

Removal and recovery of mercury from chlor-alkali petrochemical wastes using γ -Fe₂O₃ nanoparticles

Zahra Ramezani^{1,2} · Neda Pourmand^{2,3} · Abdolazim Behfar^{1,2} · Ali Momeni^{2,4}

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Abstract One of the main sources of mercury pollutions in Bandar Imam petrochemical company is its chlor-alkali unit. The unit uses mercury to convert sodium chloride (NaCl) to chlorine and sodium hydroxide. In this study, removal and recovery of mercury from wastewater of the chlor-alkali unit before its conversion to cake using γ -Fe₂O₃ nanoparticles were reported. It was shown that the magnetic nanoparticles can adsorb and remove mercury from the chlor-alkali unit wastes and the resulting sorbents effectively separated from the solution by a 1.4 T magnet. Different parameters, which could affect the adsorption process, such as the amount of nanoparticles, pH and volume of buffer, and contact time were optimized. Under the optimized conditions, 94.59 % of mercury was removed using bare nan γ -Fe₂O₃ with RSD of 1.7 % ($n = 5$). Adsorbed Hg(II) was successfully desorbed using 1 M HCl, then the resulting solution's mercury content was reduced to elemental mercury. The elemental mercury was finally collected in a hollow glass gas chromatographic column half filled with distilled water, providing a green chemistry for reuse of mercury. The method of mercury

determination was cold vapor atomic adsorption spectrometry throughout this study.

Keywords Petrochemical waste · Chlor-alkali unit · γ -Fe₂O₃ nanoparticles · Mercury, remediation

Introduction

Mercury is one of the most toxic heavy metals in wastewaters released from industrial activities, such as the pharmaceutical, agricultural and petrochemical industries into the environment and creating problems for humans as well as aquatic organisms due to its toxic and bio-accumulative properties [1]. Mercury pollution constitutes serious worldwide environmental problem [2–5]. Globally, it has been estimated that 5500 tons of mercury are discharged into the atmosphere annually. Reactive mercury (II) salts are toxic form of mercury, which are often converted by bacteria into the most toxic form, methyl mercury, which create a health risk to humans and wildlife [6]. Generally, discharge of mercury from industrial wastewater is directed to the natural water bodies, such as rivers, lakes and seas. The European Union considers mercury as a priority and hazardous pollutant and defines a maximum permissible concentration of total mercury as low as 1 $\mu\text{g L}^{-1}$ for drinking water and 5 $\mu\text{g L}^{-1}$ for wastewater discharge [7]. Volcanic eruptions, naturally caused forest fires, and biogenic emissions are natural inputs of mercury to the environment [8]. In addition, unnatural ways for mercury pollution are wastewater of chlor-alkali plants, vinyl chloride plants, plastics industry, electrical equipment, batteries, and paints [9, 10]. Chlor-alkali plants (CAP) are one important source of Hg emissions, which use metallic Hg to convert NaCl to chlorine and sodium

✉ Zahra Ramezani
zramezani@ajums.ac.ir

¹ Nanotechnology Research Center, Faculty of Pharmacy, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, IR, Iran
² Medicinal Chemistry Department, Faculty of Pharmacy, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, IR, Iran
³ Department of Chemistry, Faculty of Science, Ahvaz Branch of Azad University Science and Research Center, Ahvaz, Iran
⁴ Mahshahr Petrochemical Companies, Mahshahr, Iran

