization

3.3.1. Transmission electron microscopy (TEM)

To determine nanoparticle size, transmission electron microscopy (TEM) was used, it was obtained that the average size of the nanoparticle
is approximately 8.97 nm, in addition to a semicircular morphology. Figure 3 shows the micrograph obtained for synthesized particle in the nanometer range. In some cases, a greater degree of agglomeration can be seen, although they do not exceed 25 nm. Temperature, agitation, presence of natural extract and addition of sodium hydroxide played a transcendental role in obtaining nanoparticles of adequate size. Works reported by Hassanjani-Roshan et al. indicate that the adjustment of the obtaining conditions such as addition of sodium hydroxide, ultrasound energy, temperature and time allow obtaining nanoparticles with an average spherical size of about 19 nm and a crystalline size between 5 and 7.5 nm (Hassanjani-Roshan et al., 2011). With the size of the nanoparticles determined, it can be conjectured early that, thanks to its small size, contact area it presents will be greater and therefore the number of interactions between the surface of the nanoparticle and the analyte will be greater. Results of surface area were verified by means of the analysis with BET technique.

3.3.2. Infrared spectroscopy

To determine functional groups, present in synthesized magnetite nanoparticle, an analysis was performed by infrared (IR) spectroscopy.
technique, using an IR spectrophotometer. This technique can be applied for the identification of surface functional groups, which is important to have a general idea of the chemical structure of the possible biomolecules that are responsible for the coating and stability of the nanoparticle [28, 30]. In this case, various functional groups were found on the particle, in Figure 4 it is observed the IR spectrum of the synthesized nanoparticle which shows that around 3440.77 cm⁻¹ there is a stretching band of the hydroxyl group (–OH), although in this case the band is quite attenuated, in the same way it can see a band at 1559.26 cm⁻¹, which refers to the stretching of the carbonyl group bond (–CO). Presence of magnetite nanoparticles can be seen by appearance of a band at 445.31 cm⁻¹, which corresponds to the stretching band of the Fe–O bond of the magnetite nucleus [28, 30].

With these results it can be established that the carboxyl group (–COO⁻) has interacted with the nucleus, bonding on the surface of the magnetite particle. From these results and based on the studies carried out by Garcia, 2015, can be said that the polyphenols of the eucalyptus extract have interacted with the particle, acting as a reducing agent and stabilizer for the magnetite nanoparticle [27, 28, 30]. Figure 5a shows the infrared spectrum of the natural extract of E. grandis (Red), indicating C–H bending bands at 655.83 cm⁻¹, carbonyl group band (–CO) at 1634.40 cm⁻¹ and –OH band at 3315.71 cm⁻¹, while in the blue spectrum of figure a) nanoparticle synthesized in E. grandis extract, the C–H bending bands can be observed at 652.43 cm⁻¹, a band at 445.31 cm⁻¹, of stretching of the Fe–O bond of the magnetite nucleus, the presence of bands between 1400 and 1600 cm⁻¹ corresponding to the stretching of the carbonyl group (–CO) and the attenuation of the stretching band of (–OH) hydroxyls at 3440.77 cm⁻¹, the variation in the IR spectrum indicates the interaction of the iron oxide nanoparticle with the oxygen atoms of compounds present in the natural extracts of E. grandis.

Considering the work carried out by Pinkas et al., 2008 in Figure 5b, the red line shows the infrared spectrum of iron oxide nanoparticles synthesized by sonication in the presence of acetylacetone where important -OH elongation bands are observed at 3500 cm⁻¹, between 1400 and 1650 cm⁻¹ of elongation of the carbonyl group –CO of acetylacetone and close to 450 cm⁻¹ the Fe–O elongation band. Both in the synthesis of nanoparticles using the natural extract or by sonication, the interactions of iron with the oxygen atoms of the components of the natural extract and iron with the oxygen atoms of the acetylacetone obtained by sonication are observed. The blue color spectrum of the work carried out by Pinkas was obtained after calcining the synthesized nanoparticle and the loss of the hydroxyl group bands near 3000 cm⁻¹ and of the carbonyl interactions near 1500 cm⁻¹ were observed, showing the bands corresponding to iron oxide near 450 cm⁻¹. The foregoing indicates how the iron oxide nanoparticle can be modified depending on the synthesis environment and how this can enhance its adsorption capacity.

