



Removal of copper(II) from aqueous samples using natural activated hydroxyapatite sorbent produced from camel bones

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ABSTRACT

A simple and low-cost procedure for the removal of copper(II) ions from contaminated aqueous samples is introduced. The method depends on the adsorption of Cu(II) ions onto a natural activated hydroxyapatite (HAP) adsorbent, simply produced by recycling camel bones food waste, then chemically and physically activated. Activated sorbent samples were characterized using FT-IR, XRD, and SEM-EDX, then initially tested for Cu(II) ions adsorption. Four samples were then selected to complete the physicochemical studies including factors affecting the adsorption efficiencies and thermodynamic studies. As a result, one sorbent sample (chemically activated sample #2) that acquired the highest adsorption efficiency among other sorbents was selected to conduct industrial semi-pilot column experiments for the treatment of copper-contaminated well-water samples. This article presents a simple method for the recycling of a major food waste and environmental pollutant in Saudi Arabia to produce an activated adsorbent that had been applied successfully in the treatment of contaminated aqueous samples.

Keywords: Natural adsorbent; Activated hydroxyapatite; Removal of copper(II); Food waste recycling; Water treatment

1. Introduction

Environmental pollution caused by heavy metal ions has a primary concern due to the high ecotoxicological hazards of heavy metals through their accumulation in the living organisms [1–5]. Leaching of heavy metals to natural waters, as a main part of environment, increases continuously due to the increase of the production and utilization of such metals in many of human industrial activities, in addition to natural leaching from rocks to surface or groundwater [1].

Exceeding the intake level of copper, as an example of heavy metals, by the human body may cause gastrointestinal distress with short term exposure, while may cause liver or kidney damage with long term exposure [6]. The United States Environmental Protection Agency (EPA) stated a maximum level of copper contamination to be 1.3

ppm while The World Health Organization (WHO) recommends the maximum allowable concentration for copper to be 2 ppm. Therefore, many research efforts have been done recently for the removal of hazardous heavy metals from water/wastewater to reach the permissible levels [5].

Conventional processes for the treatment of metal-contaminated water involve several procedures, such as ion exchange, membrane filtration, chemical precipitation, co-precipitation/adsorption, and carbon adsorption processes [7]. Many adsorption studies on the treatment of waste water contaminated with copper ions and other heavy metal ions were conducted using both natural and synthetic adsorbents. Razak et al. used modified natural kenaf fibers in the removal of copper ions from waste water samples [28]. Ince et al. applied treated food wastes (including, tea leaf, chestnut shell, and banana peel) for the treatment of copper-contaminated wastewater [29]. Activated carbon membranes modified with nano Fe₂O₃/TiO₂ 3D composite were successfully used for adsorbing Cu(II) and As(V) from

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artificial wastewater samples with high removal efficiency [30]. Copper and other heavy metal ions were efficiently removed using chemically-treated orange biomass [31]. Removal of copper ions from artificial wastewater samples was again carried out using both raw and treated sea-shells, with more than 99% adsorption efficiency [32]. Mojoudi et al. introduced an efficient method for Cu(II) and Pb(II) ions adsorption based on a composite of activated carbon/thiol-modified graphene oxide [33].

Hydroxyapatite has been considered as an effective adsorbent for wastewater treatment from heavy metals. Many studies have been done on the production of hydroxyapatite from low-cost and abundant sources [8]. Several natural sources are known for hydroxyapatite production, such as fish bones, egg shells and natural corals [9,10]. Hydroxyapatite and other adsorbent materials were produced from camel bones, characterized, and applied to the treatment of heavy metals from water samples [11–13].

This work aimed to introduce a simple produce for the production of hydroxyapatite sorbent material from a cheap natural source, i.e. camel bones, which is a major food waste with high local availability and almost no cost in Saudi Arabia. The produced hydroxyapatite sorbent samples were then activated via chemical or physical treatment procedures in order to increase their adsorption efficiencies. Activated sorbent samples were used in the treatment of contaminated aqueous samples for the removal of copper ions.