hydroxide [11, 12]. Several studies have exposed that most Hg emitted from chlor-alkali plants is dispersed over long distances [13, 14]. Nevertheless, it has been reported by EPA that soils surrounding chlor-alkali plants show Hg concentrations up to 75 times the background. It should be mentioned that water contents of the chlor-alkali waste are evaporated and a solid waste that is called “cake” are released into the environment. Therefore, the removal of mercury from chlor-alkali plants wastes is necessary before the effluent is discharged into the environment [15, 16]. As a consequence, the development of effective techniques for the removal of mercury from wastewater and related sources is very important for the remediation of mercury pollution. Air emission and wastewater treatment standards are gradually becoming tighter all over the world. Research and development of pollution control technology has been focusing on improving the removal efficiency of all contaminants, minimizing water and energy consumptions [17]. A number of technologies have been developed over the years to remove toxic metal ions from water [18, 19]. Conventional methods for the removal of heavy metals include ion exchange, chemical precipitation, pre concentration, reverse osmosis, evaporation, membrane filtration, adsorption and bio sorption [20–25]. Therefore, abatement of mercury from industrial wastewater to attain the stipulated limit as prescribed by EPA is mandatory.

In recent years considerable attention has been given to remove mercury by adsorption process on various adsorbent, a number of pre concentration techniques have been used for trace metal remediation: These include coagulation, precipitation/coprecipitation and solid phase adsorption [26–29].

Nowadays, adsorption is a well-recognized technique and has been applied for cleaning up of numerous different classes of compounds in a variety of matrices by virtue of its high absorptivity, recovery, and rapid phase separation [30–33]. Separation by magnet is a relatively new solid phase adsorption method which according to the characteristics of the target systems can be used in two different ways; firstly using of external magnetic field as a separation tool of magnetic target, secondly using of external magnetic field to separate nonmagnetic target for instance organic and inorganic compounds. Separation of nonmagnetic target such as organic molecule is through formation of a complex with magnetic particles which shall then be separated by an external magnetic field [34–36].

The aim of this study is to develop a new environmentally friendly and less expensive adsorbent suitable for removal of mercury from industrial wastewater and to check whether the adsorbed metal can be recovered from the spent adsorbent for reuse. In this work, γ -Fe₂O₃ Nanoparticles (MIONs) was used for the removal and recovery of mercury from chlor-alkali plant wastewater.

The major objective of this work is to investigate the potential of γ -Fe₂O₃ as adsorbent for mercury removal from the waste. To do so, the effect of parameters such as amount of γ -Fe₂O₃ nanoparticles (MIONs), pH and volume of buffer solution, and stirring time in the removal process is optimized. Recovery of mercury (II) from spent MIONs was studied to check the reusability of the MIONs and mercury. Different adsorption isotherms were also checked and the best model was introduced.

Experimental

Instrumentation

Cold vapor atomic absorption spectrometry (CV-AAS) determination of mercury in field samples was performed by a flame AAS instrument (CTA-3000, Anal. tech England) equipped with a Mercury Vaporizer Unit MVU-1A (Shimadzu) and hollow tube with quartz windows as CV_AAS cell, placed in the light path of the spectrometer. A pH meter (632 Metrohm, Herisau, Switzerland) was used to adjust pH of the solutions. A 1.4 T super magnet (10 × 5 × 2 cm), a mechanical stirrer (E649 Metrohm, Herisau, Switzerland), and ultrasonic bath (Transistor/ultrasonic T-14, USA) were used throughout the study.

Reagents and standard solutions

All chemicals and reagents were of analytical grade unless otherwise stated. Nitric acid (HNO₃, 65 %), sulfuric acid (H₂SO₄, 98 %), hydrochloric acid (HCl, 37 %), Potassium permanganate (KMnO₄), Hydroxylamine Hydrochloride (H₄CINO), Tin (II) chloride (SnCl₂·2H₂O) were purchased from Merck (Darmstadt, Germany). Nano iron oxide (γ -Fe₂O₃) with size of 15–25 nm, SSA: 50 m² g⁻¹, and purity 95 % was purchased from Tehran petrochemical industry (Tehran, Iran). Figure 1 shows the XRD of γ -Fe₂O₃ Nanoparticles that was sent by the manufacturer. The peaks