3.3.3. BET analysis

To determine the surface area of the particle, an analysis was carried out by means of a type II isotherm for BET, from which it was obtained that the estimated surface area for the magnetite nanoparticle is 131.90 m²/g, which corroborates the first hypothesis posed by transmission electron microscopy on the large contact surface of the nanoparticle due to its small size and which is corroborated when comparing with the results obtained by Stan et al. [28] which for iron oxide nanoparticles synthesized in a similar way obtained surface areas of 187.40 m²/g according to the BET tests [28], for which it can be expected that for this specific nanoparticle, the adsorption of mercury is relatively high thanks to the resulting higher interaction between the adsorbent material and analyte of interest.
3.4. Viability of Hg retention by nanoparticles

To determine the viability of the nanoparticle as a retainer of mercury, in addition to the different tests carried out to find the optimal conditions, work was carried out considering the percentage of adsorption of the particle, which is given by Eq. (1).

$$\% \text{ Adsorption} = \frac{C_i - C}{C_i} \times 100$$

(1)

where $C_i$ (μg/L) and $C$ (μg/L) are the metal concentration in the test solution, before and after adsorption, respectively.

3.4.1. Equilibrium time, dosage and effect of pH on retention

Experimental results for the determination of equilibrium time are presented in Figure 6, which shows that contact time required for nanoparticle to reach adsorption equilibrium is within the first 12 h of starting the experiment, thus establishing that equilibrium time for the following experiments and evaluation of the different parameters (effect of pH, temperature, dosage, effect of other ions and comparison between adsorbents), was 12 h. Nanoparticle dose effect was carried out in a range of 2.5 to 15 mg of particle for mercury retention from a mercury solution of 50 μg/L and a constant temperature of 25 °C, the results obtained are shown in Figure 6 (b). Percentage increased from 66.63% to 79.26% as a result of the increase in particle amount added, this because as the...
amount of particle that is added increases, in the same way, number of active sites for retention available in the surface. From these results it is seen that the minimum required number of nanoparticles to achieve the maximum possible retention of mercury is 5.5 mg of nanoparticles, therefore, can be established that for use of these nanoparticles as an adsorbent material. It is an effective and low-cost method as it does not require large quantities to achieve good retention of pollutant in question, in this case mercury (II) ions. Regarding the effect of pH, Jiménez, 2005 reports that in studies carried out for retention of mercury, it is found that the best pH ranges for said process are at a pH greater than or equal to 4, even favoring adsorption according to the adsorbent species at a more basic pH with values around 9 [41]. This may well be due to the fact that many of the active sites present were already protonated at very low pH due to high concentration of H\(^+\) ions that are found in medium at lower pH values, neutralizing these points for their interaction with the metal [42]. To study the influence of pH on behavior of mercury adsorption, adsorption experiments were carried out in a pH range between 1 and 7. In Figure 6(c) effect of pH shown in retention of the metal and found that indeed when the pH is below 4 retention mercury tends to be quite low reaching a 23.47% maximum retention, while values above 4 the maximum retention that was obtained is around 75.05%, a significant increase in retention as the pH increases. Based on these results, it can be determined that at more acidic pH the adsorption process is affected by providing a greater amount of H\(^+\) ions capable of occupying the active sites on retaining surface, preventing interaction with other metal ions such as Hg\(^{2+}\), found in the solution. Effect of pH on the retention of mercury in a 50 \(\mu\)g/L solution is greater at higher pH, finding its best results as the solution then approaches neutrality, which can be considered an advantage when treating samples of real contaminated water in mining areas, whose pH is not far from an almost neutral value and therefore the active sites on the surface of the adsorbent material would be more available for the capture of mercury in solution.