2. Methodology

2.1. Materials and equipments

All used chemicals and reagents were obtained with analytical grade. A copper atomic absorption standard solution of 1000 mg L⁻¹ (Sigma-Aldrich, USA, www.sigmaaldrich.com) was used as a stock solution. The working standards were freshly prepared from the stock solution using bi-distilled deionized water (Barnstead, NANO pure diamond system, USA, www.barnstead-water.com). Solution pH was adjusted by a calibrated pH-meter (Hanna, model 211, www.hannainst.com) complete with a combined glass electrode. A three-zone tube furnace (MTI, model OTF-1200X-III-S, USA, www.mtixtl.com) was used for sample activation under the recommended conditions. Analysis of the concentration of Cu(II) ions was carried out using a flame atomic absorption spectrophotometer (Varian, model SpectrAA 220, USA, www.agilent.com). Fourier transform infrared spectrometer, FTIR, (Thermo Nicolet, model iS 10, USA, www.thermofisher.com) was used to identify the adsorbents functional groups. A scanning electron microscope coupled with energy dispersive X-ray spectroscopy (SEM-EDX) instrument (Jeol, model 6360 LVSEM, USA, www.jeolusa.com) was utilized to obtain the pore structure of the treated hydroxyapatite surfaces and to produce a qualitative/quantitative elemental analysis of the hydroxyapatite samples. X-ray diffraction patterns for HAP samples were obtained using a X-ray diffractometer (Shimadzu, model XRD-6000, Japan, www.shimadzu.com). Sample/adsorbent incubation and shaking was conducted using a mechanical water thermostat shaker (GFL, 1083, Germany-

www.gfl.de). Whatman filter paper, grade 42, was used to filter off the copper sample solutions after absorption for adsorbent removal.

2.2. Samples collection and pretreatment

Camel bone samples were collected from the local market in Abha city, Asserarea, KSA. The collected samples were cut to small cubes (2 cm × 2 cm) and immersed in dilute acetic acid for 24 h to easily remove the fats and tissues from bones then washed by distilled water and dried at 220°C for 48 h. After cooling, dried samples were grinded and sieved to size range from 250 μm to 500 μm.

2.3. Sample preparations and activation

2.3.1. Physical activation

Physical activation of dried camel bone samples was carried out through carbonization under N₂ gas at temperatures of 500, 700, and 900°C for 2 h, followed by activation under CO₂ gas at 600, 900, and 1200°C for 2 h.

2.3.2. Chemical activation

Chemical activation of dried camel bone samples was carried out by soaking the samples in NaOH (1:1 and 1:3, sample : NaOH ratios, w/w) or H₃PO₄ (25% and 65% V/V H₃PO₄) for 48 h at room temperature. Samples were then dried at 105°C for 72 h, followed by activation at 450, 650, and 900°C under N₂ gas for 2 h. After activating the samples at the recommended conditions, all samples were excessively washed with deionized water until the pH become in the range of 5.5–6.

2.4. Chemical preparation of hydroxyapatite

A heated solution of 5.0 M ammonia (80°C) was added drop by drop to a 1 M aqueous solution of calcium nitrate till the pH reaches 10. The resulting solution was treated by drop-wise addition of a 0.5 M (NH₄)₂HPO₄ solution until complete precipitation. The saturated solution was kept at 80°C for 1 h, then the temperature was reduced to 37°C and kept thermostated for 24 h. The precipitate was then excessively washed with water in order to wash-off all excess ammonia and nitrate ions, followed by drying at 50°C. Powders were then heated at 120°C for 1 h.

2.5. Adsorption efficiencies

Batch experiments were performed in order to obtain the optimum conditions for Cu(II) ions removal from aqueous solutions using the produced adsorbent samples. 0.05 g aliquots of dried-raw camel bone sample, chemically- or physically-activated hydroxyapatite samples were examined for the removal of copper ions from an artificially copper contaminated sample (50 mL of 50 ppm copper sulfate standard solution). Different parameters affecting the sorption of Cu(II) ions were separately studied, such as shaking time, sorbent weight, temperature, metal ion concentration and solution pH.

3. Results and discussion

A series of 9 chemically-activated and 12 physically-activated HAP adsorbent samples were prepared as described and were ran for Cu(II) ions removal from artificial polluted water samples under the same conditions. From the Cu(II) recovery results, the best sorbent samples were selected to complete the study, among which one chemically-activated and 3 physically-activated samples. Table 1 shows the adsorbent samples selected for studying the adsorption efficiencies/parameters for the removal of Cu(II) ions from aqueous solutions.

3.1. Physical characterization of HAP samples

Activated hydroxyapatite natural adsorbent samples, in association with a chemically synthesized HAP sample, a commercially available HAP sample, and a raw camel bones sample were characterized using a set of physical characterization tools. Fig. 1 represents the scanning electron microscope images (SEM), the energy dispersive X-ray graphs (EDX), the fourier transform infrared spectra (FT-IR), and the x-ray diffractograms (XRD) for sample number 2 and prepared HAP sample (Table 1), as models for the investigated adsorbents.

Morphologies of the physically activated HAP particles revealed a homogenous small particle distribution together with large agglomerates. The formed agglomerates were thought to be a result of the welding of very fine particles, where the powders displayed a significant level of agglomeration. From the EDX analysis, the obtained Ca/P ratio is very close to the ideal value (~1.78), based on atomic mass %.