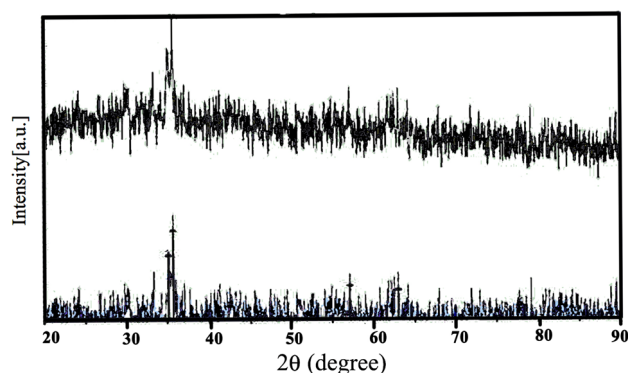


Fig. 1 XRD of γ -Fe₂O₃ magnetic nanoparticles

observed at 2Θ ranges of 30–40, 60–65 and 70–80 (weak) are indicative of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles.

Sample collection and treatments

About 10 L composite samples of chlor-alkali petrochemical wastes from Mahshahr petrochemical company (Mahshahr, Iran) were transferred to our laboratory. Its total mercury contents were determined before starting any experiments. All experiments including optimizations were performed directly on these wastes. The mean mercury contents of wastes were determined by CV-AAS and was 9.36 mg mL^{-1} .

Adsorption procedure

Adsorption of mercury on $\gamma\text{-Fe}_2\text{O}_3$ Nanoparticles (MIONs) were investigated by diluting appropriate amount of petrochemical wastewater to 50 mL by nitric acid (1 M). The resulting solution was transferred to a beaker, the pH was adjusted and appropriate amount of MIONs was added. The mixture was stirred using an ultrasonic bath for about 20 min. Mercury adsorbed MIONs was then collected by placing the beaker on the 1.4 T magnet and allowing the upper solution to become colorless, and then decanted. Removal percentage of mercury was determined by concentrations of mercury in the waste solution before and after the nanoparticle contact with aid of cold vapor atomic absorption spectrometric technique (CV-AAS) at mercury line (253.7 nm). Nitric acid (0.1 M) and 0.1 M NaOH solutions was used for pH adjustment.

Results and discussion

All the experiments were performed on the diluted petrochemical waste as indicated in the previous section. The effects of different parameters on mercury extraction were studied to reach higher removal efficiency. The results of each are discussed separately.

Effect of the amount of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles (MIONs)

The amount of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles (MIONs) used in this work was varied from 5 to 50 mg. The results are graphically shown in Fig. 2. The results indicated that the higher removal was observed at 20 mg of MIONs. Slight decrease (about 1–3 %) in removal efficiency with increase in sorbent amount may be due to variation in surface charges of the nanoparticles in the presence of the sample matrices. This was confirmed by the excess MIONs remained

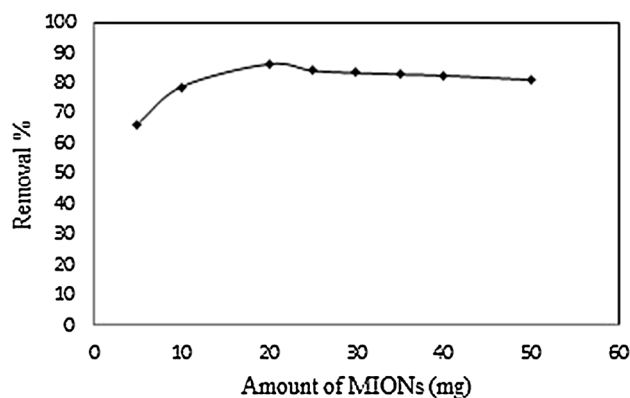


Fig. 2 Effect of different amounts of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles (MIONs) on the mercury separation (stirring time: 30 min, diluted petrochemical waste). The presented data were average of three replicated analysis

floating on the solution when applying a magnetic field. So the 20 mg was chosen as the optimum value.