Surface chemistry of nanoparticle was determined by acidic or basic character of their surface. pH was measured before and after adding the adsorbent to solution containing Hg (II). Figure 6(d) of initial pH versus final pH allowed to determine a pH\(_{pzc}\) of 8.8, pH in which a zero-surface charge and neutralization of charges is presented. Acidic means a positive surface charge and basic means negative surface charge. pH\(_{pzc}\) of 8.8 indicated that at this pH value, the surface of the nanoparticle is neutral, decreasing the positive and negative charge. However, Hg (II) presents better adsorption conditions over pH 4.

3.4.2. Influence of temperature

In order to establish the experimental parameters in the retention of mercury in synthesized particle, effect of temperature was evaluated in three different values of controlled temperature, these being 25, 30 and 50 °C respectively, a dose of nanoparticle 5.5 mg and an analyte concentration of 50 \(\mu\)g/L. Experimental results are shown in Figure 7 and it is observed that as temperature increases, there is a slight reduction in the percentage of mercury adsorption. For materials with such a small particle size, temperature is an aspect to consider as they are more susceptible to changes in temperature and therefore to alter their properties if temperatures are raised too high. Iron nanoparticles synthesized under a green procedure using pear extracts were used for the retention of Cr (VI), observing an increase in retention from 55 to 90% when temperature increased from 25 to 55 °C, due to an increase in energy with temperature which increases the diffusion of Cr (VI) through the nanoparticle (Ron et al., 2020). However, in case of Hg results obtained
show that variation in its adsorption capacity towards mercury is quite small, showing its stability at different working temperatures.

### 3.4.3. Influence of other IONS

In practical application, adsorption selectivity is very important in evaluating adsorbents. Before determining its performance as a mercury adsorbent in real samples, the influence of coexisting ions on analyte adsorption was investigated in order to identify interferences from these metal ions. To study the influence of metal ions, a series of mixtures with different metal content and a fixed concentration for selenium, cadmium, and mercury ions of 50 μg/L were stirred under conditions of temperature of 25 °C, pH at values of 4.00, an amount of magnetite nanoparticle of 5.5 mg and a time to equilibrium of 12 h. The experimental results of testing the nanoparticle against various metal ions are presented in Figure 8.

To get as close as possible to water real samples to be compared, metals that could be present in them were considered, these samples come from areas of high mining activity and are therefore rich in different minerals. Types of minerals and metals that are also released during the gold vein extraction process and that, being present in the rocks from which the gold is extracted, will also become part of the process wastewater, which can condition the effectiveness of the nanoparticles when it comes to retaining mercury by interference from other ions, in this case Se and Cd. Although the quantitative retention of mercury is around 79.59% when there is only the presence of mercury, it is observed that metal retention decreased in presence of other ions such as selenium or cadmium. However, this decrease in the retention of Hg (II) was not reduced below 70.00%, showing that despite the presence of other ions there is a certain selectivity of the adsorbent towards the analyte of interest by the organic groups available on nanoparticle surface. According to Cabañero [43], who reports in his work the antagonism between selenium and mercury where the content of adsorbed mercury was reduced by up to 60% in presence of selenium; in the study carried out for mercury adsorption with the nanoparticle, the fact that selenium turned out to be the major interfering factor for the adsorption of mercury may be due to the competitiveness that exists between both elements, influenced by chemical form of Hg and Se present in solution and concentration administered to each of these elements during adsorption process on the surface of nanoparticles [43]. This remarkable selectivity of the particle towards Hg (II) over other metal ions is enormously useful for mercury recovery in solution and, the coexisting metal ions had little effect on mercury adsorption.