SEM images of chemically-activated hydroxyapatite revealed spherical microstructure with 1–5 μm in diameter. Highly crystalline HAP was obtained in all samples with the characteristic peaks of calcium, oxygen, and phosphorus. The average Ca/P ratio, calculated from EDX analysis, were slightly low (1.74), based on atomic mass %. Additionally, other elements (magnesium and carbon) were present in some samples with minor levels.

The IR-spectra of HAP samples revealed wide bands of H–O–H lattice water covering the regions 1600–1700 cm^{-1} and 3200–3600 cm^{-1} ; $[\text{OH}]^-$ stretching mode bands at 3400–3600 cm^{-1} ; ν_1 $[\text{PO}_4]^{3-}$ bands at 1030 cm^{-1} –1100 cm^{-1} ; ν_2 $[\text{PO}_4]^{3-}$ bands at 960 cm^{-1} –975 cm^{-1} ; ν_3 $[\text{PO}_4]^{3-}$ bands at 603 cm^{-1} and 565 cm^{-1} . The $[\text{PO}_4]^{3-}$ vibrational bands depend on

the activation temperature, and the sharpness of the 550 cm^{-1} –650 cm^{-1} bands indicate a well-crystallized HAP. Characteristic vibration bands of the C–O in the carbonate group were observed at 1410–1460 cm^{-1} .

The XRD analyses revealed straight baselines and sharp peaks confirming that hydroxyapatite was formed in all samples, and the produced calcium phosphate was well crystallized. In addition, it was found that the crystallinity of hydroxyapatite increases with increasing activation temperatures.

3.2. Effect of shaking time

The effect of shaking time (2–120 min) on the removal efficiency of 50 ppm Cu(II) ions from aqueous solutions using 0.05 g of the sorbent samples, mentioned in Table 1, was studied at 250 rpm, pH 6.2 and temperature of $22 \pm 0.1^\circ\text{C}$. Removal percentage of Cu(II) was found to increase from 6.1% at 2 min to 21.2% at 30 min with raw camel bone adsorbent sample, while increased from 39.5% (at shaking time 2 min) to 100% (at 30 min shaking time) when using sample 2, as shown in Fig. 2a. Also, it is noticed that the removal efficiency for copper is not affected with increasing the shaking time from 30 to 120 min. with all examined sorbent samples. Therefore, equilibration time of 30 min was chosen in the subsequent studies.

3.3. Effect of pH

The effect of solution pH on the removal efficiency of 50 ppm Cu(II) ions from aqueous solutions by 0.05 gm of the investigated sorbents was studied at $22 \pm 0.1^\circ\text{C}$ in the pH range 2–6.2. As shown in Fig. 2b, the removal percent of Cu(II) ions increases with increasing pH from 2 to 6.2 with all adsorbents tested.

At lower pHs, much more H^+ ions are found in solution, which compete with Cu(II) ions for the active sites on the sorbent surface, a process that will reduce the removal of copper metal ions from solution. On the other hand, as the pH value increases, protonation of sorbent functional groups by H^+ ions may decrease and the interaction between metal ions and the active sites may increase [14]. After pH 6.5, slight precipitation of copper hydroxide appeared. From the data obtained, it was found that the removal percent increased from 13.05% at pH 2 to 20.3% at pH 6.2 with raw camel bone sorbent while raised from 96.15% at pH 2 to

Table 1
Adsorbent samples selected for studying the adsorption efficiencies on the removal of copper ions

Sample code	Sample type	Activation type	Preparation conditions	Surface area, m^2/g
1	CB	Physical	N_2 at $500^\circ\text{C}/\text{CO}_2$ at 600°C	410.97
2	CB	Chemical	N_2 at $450^\circ\text{C}/1\text{CB}:3\text{NaOH}$	952.5
3	CB	Chemical	N_2 at $650^\circ\text{C}/1\text{CB}:1\text{NaOH}$	673.38
4	CB	Chemical	N_2 at $450^\circ\text{C}/25\% \text{H}_3\text{PO}_4$	571.35
Prep HAP	Prepared hydroxyapatite	Chemically prepared at our Lab	Preparation entitles mentioned in first annual report	603.36
Ref HAP	Reference hydroxyapatite	As purchased	Bio Rad Laboratories	675.72
Raw CB	Raw camel bone	–	–	–