Effect of pH

The effect of pH was examined by varying the pH of the test solution in the range of 2–10. The pH of 1 mL of wastewater solution (9.36 mg L^{-1}) was adjusted to the desired value using HNO_3 and/or NaOH solution (0.1 M), diluted to 50 mL and 20 mg of MIONs was added as the adsorbing agent. As the Fig. 3 indicates the removal efficiency of the $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles (MIONs) are approximately the same (more than 86.15 %) in the pH ranges of 3–8. At lower pH, the solution became dark brown due to dissolution of iron oxide nanoparticles. On the other hand in solutions with high pH values (above pH 8), the particles were converted to a colloidal form that did not settle by the

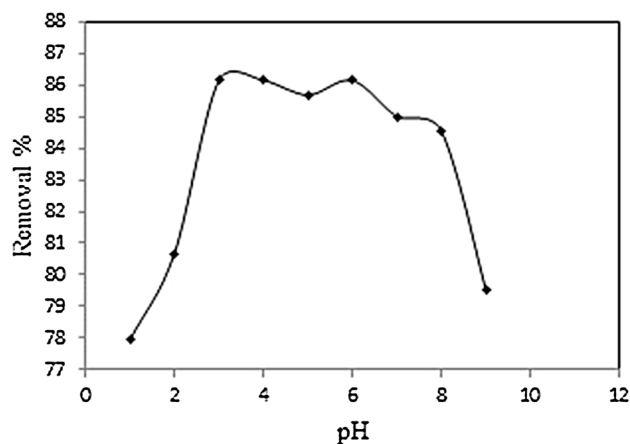


Fig. 3 Effect of pH on the mercury adsorption (conditions: 0.02 g of MIONs; stirring time: 30 min, diluted petrochemical waste). The presented data were average of three replicated analysis

applied magnetic field (Fig. 3), indicating strong adsorption of hydroxide ions. Thus, pH is not a critical limiting factor on the proposed removal process and pH in the range of 3–8 can be selected. Therefore, in further experiments, the pH of the solutions was adjusted to 5. It is to be mentioned that the waste had pH over 9.

Effect of buffer volume

The effect of buffer volume on the mercury removal of the petrochemical waste ($0.1872 \mu\text{g mL}^{-1}$) by the present magnetic adsorbent (MIONs) was investigated. The results indicated that a slight decrease in removal efficiency was observed at different buffer volume (pH 5 and 20 mg of MIONs). So, minimum amount of the acid is required to adjust pH of the waste to the desired value. This may be because of the wide obtained pH optimization range.

Effect of stirring time

The effect of stirring (contact) time on the mercury removal of the chlor-alkali waste solution after addition of MIONs is shown in Fig. 4. As can be seen from the figure, the removal increases with increase in the stirring time up to 20 min, afterward a slight decrease was observed (about 9 percent decrease on 20 min increase in contact time). Since no modification is made to selectively adsorb the mercury, the small decrease was due to adsorption desorption equilibrium of the other competitive ions in the waste. Therefore, at bare $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles adsorption rate was indicated by the removal of more than 94.59 % of mercury in the 20 min at optimum values of other factors indicated in Fig. 4 captions. So the 20 min contact time is the best choice.

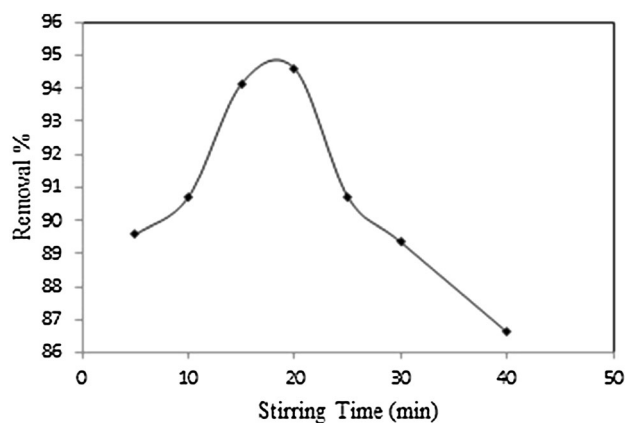


Fig. 4 Effect of stirring time on the mercury adsorption (conditions: 0.02 g of MIONs; pH 5, buffer volume = 4 mL). The presented data were average of three replicated analysis