### 3.4.4. Adsorption isotherm

Adsorption isotherm was studied by varying the initial mercury concentrations in the test solution. For which equilibrium concentration given in μg/L was plotted against the amount of metal adsorbed by the nanoparticle (q) expressed in mg/g, which is calculated according to Eq. (2).

\[ q = \frac{C_i - C_f}{w} V \]  

where \(C_i\) (μg/L) and \(C_f\) (μg/L) are the metal concentration in the test solution, before and after adsorption respectively, \(w\) (g) and \(V\) (L)

\[ \text{Log}_q = \text{Log}_K_f + \frac{1}{n} \text{Log}_C_e \]  

where Langmuir equation in Figure 10(A), \(C_e\) (μg/L) and q (mg/g) represent concentration equilibrium of metal ion in the liquid phase and metal ion amount retained per unit mass of adsorbent respectively, while \(q_m\) and \(b\) are constants related to maximum sorption capacity for a complete monolayer (mg/g) and with affinity between adsorbent and adsorbate (L/mg), respectively [44]. For Freundlich equation in Figure 10(B), \(C_e\) and q have the same meaning as in Langmuir case, while \(K_f\) and \(n/\) refer to equilibrium constants (mg/g) and affinity between adsorbent and adsorbate (L/mg) respectively [44].

From results obtained, it is found that value of correlation coefficients \(R^2\) makes it possible to infer favorability on surface of the prepared adsorbent and therefore indicates type of isotherm and calculations to be carried out. It should be considered that value of \(R^2\) must be closest to one to be favorable [45]. Comparing results obtained from the two models, it indicate the dry weight of particle and volume of the test solution, respectively. As shown in Figure 9, it is evident that the amount of mercury retention increased with increasing metal concentration in solution tending to approach a constant value at higher concentrations of about 274.9 mg Hg/g adsorbent.

From experimental results obtained from equilibrium, the parameters of Langmuir and Freundlich isotherm models were determined. Results of retention mercury in nanoparticles were linearized considering equations models of isotherms studied. Figure 10 shows results of linearization by models, where correlation value index \(R^2\) plays an important role in determining the model that is best adjusted to adsorption process as this value approach 1 and therefore allowing to discern whether nanoparticles adsorption is physical or chemical.

Eqs. (3) and (4), which represent linearized equations of both models, are used in the same way to determine constants values in each case, values shown in Table 1.

\[ \text{Langmuir} : \frac{C_e}{q} = \frac{1}{q_m b} + \frac{C_e}{q_m} \]  

\[ \text{Freundlich} : \text{Log}_q = \text{Log}_K_f + \frac{1}{n} \text{Log}_C_e \]  

\[ q_m \]

Figure 8. Influence of other ions on Hg (II) adsorption.

Figure 9. Adsorption isotherm of Hg (II) on magnetite nanoparticle at 25 °C.
is found that for Hg (II) retention, the best fit was obtained under Freundlich model, with $R^2$ values of 0.857 compared to Langmuir model which presents a value for $R^2$ of 0.1704. Standard errors respect to the fit to the Freundlich and Langmuir models were 13.43% and 82.79%, respectively. Under analysis of these results, it can be inferred that for data of adsorption isotherm of Hg (II), the model that best describes the behavior in the range of concentrations studied is Freundlich model. This model makes it possible to determine that adsorbent surface is in fact of a heterogeneous type, which indicates that there are many sites available for adsorption, that is, the number of functional groups present on the surface of the particle is greater and more varied, therefore it is more likely that there is a greater interaction and therefore a greater probability of retention by these groups of the analyte in the magnetite particle, due to the presence of non-ionizable organic compounds such as poly-phenols on the particle surface obtained using foliage extract of $E$. grandis [35], due to its mostly activated groups, presented, like activated patula [35] and commercial activated carbon can be observed in Figure 12, where it is shown that the percentage of mercury adsorption in the synthesized nanoparticle using extract from $E$. grandis foliage is lower than other materials studied. Said behavior and apparent improvement in adsorption capacity of the other adsorbents towards Hg (II) is probably due to the presence of non-ionizable organic compounds such as polyphenols on the particle surface obtained using foliage extract of $E$. grandis [50] which would explain why its lower capacity to retain mercury compared to activated carbon or resin obtained from the modification of $Pinus$ patula tannins [35]. Synthesized particle present very low solubility in water and is effective for absorption of Hg (II) in 79.26% under experimental condition developed therefore can suitably be used in retention experiments, capture and recovery of mercury in solution, in addition to presenting advantages due to its magnetic behavior, for which the particle can be recovered from the environment more easily using magnetic fields, its low toxicity and the ability to modify its surface by functionalization to improve its retention properties of the target metal, in this case mercury.

