ORIGINAL ARTICLE

Magnetic Fe$_3$O$_4$ nanoparticles coated with Thiol functionalized mesoporous Silica as a novel adsorbent for Pb^{2+} and Ag$^+$ removal

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Abstract
Magnetic Fe$_3$O$_4$ nanoparticles coated with thiol functionalized mesoporous silica (TFMS) were prepared and used as a novel adsorbent for Pb2+ and Ag+ removal. FTIR spectra confirmed the Fe$_3$O$_4$ nanoparticle cores coated with mesoporous silica and indicated the presence of thiol groups on the surface. XRD analyses showed that synthesized adsorbent has a face-centered cubic magnetite phase structure. The best removal results were obtained at pH=5-7 and a stirring time of 15 minutes. The lowest amount of 3M nitric acid for stripping the target species from adsorbent was 40 mL. The data was found to fit the Langmuir model, and the respective maximum capacities of the adsorbent for Pb2+ and Ag+ ions was 1000.0 (±1.5) μg and 1111.0 (±1.2) μg of the target species per mg of the adsorbent. The developed adsorbent was successfully applied in wastewater samples.

Keywords: *Magnetic Fe$_3$O$_4$; Mesoporous Silica; Removal; Thiol Functionalized; Ag$^+$; Pb^{2+}.*

INTRODUCTION

Heavy metals are the source of significant threats to living animals. The lead ions present in the environment come from natural and anthropogenic sources. Lead compounds are used in batteries, petroleum additives, alloys, pigments, cables, and ammunitions. Drinking water, food, air, and soil constitute the significant sources of exposure to lead ions. In high concentration of lead, it can meddle with the synthesis of hemoglobin; influence the kidneys, gastrointestinal tract, joints, reproductive system; and causes acute or chronic damages to the nervous system [1]. Contact with silver or its compounds can lead to severe corneal injury and skin irritation. The adverse effects reported at high concentrations include drowsiness, staggering, confusion, unconsciousness, coma, or death. All these make it necessary to develop methods and materials for removing these species from the environment [2].

Preparation of adsorbents to remove heavy metals is a hot topic in the field of environmental pollution [3-7]. Most of the materials used for

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this, e.g., alumina, clays, and silicates, suffer disadvantages of low mechanical and thermal stability and lack of chemical inertness. Metal or metal oxide nanoparticles offer various advantages, including large surface area/volume ratios, high effectiveness at low amounts, facile and fast separation and regeneration, etc. [8]. The recently developed hybrid sorbents further offer new properties and create novel application opportunities [9-13]. These modified materials combine various removal mechanisms like physical and electrostatic adsorption, ion-exchange, and hard/soft acid-base interactions [14] and hence offer enhanced properties.

Consequently, the design and preparation of new magnetic nanoparticles coated with functionalized mesoporous silica can have exciting results, which is reflected in recent works in this field [9, 10, 15-19]. Mesoporous silica materials are suitable for various applications, due to their large specific surface area, limited pore size distribution, and high surface density of hydroxyl groups. The silanol groups of these materials can be easily modified through reacting with organosilane compounds, and their hydrophobic surfaces make them good candidates for use as adsorbents in aqueous media. Hence, different mesoporous materials are developed and used as adsorbents for metal ions [20–27], organic compounds [28], dyes [29-31], radionuclides [32], and anionic complexes [33, 34].

Based on what was said, in the present work, we focus on the development of a new hybrid sorbent by coating magnetic Fe_3O_4 nanoparticles with thiol functionalized mesoporous silica (TFMS). To this end, the magnetic nanoparticles were prepared and coated with mesoporous silica, and then the coating was modified with thiol groups (Fig. 1). The resulting adsorbent was used to remove Pb^{2+} and Ag^+ from water media. As far as our search reveals, no previous work has reported the development and application of TFMS-coated Fe_3O_4 magnetic nano adsorbents for Pb^{2+} and Ag^+ removal.