Effect of the petrochemical waste volume

Different amounts of the petrochemical waste having mercury concentration in the range of $0.1872\text{--}9.36 \mu\text{g mL}^{-1}$ at optimum conditions (pH 5, 20 mg sorbent) were mixed and stirred by sonication for 20 min. About 91 % mercury removal was observed for mercury concentrations up to $1.872 \mu\text{g mL}^{-1}$. At higher mercury contents, twofold increase in mercury contents results in 25 % decrease in mercury uptake by the sorbent. This may happen because of maximum sorbent capacity of the mercury is reached (Fig. 5). It indicated that the waste dilution should be controlled to keep the mercury level at about 0.4 ppm in treatment vessels, otherwise, the sorbents amount must be increased. By conducting different experiments at optimum conditions on the diluted waste, it was concluded that mercury in the diluted wastes can be reduced below the permitted level reported by the European Union (5 ng mL^{-1}) for waste water.

Maximum adsorption capacity

Maximum adsorption capacity of the sorbent was studied by contacting 10 mL portions of solutions containing $50 \mu\text{g mL}^{-1}$ standard mercury with 0.5 g of MIONs for predetermined time followed by determination of the effluent and retained mercury using CV-AAS. The maximum capacity was calculated as 234 ng mg^{-1} . The adsorption capacity was also determined from different adsorption isotherms presented in Table 1.

Recovery

Mercury released into the environment enters the human body through the food chain. Chronic exposure to Hg°

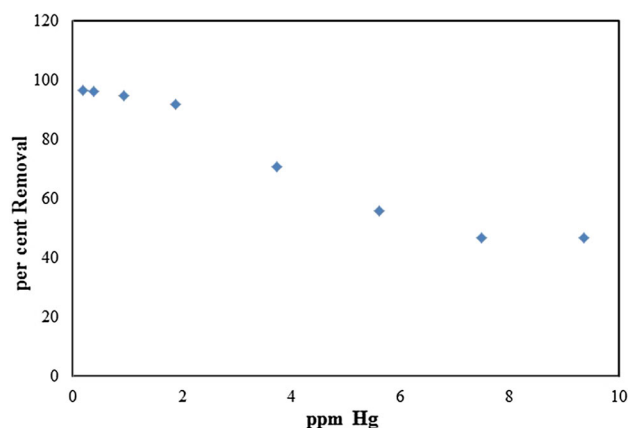


Fig. 5 Effect of the petrochemical waste concentration on the mercury adsorption (conditions: 0.02 g of MIONs; pH 5, buffer volume = 4 mL; stirring time: 20 min). The presented data were average of three replicated analysis

Table 1 Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm constants for the adsorption of mercury on the γ -Fe₂O₃ nanoparticles

Parameters	Langmuir			Freundlich			Temkin			Dubinin–Radushkevich		
	Q_m (mg g ⁻¹)	K_L L mg ⁻¹	R_L	$1/n$	n	K_f (mg g ⁻¹)	A_T L g ⁻¹	b_T	B J mol ⁻¹	q_s (mg g ⁻¹)	K_{ad} (mol ² /J ²)	E (KJ mol ⁻¹)
	0.69348	497.24	0.1773	1.6321	0.6127	2018.8	7.15×10^{20}	20458.9	0.1211	2.1877	1×10^{-9}	22.36
R^2	0.9927			0.9926			0.9584			0.9991		

vapors also can damage the kidneys and neurologic system. However, before release of the chlor-alkali sewage into the environment it is strongly recommended to remove mercury. Also the sorbents used for mercury remediation such as the present nanoparticles should not be released into the environment. So the recovery and reusability of the nanoparticles and the mercury seems necessary.