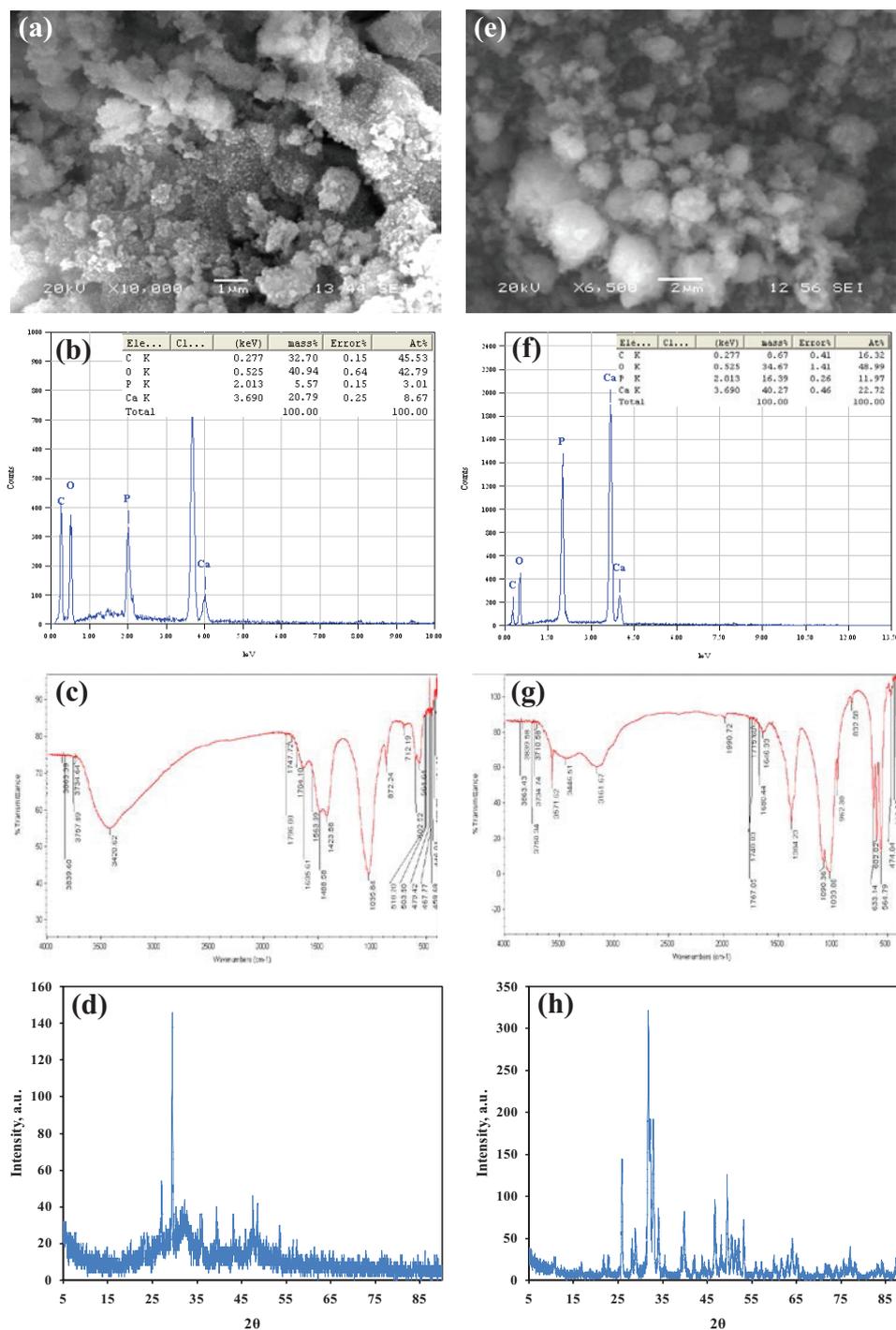


Fig. 1. SEM images (a,e); EDX graphs (b,f); IR spectra (c,g); and XRD diffractograms (d,h) for sample 2 (a,b,c,d) and prepared HAP (e,f,g,h).

100% at pH 6.2 when using sample 2. Therefore, pH 6.2 was chosen in all subsequent studies.

3.4. Effect of sorbent weight

The effect of sorbent samples weight on the removal percent of copper ions from aqueous solutions was stud-

ied in the range 0.01–0.1 g sorbent using 50 ml of 50 ppm Cu(II) ion solution at $22 \pm 0.1^\circ\text{C}$, shaking speed 250 rpm, shaking time 30 min and pH 6.2 (Fig. 2c). The results obtained show an increase in the removal percent of Cu(II) ions within the range of 0.01g up to 0.05 g sorbent, then it remains almost constant with further increase in sorbent weight up to 0.1 g. This could be explained by