EXPERIMENTAL PROCEDURES
Reagents

Ferrous chloride tetrahydrate (98%), Ferric chloride hexahydrate (98%), absolute ethanol, glycerol (99%), aqueous ammonium solution (25%), and the organic solvents used were purchased from Merck. Tetraethyl orthosilicate (TEOS, 98%), 3-Mercaptopropyl trimethoxysilane

were from Sigma-Aldrich. Analytical grade sodium, manganese, magnesium, cobalt, silver, nickel, zinc, cadmium, lead, chromium, and copper nitrates (Merck, Darmstadt, Germany) were used without any further treatments. Doubly distilled water (DDW) was used in all experiments. The stock solutions of the metal ions were 1000 mg L^{-1} solution in DDW, and the working standard solutions were prepared by diluting them to the desired concentration [2].

Apparatus

Fourier transform infrared (FT-IR) spectra were acquired in the range of 400 to 4000 cm^{-1} using a RAYLEIGH WQF-510A FT-IR spectrophotometer through the KBr pellet technique. The crystallinity of the products was studied by X-ray diffraction (XRD) using an X'Pert Pro MPD diffractometer with Cu K_α radiation (λ= 1.5418 Å). The XRD results were recorded at 40 kV and 40 mA. The pH studies were performed using a Jenway 3520 pH meter and a combined glass-calomel electrode. A UP 400S Hielscher ultrasonication probe was used for dispersing the species at an operating voltage of 450 V. The separation of the magnetic adsorbents was performed using a 5 cm × 5 cm × 4 cm 1.4 T magnet [35].

The quantitative analysis of the species concentration was performed by a PG-990 flame atomic absorption spectrometer, with hollow cathode lamps and an air-acetylene burner. The flame atomic absorption spectrometry analyses were performed at slit width: 0.4 nm, lamp current: 5.0 mA, and wavelength 273.3 nm, and 328.1 nm for Pb^{2+} and Ag^+. In the case of other cations, the corresponding recommended conditions were used.

Synthesis of Fe_3O_4 nanoparticles

The magnetite nanoparticles (MNPs) were precipitated from aqueous solutions of Fe(II), and Fe(III) salts in an alkaline medium as described elsewhere [12]. This typically involved dissolving $FeCl_3 \cdot 6H_2O$ (0.02 mol, 5.84 g) and $FeCl_2 \cdot 4H_2O$ (0.01 mol, 2.15 g) at a molar ratio of 2:1, in 100 mL of DDW. Then 15 mL of a 28% v/v NH_4OH solution was added to this mixture under a nitrogen atmosphere as a co-precipitating agent. After half an hour of sonication, the product (10 nm Fe_3O_4 nanoparticles) was cleaned using deionized water and ethanol (twice), a 0.02 mol L^{-1} NaCl solution, and deionized water (three times), before storing
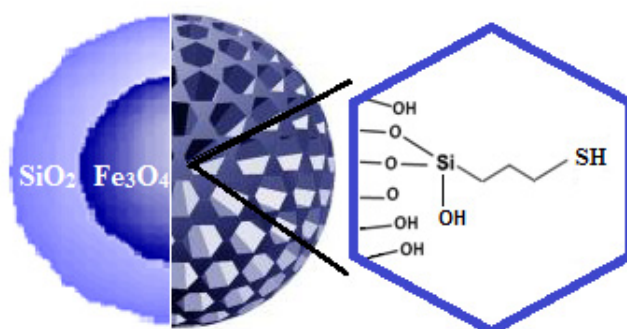
Fig. 1. Structure of thiol functionalized silica coated Fe₃O₄ magnetic nanoparticles.

at a concentration of 40 mg mL⁻¹ [12].

Synthesis of Silica-coated MNPs

The nanoparticles were prepared as described before [10]. The method included transferring 25 ml of a suspension of the magnetite nanoparticles (MNPs) into an Erlenmeyer flask. Then the MNPs have separated from the supernatant using a magnet and then dispersed in 80 mL of a 10% v/v aqueous solution of tetraethoxysilane (TEOS). Next, 60 mL of glycerol was added, and the suspension was sonicated in a bath for 5 min, before its pH was set below 5 using acetic acid. This mixture was stirred at 85 °C for 2 hours under a nitrogen atmosphere, and the product was separated, washed three times with 200 mL deionized water, and with 200 mL methanol, and eventually once with 200 ml of DDW. The final product was stored as a 40 g L⁻¹ mixture in DDW [10].