Hydrochloric acid is commonly used for some metal ions elution, including Hg(II), from adsorbents surfaces due to its common usage in industry. Recovery of the adsorbate may be a secondary objective, and the more concentrated the adsorbate is in desorption fluid the more likely the success of the process. Therefore, in this work, we added hydrochloric acid on the spotty nanoparticles for recovery of mercury and recycling of nanoparticles. Finally, the recovered mercury ions were recycled as metallic mercury.

Influence of hydrochloric acid concentration

When using strong acid it is possible that desorption could occur along with nanoparticles dissolution as a result of acid solubilization of the nanoparticle. This was checked using different concentration of HCl in a desorption trial. The results showed that nanoparticles were dissolved in HCl with concentrations higher than 1 M. The addition of 10 mL portions of acceding concentration of HCl (0.1, 0.5, 0.7 and 1.0 M) as a recovery agent, indicated an increase in mercury desorption up to 1 M. So, 1 M HCl was used as the recovery solvent.

Influence of hydrochloric acid volume

Different amounts of 1 M hydrochloric acid were added to the spotty γ -Fe₂O₃ nanoparticles to desorb the mercury from the surface. Figure 6 shows that desorption efficiency increases with increase in HCl volume. A maximum mercury recovery of 93.92 % was observed for 8 ml of 1.0 M HCl solution as the elution solvent.

Recovery of elemental mercury (Hg⁰) from spotty Hydrochloric acid

A system presented in Fig. 7a was designed to recovered mercury from contaminated HCl in our laboratory. The

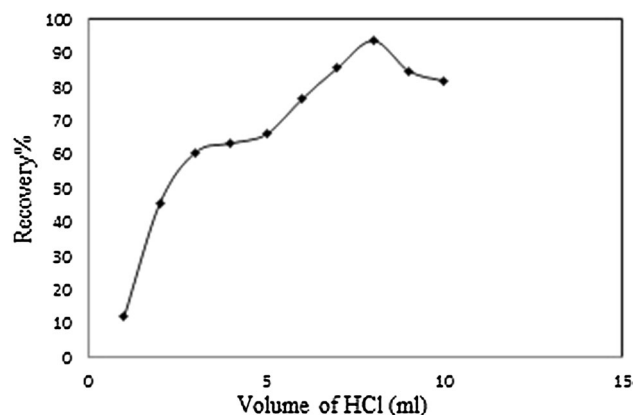


Fig. 6 Influence of hydrochloric acid volume on mercury elution from the nanoparticle surface

system is much like the cold vapor system except for mercury trapping segment. Tin (II) chloride was used to reduce Hg²⁺ to Hg. The generated Hg was passed through the system by means of nitrogen gas. As it can be seen from the Fig. 7b, a hollow glass gas chromatography column half filled with distilled water which was completely covered by ice was placed in the mercury reduction line (Fig. 7a) to trap metallic mercury on cooling the Hg vapors. The elemental mercury can be reused in chlor-alkali plant and thus protecting the environment. To prevent release of traces of mercury into the environment, the acidic permanganate solution was placed at the end of the transfer line. The mercury recovery was about 94 %.