In comparison, modified tannin resin obtained from bark of $Pinus$ patula [35], due to its mostly activated groups, presented, like activated carbon, a greater adsorption in the medium, this due to activated groups present on its surface and that interact on a larger scale with mercury in solution. This implies that although this magnetite particle is capable of retaining mercury in its current state, an activation or functionalization
Activated coal
Modified resin

EM3 87.92 102.42 97.58 39.61 44.44 39.61 7.38 2.79 57.05
ET2 92.75 97.58 87.92 54.11 58.94 63.77 4.83 4.83 36.46
ET3 305.31 300.48 305.31 136.23 131.40 141.06 2.79 4.83 55.14
EM2 261.84 266.67 252.17 213.53 208.70 218.36 7.38 4.83 17.95
Low [Hg] 39.61 34.78 44.44 15.46 25.12 20.29 4.83 4.83 48.78

*Ci: Initial concentration, Cf: Final concentration, SDi: Initial standard deviation, SDf: Final standard deviation.

Figure 12. Comparison between magnetite nanoparticle, activated carbon and modified resin.

process of its surface with more receptive compounds would improve its ability to retain the analyte of [50]. However, one must consider the fact that in relation to the adsorbent’s affinity with respect to adsorbate (1/n), the nanoparticle has a higher value (0.6269 L/mg) compared to modified resin (0.5303 L/mg) and activated carbon (0.2299 L/mg) [36], which would indicate that although adsorption percentage of the particle is lower compared to the other two adsorbents, adsorption on the particle is much stronger.

3.7. Holding capacity in water samples

Mercury retention in drinking water was carried out in order to evaluate the effect of the matrix on mercury retention by the particle, results obtained showed that retention of mercury in drinking water reached a total retention percentage of 78.74%, which compared to the previous results shows that effect of the matrix on adsorption to drinking water is zero and the process can be carried out without problems, in addition, as a control, the same procedure was carried out with a sample of drinking water without doping subjected to the same process, obtaining an absorption of 0, proof that the equipment used for the analysis by atomic absorption spectroscopy by the cold vapor method (CVAAS) worked properly and that there was no interference of any kind. The sampling station for sewage collection is contaminated by mercury in the amalgam-forming process. In Suarez-Cauca area, the following sampling stations were chosen Vereda 1: Maravelle (Entanglement-Sample station: EM1-Zona de balde, EM2-Mina de Hugo, EM3-Maravelle), Vereda 2: Tamboral (Entanglement-Sample Station: ET1-Batea, ET2-La marrana, ET3-La canaleta). Table 2 shows mercury retention by the nanoparticle in samples of these wastewater from 6 tables where gold is obtained by hand with amalgamation. Waters were taken after Hg retention process by the nanoparticle, and it is found that in all cases a retention of the metal is achieved, in some cases the adsorption was lower than in others in terms of adsorption percentage. Samples of water sources where residues of artisanal mining activity arrive were analyzed and showed pH values close to neutrality with some samples having a pH lower than 7. The conductivity values varied between 62.12 µS/cm and 358.67 µS/cm, the maximum acceptable value being 1000 µS/cm, where conductivity indicates the ionic strength of a saline solution and higher values may indicate a high concentration of salt mixtures. DO values were above 100% for all samples indicating rapid aeration, values of 5 mg/L for BOD5 indicated low biodegradation of organic material, alkalinity values were between 5.19 mg/L CaCO3 and 17 mg/L CaCO3 indicating the possible dissolution of rocks and runoff effect, these values are classified as low as they are below 75 mg/L of CaCO3 [51]. The wastewater samples from the selected stations have been previously analyzed and have shown Hg concentrations between 0.5 µg/L and 78.4 µg/L. Water currents where wastewater from mining activity arrives showed Hg concentrations between 0.094 µg/L and 1.0 µg/L [51, 52].