Thiol functionalization of the silica-coated MNPs

Organosilane compounds were used at this stage [36]. According to the procedure, 1 g of the prepared silica-coated MNPs (SC-MNPs) was dispersed in 50 mL of water-free toluene under sonication, and then 1 mL of (3-Mercaptopropyl) trimethoxysilane together with 30 mL of the same solvent were added to the reaction vessel in a drop-wise manner to vessel. Once the reaction was over, the thiol functionalized silica-coated Fe₃O₄ nanoparticles (TFMS-MNPs) were filtered and washed with toluene and dried at 60 ºC under vacuum [36].

Extraction experiments

The general extraction procedure using the TFMS-MNPs involved adding 5mg of the adsorbent to suitable volumes of a 3 mg L⁻¹ solution of Pb²⁺

and Ag⁺ and stirring the mixture for at least 15 min. Then, the adsorbent was filtered, and the extracted ions were stripped using 40 mL of a 3.0 mol L⁻¹ solution of nitric acid and assessing the concentrations of the species in sample and stripping solutions [2].

Equilibrium Studies

Adsorption isotherms determine the mathematical dependence of the solute adsorbed mass by each gram of an adsorbent, qe (mg/g), and the solute concentration in the solution under equilibrium, Ce (mg/L). Freundlich and Langmuir isotherm models were evaluated in these studies. The former model has been derived from the assumption a heterogeneous surface with a non-uniform distribution of heat of adsorption. While Langmuir model is build based on the assumption that the sorption process takes place at specific homogeneous sites within the make-up of the adsorbent [35, 37].

The linear form of the Langmuir model can be expressed as [38]:

$$C_e / q_e = 1/b \, q_m + C_e / q_m \qquad (1)$$

In this equation, q_m is the maximum adsorption capacity (which happens when a complete monolayer covers the adsorbent), and b is the equilibrium constant (L/mg).

The linear expression of the Freundlich model can be as below [39]:

$$\text{Log } q_e = \log K_f + \frac{1}{nf} \log C_e \qquad (2)$$

In this equation, K_f is a rough indicator of the adsorption capacity, and $1/n_f$ expresses the adsorption intensity, which is a measure of the
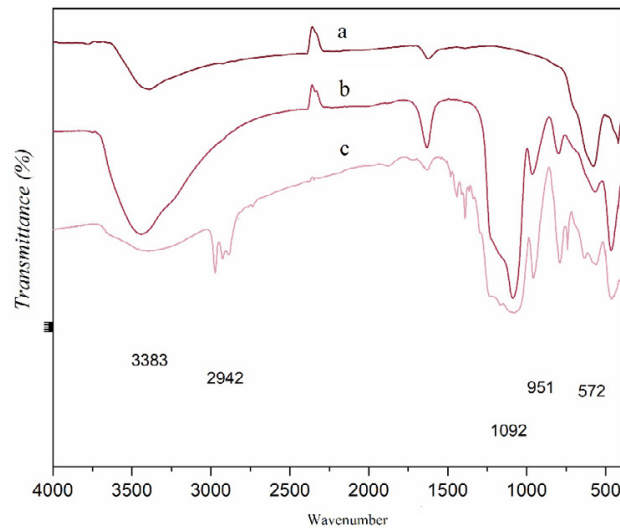
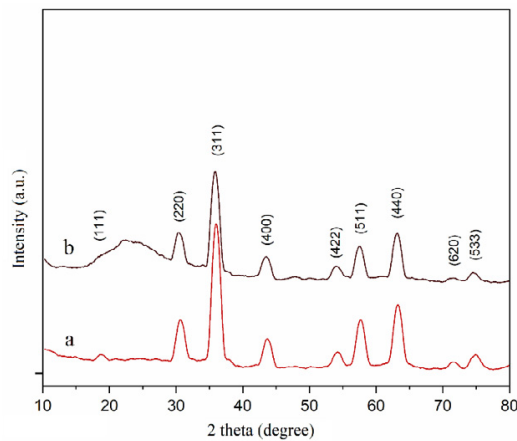Fig. 2. FT-IR spectra of a) Fe$_3$O$_4$, b) silica coated Fe$_3$O$_4$ and c) thiol functionalized magnetic nanoparticles.

Fig. 3. X-ray diffraction patterns of a) Fe$_3$O$_4$ and b) thiol functionalized magnetic nanoparticles.

adsorption intensity or surface heterogeneity and ranges from 0 and 1, smaller values reflecting higher heterogeneity.