Sorption isotherms

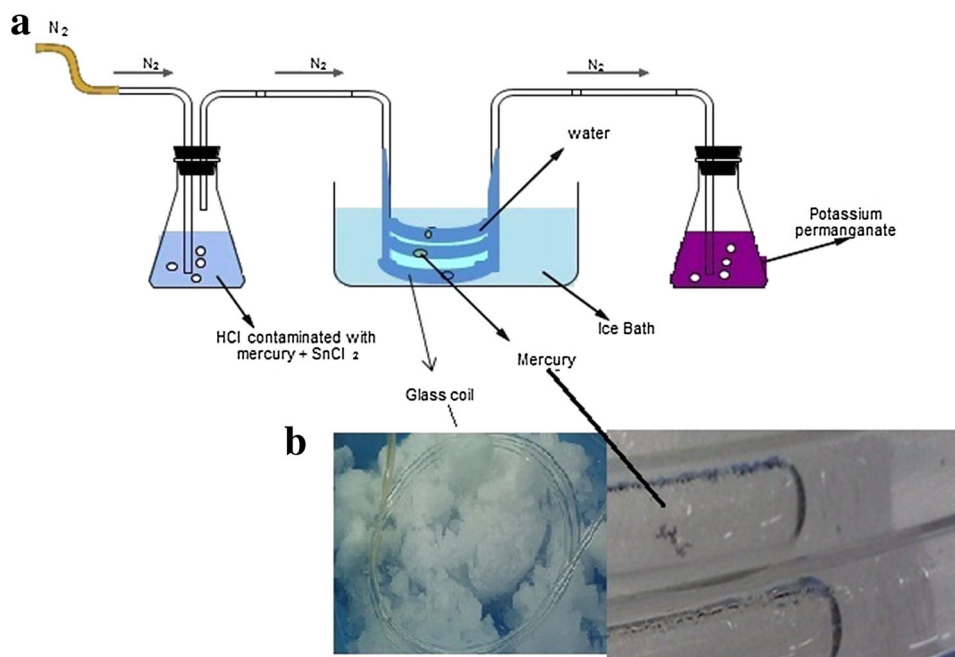
Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherms models were fitted to determine the adsorption mechanism of the mercury from the petrochemical waste onto the γ -Fe₂O₃ nanoparticles. The equations and their linear form used for evaluation of the sorption systems are briefly described below.

Langmuir Adsorption Isotherm equation [37] is:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

and its linear form which is used to calculate the corresponding isotherm parameters is:

Fig. 7 **a** schematic design for conversion of mercury contaminated HCl to elemental mercury, **b** released mercury that is trapped in the glass coil placed on ice



$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

where C_e = the equilibrium concentration of adsorbate (mg L^{-1}), q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg g^{-1}), q_m = maximum monolayer coverage capacity (mg g^{-1}), K_L = Langmuir isotherm constant (L mg^{-1}).

The essential features of the Langmuir isotherm can be expressed in terms of R_L , which is a dimensionless constant referred to as separation factor and defined as:

$$R_L = \frac{1}{(1 + K_L C_0)}$$

where C_0 is initial concentration.

R_L value indicates the adsorption nature. The $R_L > 1$, $R_L = 1$, $0 < R_L < 1$, and $R_L = 0$ identify unfavorable, linear, favorable, and irreversible adsorption, respectively. In this study, the present adsorption system evaluated by Langmuir isotherm indicates the favorable adsorption with $R_L = 0.1773$ as can be seen in Table 1.

Freundlich adsorption isotherm is commonly known to describe the heterogeneous adsorption [38]. The empirical equation proposed by Freundlich is

$$q_e = K_f C_e e^{1/n}$$

where K_f = Freundlich isotherm constant (mg g^{-1}), n = adsorption intensity; C_e = the equilibrium concentration of adsorbate (mg L), q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg g).

Linear form of the equation has the following form:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

The constant K_f is an approximate indicator of adsorption capacity, while $1/n$ determines the adsorption strength in the adsorption process [39]. The values more than 1 for $1/n$ parameter implies to the fact that a cooperative adsorption occurs [40]. In this study not only the experiments are directly performed on waste, which contains some cations and anions, but also no modification on the sorbent surfaces for selective adsorption of mercury is done. Therefore, as it is indicated in Table 1 the $1/n$ value of 1.6321 confirms occurrence of cooperative adsorption in mercury removal from the waste using bare $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles.

The Temkin model is given by the following equation [41]

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e$$

$$B = \frac{RT}{b_T}$$

A_T = Temkin isotherm equilibrium binding constant (L g^{-1}), b_T = Temkin isotherm constant, R = Universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}$), T = Temperature at 298 K, B = Constant related to heat of sorption (J mol^{-1}).