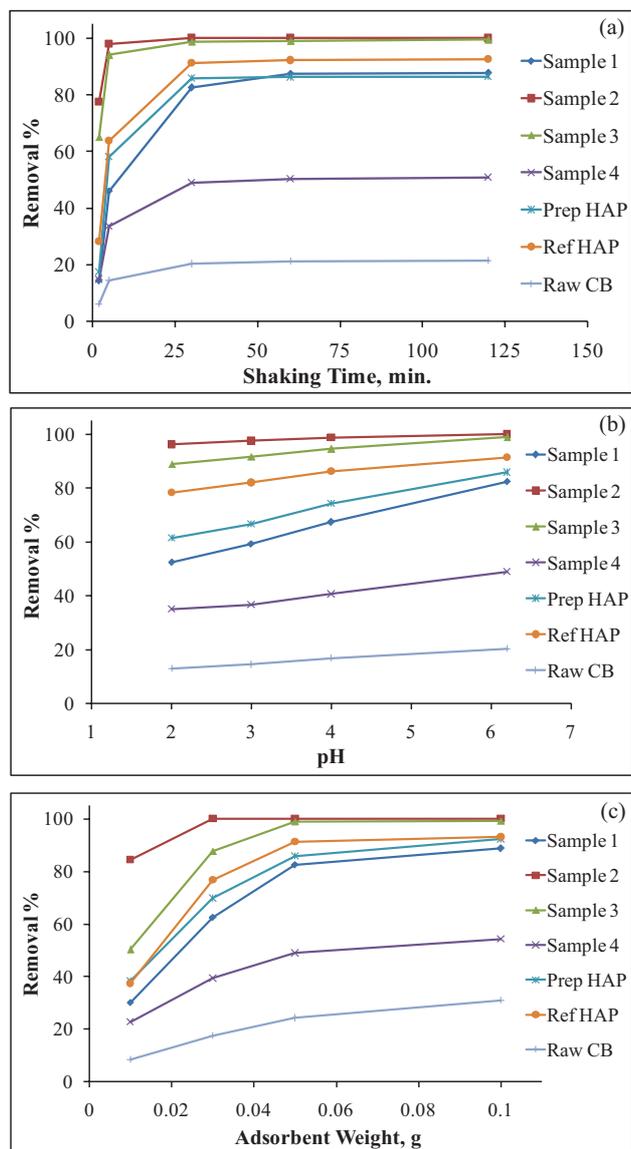


Fig. 2. Effects of: (a) Shaking time (experimental conditions: Sample vol. = 50 ml, sorbent wt. = 0.05 g, pH = 6.2, temp = $22 \pm 0.1^\circ\text{C}$, $[\text{Cu}^{2+}] = 50$ ppm, shaking speed = 250 rpm); (b) pH (experimental conditions: sample vol. = 50 ml, sorbent wt. = 0.05 g, temp = $22 \pm 1^\circ\text{C}$, $[\text{Cu}^{2+}] = 50$ ppm, shaking time = 30 min, shaking speed = 250 rpm); and (c) sorbent weight (experimental conditions: sample vol. = 50 ml, temp = $22 \pm 0.1^\circ\text{C}$, $[\text{Cu}^{2+}] = 50$ ppm, pH = 6.2, shaking time = 30 min, sorbent wt. = 0.05–0.1 g, and shaking speed = 250 rpm) on the removal percent of Cu(II) from aqueous solutions using the sorbent samples.

the increase in the number of surface functional groups and the increase in surface area with increasing sorbent weight up to 0.05 g [15]. The direct proportionality of the removal percent with adsorbent weight is a result of the availability of free (unsaturated) adsorption sites during the adsorption reaction. Besides, core aggregated particles may adsorb some of the loosely-bound Cu(II) ions on the adsorbent surfaces [16]. The removal percent of Cu(II) ions then becomes constant from 0.05 to 0.1 g, an effect that is related with high sorbent concentration, where

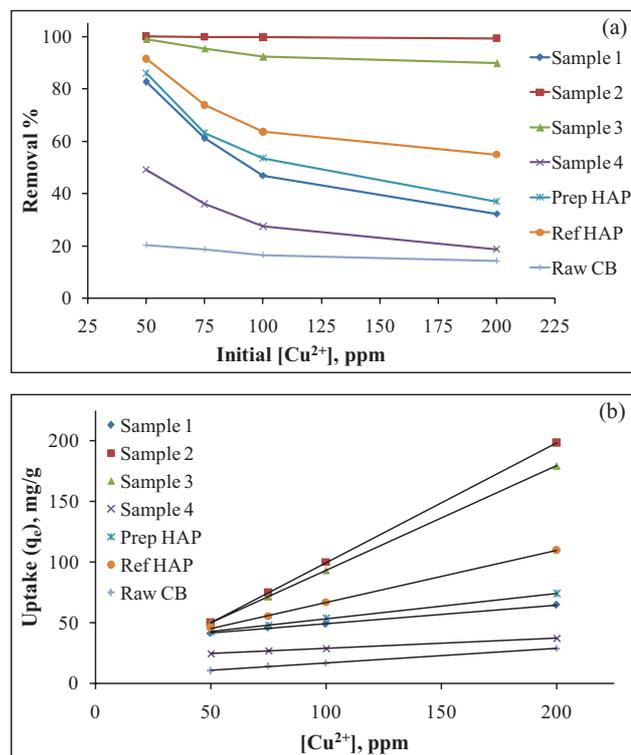


Fig. 3. Effect of initial concentration of Cu(II) ions on (a) the removal percent, and (b) uptake (q_e) of Cu(II) ions from aqueous solutions using the sorbent samples (experimental conditions: sample vol. = 50 ml, temp = $22 \pm 0.1^\circ\text{C}$, $[\text{Cu}^{2+}] = 50$ –200 ppm, pH = 6.2, shaking time = 30 min, sorbent wt. = 0.05 g, and shaking speed = 250 rpm).