A set of solutions with various concentrations in the range of 10-800 mg L^{-1} of the ions was used for adsorption isotherm studies.

RESULTS AND DISCUSSION

Characterization of the adsorbent

The FT-IR spectra of the modified and unmodified silica-coated Fe$_3$O$_4$ magnetic nanoparticles are presented in Fig. 2. All spectra contain two absorption bands at about 453 cm^{-1} and 572 cm^{-1}, corresponding to the stretching vibrations of the Fe^{2+}–O and Fe^{3+}–O, which confirm the nature of the Fe$_3$O$_4$ nanoparticle cores in all cases. The characteristic peak of the O–H group

can be observed at 3383 cm^{-1} for all samples. Also, the four characteristic bands reflecting the vibrations of Si–OH and Si–O–Si vibrations can be seen at 951, 1092, and 1211 cm^{-1} in the case of the silica-coated nanoparticles. Further, the stretching vibration of aliphatic –CH$_2$ present in organic compounds of thiol-functionalized product is evident at 2942 cm^{-1} [12, 36 and 40-42].

The crystallinity of the modified and unmodified nanoparticles was studied by X-ray diffraction analysis, and the results are seen in Fig. 3. The respective diffraction peaks at 2Θ = 30.1º, 35.2º, 43.2º, 53.1º, 57.4º, and 62.3º correspond to the (220), (311), (400), (422), (511) and (440) planes, respectively, which agreed well with the magnetite database (JCPDS No. 19-1 0629) and indicating that the magnetite (Fe$_3$O$_4$) phase has
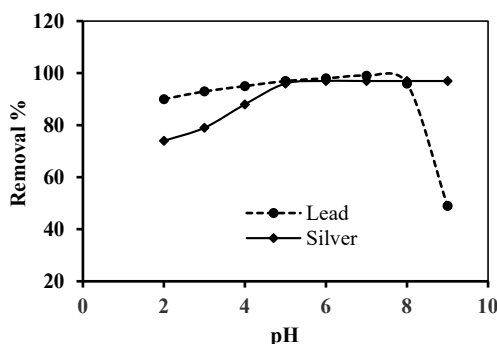
Fig. 4. Effect of pH on the removal efficiency of Pb^{2+} and Ag^+ ions.
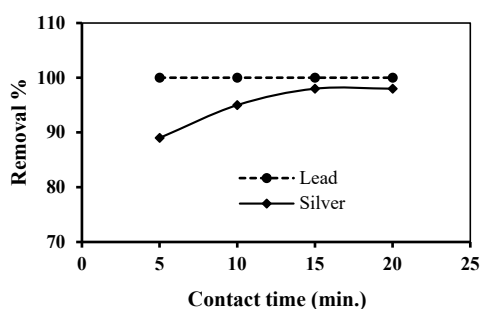
Fig. 5. Effect of contact time on the removal of Pb^{2+} and Ag^+ ions.

a face-centered cubic (fcc) structure. No other iron oxides, e.g., Fe_2O_3, could be observed, which illustrates the purity of the samples. Further, the pattern includes a broad reflection at $20 - 30^\circ$, due to the coating of the amorphous SiO_2 [12].

Effect of pH on the extraction

The extraction of the target species by the TFMS-MNPs adsorbents was evaluated at different pH range of 2.0 to 9.0. The changes in the solution pH were created using 1 mol L^{-1} solutions of nitric acid or sodium hydroxide, and the results are presented in Fig. 4. The results show that Pb^{2+} and Ag^+ can be effectively extracted with the developed adsorbent in the pH range of 4-8. This is because the functional groups present on the surface of the surface groups of TFMS-MNPs change based on pH. At acidic pH, the majority of these binding sites are protonated, and the surface of TFMS-MNPs is covered with hydronium ions, inhibiting their interaction with the target ions. Increasing the pH, on the other hand, deprotonates the surface groups have been increased the negatively charged sites. Consequently, Pb^{2+} and Ag^+ cations are adsorbed due to electrostatic attractions.