Dubinin–Radushkevich isotherm (DRK) model and its linear form are described by the following equations

$$q_e = q_s e^{(-B_{DR} \epsilon^2)}$$

$$\ln q_e = \ln q_s - B_{DR} \epsilon^2$$

Table 2 Comparison of mercury removal methods used for industrial waste treatments

Adsorbate	pH range	Capacity	Time	Con (ppm)	Adsorption %	References
<i>Acetobacter xylinum</i> cellulose	5–8	65 $\mu\text{g g}^{-1}$	10 min	9.638	95.64	[45]
MBI-Clay ^a	4–8	250 mg g^{-1}	8 h	28–100	75–99	[5]
SA-activated carbon ^b	4–9	188.7 mg g^{-1}	4 h	50–100	Above 90	[33]
NAC-activated carbon ^c	6–9	Below 188.7	4 h	50–100	Above 60	[33]
Bare $\gamma\text{-Fe}_2\text{O}_3$	3–8	234 mg g^{-1}	20 min	0.1–0.400	83–94.5	Present method

^a 2-Mercaptobenzimidazole-clay (MIB-clay)

^b Sulfur activated

^c Non activated

Dubinin–Radushkevich isotherm is generally applied to express the Gaussian energy distribution onto a heterogeneous surface [42].

where q_e = amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}), q_s = theoretical isotherm saturation capacity (mg g^{-1}), B_{DR} = Dubinin–Radushkevich isotherm constant (mol^2/J^2).

The model was usually applied to distinguish the physical and chemical adsorption including ion exchange of metal ions on solid sorbents. Mean free energy of adsorption (E) can be determined by $E = \frac{1}{\sqrt{2B_{\text{DR}}}}$ [43]. The ε can be calculated using $\varepsilon = RT \ln \left[1 + \frac{1}{C_e} \right]$ With the obtained $E = 22.36 \text{ kJ mol}^{-1}$ for the DRK model applied on the results (Table 1), it should be concluded that a chemisorption process has been occurred. From R^2 presented in Table 1, it can be seen that Langmuir and Freundlich isotherms have shown approximately the same correlation coefficient whereas the Temkin has the least correlation among the considered models, and DRK with the $R^2 = 0.9991$ shows the best correlation. However, the adsorption obeyed DRK model. It should be recalled that the DRK model is usually capable to describe the metal adsorption on the surface of the inorganic sorbents as it is the case in this study. It should be noticed that the presence of both mercury ion and metallic mercury is appropriate in this waste. R^2 value of the Langmuir isotherms that usually describe gas phase adsorption, and that of Freundlich both indicate these two forms of mercury in the waste.

To our knowledge, there was limited works on chlor-alkali mercury removal using adsorption technology. Some of them are listed in Table 2 for comparisons. As it is indicated on the table, the present sorbent is capable of removing mercury at trace levels without any surface modification with good capacity at short time.

Conclusion

In conclusion, $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles (MIONs) are an effective sorbent for separation and pre-concentration of trace amounts of mercury from the wastewater of chlor-alkali unit. As it is reported by other researcher, some sorbent can be used for mercury removal without any modifications. Even chloride and oxide forms of mercury can be adsorbed on the surface of the sorbents better than mercury itself [44]. In petrochemical waste, chloride ion is present and probably the mercury chloride produced is simply adsorbed on the $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles. The results also indicated that no modification of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles was required. It may be because of the self-modification by the matrix components (cooperative adsorption) as it was also concluded from $1/n$ value obtained by the Freundlich isotherm. With concise control of the parameters affecting the sorption of the mercury removal efficiency reached 94.59 % in the present waste. The greatest improvement of this method is that the desired materials are separated from the petrochemical waste by a simple and efficient process while less or even no secondary wastes are produced. Other improvement is the conversion of Hg(II) to Hg^0 for reuse in chlor-alkali plant. However, simple, rapid, reproducible, and low cost system is introduced. It was also found that MIONs did not keep any magnetization after the removal of an external magnetic field which proved the super paramagnetic characteristic of these nanoparticles. Above all the main advantage is that the mercury content of petrochemical cake, the final form of chlor-alkali waste, released in the environment reaches below the waste permitted levels (5 ng mL^{-1}).

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