adsorbent particles aggregates. This aggregation reduces the adsorption of metal ions as a result of the reduction of the sorbent total surface area and the increase in the diffusion path length [17,18]. From the data obtained, it was found that the removal percent increases from 8.5% at 0.01 g to 31% at 0.1 g with raw camel bone sorbent, while increases from 84.5% at 0.01 g to 100% at 0.1 g when using sample 2, therefore 0.05 g sorbent was chosen in the subsequent studies.

3.5. Effect of initial copper concentration

The effect of initial concentration of Cu(II) ions on the removal percent and uptake values of the sorbent was studied by changing the initial metal concentration from 50 to 200 ppm under the mentioned conditions in Figs. 3a and 3b.

As shown in the figures, the removal percent of Cu(II) ions slightly decreases with increasing initial copper concentration. The apparent stability in Cu(II) ions uptake (mg/g) with the increase of its initial concentration could be attributed to the establishment of a concentration gradient rather than an increase in the initial Cu(II) ion concentration [19]. From the data obtained, it was found that the removal percentage slightly decreased from 99.9% at 50 ppm to 99.2% at 200 ppm with sample 2 sorbent, while remarkably decreased from 91.35% at 50 ppm to 54.85% at 200 ppm when using the Reference HAP sample.

3.6. Effect of temperature

The effect of temperature on the removal efficiency of 50 ppm Cu(II) ions from aqueous solutions using 0.05 g of each investigated sorbent was studied at different temperatures, ranging from 22 to 40°C, at pH 6.2, shaking time 30 min, and at 250 rpm. It is observed from the results that the removal percent of Cu(II) ions is slightly decreased with increasing temperature (Fig. 4). The adsorption capacity of Cu(II) decreased from 100% to 98.75% when using sample 2, while decreased from 49.00 to 26.05% using sample 4 with increasing temperature from 22 to 40°C (293 to 313K). This behavior indicates that the sorption process of Cu(II) from aqueous solutions, using all sorbents, is an exothermic process [20]. The decrease in the uptake of copper (II) at high temperatures may be attributed to the increase in the metal ions mobility that enhances the reverse desorption process, according to Le-Chatelier's principle [16,21].

The thermodynamic parameters obtained for the sorption processes (ΔH° , ΔS° , and ΔG°) were calculated using Eqs. (1) and (2) as follows [22]:

$$\ln K_d = \Delta S^\circ/R - \Delta H^\circ/RT \quad (1)$$

where K_d is the distribution coefficient (mLg^{-1}), ΔH° is the standard enthalpy (kJ mol^{-1}), ΔS° is the standard entropy ($\text{J mol}^{-1} \text{K}^{-1}$), T is the absolute temperature (K) and R is the general gas constant ($8.314 \text{ J mol}^{-1} \text{K}^{-1}$). ΔS° and ΔH° values were obtained using the slopes and intercepts of the linear relations between $\ln K_d$ and $1/T$ (Fig. 5).

The values of the standard Gibbs free energy, ΔG° (kJ mol^{-1}), were calculated from Eq. (2):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2)$$

The negative Gibbs free energy values for samples 1, 2, 3, 4, prepared HAP and reference HAP indicate that the adsorption process is spontaneous and does not need an induction time (Table 2). On the other hand, positive Gibbs free energy values, associated with raw camel bone sample, indicate that this process needs an induction period to

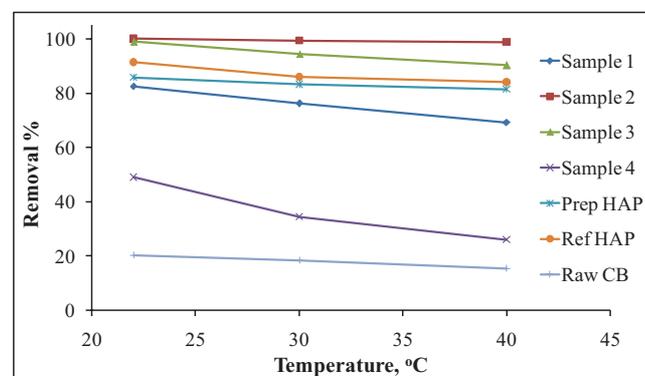


Fig. 4. Effect of temperature on the removal percent of Cu(II) from aqueous solutions using the sorbent samples (experimental conditions: sample vol. = 50 ml, temp = 22–40 ± 0.1°C, $[\text{Cu}^{2+}] = 50$ ppm, pH = 6.2, shaking time = 30 min, sorbent wt. = 0.05 g, and shaking speed = 250 rpm).

start the reaction and cannot proceed spontaneously. Also, it is noticed that the uptake for copper using this adsorbent sample was inferior (10.15 mg/g).