The effect of the extraction time

The effect of time on the extraction efficiency was studied using a series of solutions containing 75 mg of Pb^{2+} and Ag^+ ions, and the results are presented in Fig. 5. The overall adsorption process occurs in three phases, i.e., the initial fast uptake, the slow uptake, and the equilibrium phases. The initial stage occurs due to the existence of considerable concentration gradients between the surface of the adsorbent and the bulk solution due to a large number of vacant sites available. Consequently, the adsorption rate is high at this stage. With time the gradient and the number of adsorption sites reduce due to the accumulation of target species on the adsorbent, gradually decreasing the adsorption rate until the final equilibrium state is reached.

As is seen, the equilibrium times for Pb^{2+} and Ag^+ were 5 and 15 min and more. Thus, these values were chosen and used in the rest of the experiments.

Amount of the adsorbent

To determine the required amount of TFMS-MNPs for maximum removal of Pb^{2+} and Ag^+ ions, experiments were conducted using different amounts of the TFMS-MNPs. It was found that both target ions could be removed between 98%-

Table 1. Removal of Pb^{2+} and Ag^+ ions from triple mixtures[a].

Divers' ions	Amount taken(µg)	Removal of Pb^{2+} (%)	Removal of Ag^+ (%)
Na^{2+}	1250	100.0(1.2) [b]	100.0(0.9)
Mg^{2+}	1250	100.0(1.4)	99.7 (1.0)
Cr^{3+}	750	99.5 (0.8)	99.8 (0.9)
Co^{2+}	750	100.0 (0.9)	98.0 (0.7)
Cd^{2+}	750	99.2 (1.5)	100.0 (1.3)
Ni^{2+}	1250	100.0 (1.1)	100.0(1.0)
Zn^{2+}	750	97.0 (0.9)	99.0 (0.8)
Cu^{2+}	1250	99.8 (1.3)	100.0(1.4)
Mn^{2+}	750	100.0 (0.8)	99.3 (1.0)

[a] Initial samples contained 75µg Pb^{2+} and Ag^+ ions in 25 ml water.
[b] Values in parentheses are RSDs based on three replicate analysis.

Table 2. Values of isotherm constant for sorption of Pb^{2+} and Ag^+ ions.

Isotherm	Parameters	Pb^{2+}	Ag^+
Langmuir	q_m(mg g^{-1})	1000	1111
	K_L(L mg^{-1})	0.026	0.009
	R^2	0.9713	0.973
Freundlich	1/n	0.547	0.651
	K_f(mg g^{-1})	44.10	20.12
	R^2	0.9352	0.9648

99% by increasing adsorbent value from 5 to 20 mg. Consequently, the later extraction tests were carried out using the minimum optimal value of 5 mg of TFMS-MNPs.

Removal of target species in three-component mixtures

The removal of Pb^{2+} and Ag^+ from water samples containing different metal ions was investigated. 25 mL aliquots of aqueous solutions containing 75 µg of Pb^{2+} and Ag^+ and different amounts of other cations were subjected to the extraction experiments under optimal conditions. The obtained results are given in Table 1. The target species are completely removed by the TFMS-MNPs under these conditions, at up to relatively high amounts of the third component, and no significant interference effects were observed (Table 1).

Adsorption isotherms

In order to optimize the use of TFMS-MNPs, the most appropriate adsorption isotherm must be determined. Hence tests were run, and the results are summed up in Table 2.

Parameters of each adsorption isotherm were determined through linear regression analysis, and the squared correlation coefficients (R^2) were calculated. Based on the results, equilibrium data for both target species were fitted better into the Langmuir isotherm model than Freundlich model, with correlation coefficients (R^2) of 0.9713 and 0.973 for Pb^{+2} and Ag^+ respectively. It was hence concluded that Pb^{2+} and Ag^+ form a homogeneous monolayer on the adsorbent.

Using the Langmuir model, the respective maximum adsorption capacities for Pb^{+2} and Ag^+ were determined as 1000 and 1111 µg/mg of the adsorbent.

Desorption and reuse study

The regeneration reusability of an adsorbent is a crucial factor in its evaluation. Hence, experiments were carried out to determine the proper volume of nitric acid for the recovery of extracted Pb^{2+} and Ag^+ ions from TFMS-MNPs. Different volumes of the acid solution were used, and according to the results (Table 3), 40 mL of a 3.0 mol L^{-1} nitric acid led to the best results.