This may be due to the matrix effect of the residual water samples taken from the artisanal gold mining areas of the tables shown in Figure 1, where due to presence of other components in the sample, there is a decrease in the instrumental response on the analyte, this means that concentration of the analyte in a real sample will not provide the same instrumental response with a pure sample [53], this is corroborated the results to the comparison between samples of water residue signal of the strike up and the water sample potable was fortified, which is previously treated for drinkability, by which any possible interference present was removed allowing greater ease in capturing ions Hg (II) present therein with nanoparticles.

4. Conclusions

Obtaining iron oxide nanoparticles is feasible through the use of plant extracts such as E. grandis, which gives greater stability to the nucleus of the nanoparticle by avoiding its interaction with the air which would result in a degradation of it and thereby losing some of its properties. In addition to the addition of the extract, a more efficient surface area is granted for processes such as adsorption by providing more ideal points that interact with better retention capacity of the analytes, the high performance and the large surface area presented, demonstrates the effectiveness of the process. Effects of pH showed that the system works better in relatively acidic media thus avoiding the protonation of many of its active sites in addition to favoring adsorption as the pH is closer to 7, in the same way it shows that in media with a greater number of ions in addition to the analyte ions, it presents a relatively good selectivity and predisposition for the capture of Hg, being only him it is an interference to consider, this because of the competition that exists between both metallic species. Compared to other types of adsorbents tested during the Hg retention process, it was observed that the nanoparticles in fact had a lower retention capacity compared to their homonyms, most likely due to the number of spaces available on the surface of each adsorbent, however it should be noted that although the adsorption capacity of the nanoparticle is lower compared to their counterparts, if it presents a greater

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### Table 2. Results of adsorption on doped and residual water samples from the establishments in the artisanal gold mining area of Suarez, Cauca.

| Sample          | Ci (µg Hg/L) | Cf (µg Hg/L) | SDi | SDf | Adsorption Average (%) |
|-----------------|-------------|-------------|-----|-----|------------------------|
|                 | 1  | 2  | 3     | 1  | 2  | 3                     |                             |
| Low [Hg]*      |    |    |      |    |    |                       |                             |
| EM2             | 261.84 | 266.67 | 252.17 | 213.53 | 208.70 | 218.36 | 7.38 | 4.83 | 48.78 |
| EM1             | 228.02 | 232.85 | 228.02 | 194.20 | 189.37 | 199.03 | 2.79 | 4.83 | 15.43 |
| ET3             | 305.31 | 300.48 | 305.31 | 136.23 | 131.40 | 141.06 | 2.79 | 4.83 | 55.14 |
| ET2             | 92.75  | 97.58  | 87.92  | 54.11  | 58.94  | 63.77  | 4.83 | 4.83 | 36.46 |
| ET1             | 203.86 | 199.03 | 199.03 | 83.09  | 87.92  | 83.09  | 2.79 | 2.79 | 57.78 |
| EM3             | 87.92  | 102.42 | 97.58  | 39.61  | 44.44  | 39.61  | 7.38 | 2.79 | 57.05 |
| Doped water     | 50.01  | 50.00  | 49.99  | 10.63  | 15.46  | 15.46  | 0.01 | 2.79 | 78.74 |

*Ci: Initial concentration, Cf: Final concentration, SDi: Initial standard deviation, SDf: Final standard deviation.
affinity between adsorbent and adsorbate, thus allowing a greater strength in the retention of the analyte of interest on the adsorbent surface, in addition to presenting the possibility of making more functionalized systems on its surface, which will result in an increase in its retention capacity. It is recommended for further studies, to evaluate the functionality of nanoparticles with other molecules with retarding capacity. It is recommended for further studies, to evaluate the functionality of nanoparticles with other molecules with retaining capacity. It is recommended for further studies, to evaluate the functionality of nanoparticles with other molecules with retaining capacity.

Declarations

**Author contribution statement**

Santiago Pabón Guerrero: Conceptualized and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Ricardo Benítez Benítez, Rodrigo Andres Sarria-Villa: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

José Antonio Gallo Corredor: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Data availability statement

Data included in article supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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