A negative entropy of adsorption reveals the affinity of adsorbent materials for holding Cu(II) ions on their surfaces well consistently with restricted mobilities of copper ions. The negative ΔH values indicate the exothermic nature of the process. Small ΔH values (between -13.49 to -42.47 kJ/mol), associated with samples 1, 4, Prepared HAP, Reference HAP, and Raw CB, support a physical adsorption process over chemical adsorption. Different amounts of energies are released during the adsorption process according to the type of bonds formed, among which are Van der Waals (4 – $10 \text{ kJ}\cdot\text{mol}^{-1}$), hydrophobic bonds ($5 \text{ kJ}\cdot\text{mol}^{-1}$), hydrogen bonds (2 – $40 \text{ kJ}\cdot\text{mol}^{-1}$), coordinate bonds (about $40 \text{ kJ}\cdot\text{mol}^{-1}$), dipole-dipole interaction (2 – $29 \text{ kJ}\cdot\text{mol}^{-1}$) and chemical bonds (about $60 \text{ kJ}\cdot\text{mol}^{-1}$) [23]. In our study, the ΔH values for the adsorption of Cu(II) ion onto the studied sorbents suggest that the type of adsorption forces is not Van der Waals, hydrophobic, nor dipole–dipole interactions, as the amounts of energy associated with these types of interaction is less than the obtained values. Only samples 2 and 3 falls in the range of chemical adsorption, and this may interpret why these two samples give higher uptake values with copper ions.

3.7. Sorption isotherm models

Sorption equilibrium can be expressed using an isotherm equation that involve constants reveal the sorbent surface properties and its affinity towards sorbates. The sorption isotherm represents the relation between the sorbate concentration on the surface of the sorbent against its equilibrium concentration in the solution phase. In this concern, two isotherm modes; Langmuir and Freundlich, were tested with the obtained experimental data for the sorption of Cu(II) ions onto the investigated adsorbent samples selected for studying the adsorption efficiencies.

Langmuir isotherm is often used to describe the saturated monolayer sorption. This model postulates that the adsorption process takes place on the surface of structurally homogenous sorbents, where the sorbent —active sites are equi-energetically [24]. It can be represented as follows:

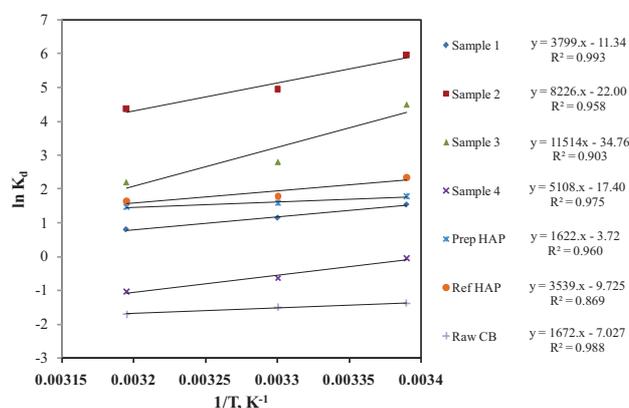


Fig. 5. Graphical determination of ΔS° and ΔH° .

Table 2
Thermodynamic values (ΔH , ΔS and ΔG) for the removal of Cu(II) using the investigated sorbent samples

Sample	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)		
			295 K	303 K	313 K
1	-31.589	-94.342	-3.758	-3.003	-2.060
2	-68.396	-182.927	-14.432	-12.969	-11.140
3	-96.787	-291.224	-10.876	-8.546	-5.634
4	-42.471	-144.717	-0.220	-1.378	2.825
Prepared HAP	-13.486	-30.928	-4.362	-4.115	-3.806
Reference HAP	-29.429	-80.853	-5.577	-4.930	-4.121
Raw CB	-13.908	-58.425	3.327	3.795	4.379