Experiments on the regeneration capacity of the TFMS-MNPs included repeated use/ regeneration of the adsorbent. It was found that the recovery efficiency of the adsorbent after reduced about 4% for Pb^{2+} and was constant for Ag^+ after three regeneration rounds.

Real wastewater samples

The applicability of the developed adsorbent was evaluated using the wastewater samples of Islamic Azad University of Yadegar-e-Imam

Table 3. Effect of volume of stripping acid on the recovery of ions.

Volume of HNO₃ (3M)	Recovery (%)	
	Pb^{2+}	Ag^+
25 mL	100	51
30 mL	100	68
40 mL	100	100

Table 4. Removal of Pb^{2+} and Ag^+ ions from wastewater samples.

Samples	Concentration of Pb^{2+}(mg L⁻¹)	Removal of Pb^{2+} (%)	Concentration of Ag^+(mg L⁻¹)	Removal of Ag^+ (%)
wastewater sample	2.2 (1.1)ᵃ	97.4 (1.4)	2. 8 (1.0)	95.3 (1.2)

ᵃValues in the parentheses are RSDs based on three replicate analysis.

Table 5. Comparison of the proposed method with the previously reported.

Adsorbent	Maximum capacity (mg g⁻¹)	Removed ions	Ref.
Fe₃O₄ nanoparticles	9.5	Pb^{+2}	43
sulfonated Fe₃O₄ magnetic nanoparticle	108.9	Pb^{+2}	44
amino-functionalized Fe₃O₄ nanoparticles	40.1	Pb^{+2}	45
Guanidine functionalized SBA-15	89.1	Pb^{+2}	24
ZnO-Chitosan core-shell nanocomposite	476.1	Pb^{+2}	13
Waste coffee grounds	49.5	Ag^+	46
Chitosan/montmorillonite	43.5	Ag^+	42
Fe₃O₄-decorated and silica-coated graphene oxide modified with a polypyrrole-polythiophene copolymer	49	Ag^+	48
Fe3O4 modified with ethylenediamine	90.3	Ag^+	49
Fe3O4@SiO2 modified with poly(2-aminothiophenol)	78.2 52.3	Pb^{+2} Ag^+	50
amino-functionalized Fe₃O₄@SiO₂ modified with EDTA	29.0	Pb^{+2}	51
Diglycolic acid functionalized core-shell silica coated Fe₃O₄ nanomaterials	62.4	Pb^{+2}	52
Thiol functionalized mesoporous Silica Coated Fe₃O₄ magnetic nanoparticles	1000 1111	Pb^{+2} Ag^+	(This work)

Khomeini (RAH), Shahre Rey. The tests were performed through the standard addition method, and the initial and final concentrations of the target species were determined. Based on the results (Table 4), the developed adsorbent could be successfully used to remove Pb^{2+} and Ag^+ ions in wastewater samples.

Comparison with former studies

The maximum capacity of the adsorbent and those of some previously reported adsorbents for the same target species are summarized in Table 5. The results indicate the superiority of the adsorbent to the formerly reported ones [13, 24 and 43-52]. Interestingly the developed adsorbent has higher adsorption capacities than other modified Fe_3O_4 nanoparticles [44, 45 and 49-52] and functionalized mesoporous SBA-15 [24].

CONCLUSION

The main objective of the present research was to develop a simple, fast, and practically efficient method for removing Pb^{2+} and Ag^+ from water and wastewater samples. To this end, thiol functionalized silica-coated Fe_3O_4 nanoparticles were developed and evaluated as adsorbents.

Pb^{2+} and Ag^+ ions were entirely removed at pH 4-8 after stirring for 15 min; in 25 mL of 3 mg L^{-1} solutions of the target species using 5 mg of TFMS-MNPs. Isotherm studies proved that the Langmuir model fits the experimental data better than the Freundlich models. The highest adsorption capacities were 1000 and 1111 µg /mg TFMS-MNPs, for the Pb^{2+} and Ag^+ ions, respectively. The main advantages of the adsorbent are concise sample processing time, rapid and simple separation process, the high adsorption capacity of adsorbent, and reducing the need for channeling results. Of course, since this adsorbent is selective but not specific, it can also remove some other inorganic ions. Only the optimum conditions for the removal of each ion must be determined.

ACKNOWLEDGMENT

CONFLICT OF INTEREST

Authors have no conflict of interest

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