Table 3
Constants of Langmuir and Freundlich isotherm models

Sample	Isotherm models					
	Langmuir constant values			Freundlich constant values		
	Q_o (mg/g)	b (L/mg)	r^2	K_f	$1/n$	r^2
1	71.42	0.074	0.985	27.9	0.157	0.892
2	250	0.16	0.944	158.12	0.410	0.976
3	250	0.16	0.891	54.32	0.342	0.918
4	43.4	0.0385	0.989	11.428	0.226	0.967
Prepared HAP	83.33	0.063	0.977	27.98	0.183	0.868
Reference HAP	142.8	0.0448	0.926	27.54	0.277	0.874
Raw CB	66.66	0.00429	0.939	1.294	0.698	0.996

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (3)$$

where C_e is the metal ion equilibrium concentration (mg/L), q_e is the fraction of sorbed ion (mg/g), q_m equals q_e for a complete monolayer (mg/g), and K_a is the sorption equilibrium constant. The linear form of Eq. (3) was utilized to calculate the sorption capacity for a certain range of Cu(II) ions concentration. Generally, the Langmuir isotherm can be linearized in four different ways, one of which is represented by Eq. (4) and was selected to graphically illustrate the relation between $\frac{C_e}{q_e}$ vs. C_e . The constants Q_o and b can be determined from the linearized form [25].

$$\frac{C_e}{q_e} = \frac{C_e}{Q_o} + \frac{1}{Q_o b} \quad (4)$$

The numerical values of the Langmuir constants, together with the sorption capacity of the saturated monolayer, Q_o , as well as the equilibrium constant, b , are calculated from the linear relations of copper sorption onto all investigated sorbents and listed in Table 3. The values provided an adequate linear fit with respect to the obtained experimental results for the sorption of copper ions onto all investigated sorbents at $22 \pm 0.1^\circ\text{C}$. The values of the coefficient of variation, r^2 , of the linearized relations, which are all approach unity, strongly indicate that the sorption process of copper ions onto all sorbents follow the Langmuir

isotherm. The values of r^2 confirm the monolayer sorption of copper (II) ions onto the investigated sorbents. The maximum value of sorption capacity, Q_o , a measure of the required sorption capacity to form a complete monolayer, is higher in case of copper (II) sorption onto adsorbent samples 2 and 3, which equals (250 mg/g) for both sorbents and increase in the following order: sample 2 = sample 3 > Reference HAP > Prepared HAP > sample 1 > Raw CB > sample 4. The Langmuir constant (b) is related to the affinity of the sorbent for the sorbate. A low value of (b) for sorption of Cu(II) ions onto all investigated sorbents was suggestive of high affinity of the sorbents for copper (II) ions [26].

On the other hand, Freundlich isotherm describes a sorption process with heterogeneous sorbent surface, where the heat of sorption is not distributed and multi-layered processes or other complicated processes are discussed [27]. The process is well described using Eq. (5):

$$q_e = C_e^{1/n} \cdot K_f \quad (5)$$

where q_e is the fraction of sorbed ion (mg/g), C_e is the concentration at equilibrium (mg/L), K_f and $1/n$ are constants representing both the sorption capacity and sorption intensity, respectively. Freundlich model is linearized as follows:

$$\log q_e = \frac{1}{n} \log C_e + \log K_f \quad (6)$$

The plot of $\log q_e$ vs. $\log C_e$ of Eq. (6) should result in a linear relation, where the values of $1/n$ and K_f were obtained

from the slope and the intercept values, respectively [26,27]. The possibility of applying Freundlich isotherm on the sorption process was also examined using Eq. (6). The resultant relation between $\log q_e$ vs. $\log C_e$ for different initial concentrations Cu(II) ions showed a linear correlation, reflecting the feasibility of applying this sorption isotherm to our sorbate-sorbent system. The linear data fitting with Freundlich isotherm reflects that more than one class of sites is involved within the sorption process based on surface heterogeneity. Moreover, based on the slope and intercept of the relations, the values of sorption capacities (K_f) and sorption intensities ($1/n$) for copper (II) were obtained and are recorded in Table 3. The slope values of the Freundlich isotherm for copper sorption onto all investigated sorbents are less than 1, show favorable sorption of Cu(II) onto sorbents used. The high values of (K_f) show a high feasibility for the sorption of Cu(II) onto all the investigated sorbents [26]. The values of the maximum sorption capacity, Q_m , which is a measure of the sorption capacity to form a monolayer, are higher in case of copper (II) sorption onto adsorbent samples 2 and 3, which equal 158.12 and 54.32 mg/g respectively and increase in the following order: sample 2 > sample 3 > Prepared HAP > sample 1 > Reference HAP > sample 4 > Raw CB.

3.8. Comparative study between current HAP adsorbent and previously reported adsorbents in the removal of Cu(II) and/or other heavy metal ions

Table 4 introduces a comparison between efficiencies of our naturally produced HAP adsorbent and previously synthesized/produced natural/synthetic adsorbing materials in the removal of copper and/or other metal ions from wastewater/synthetic wastewater samples. It is clear from the results that our natural HAP adsorbent introduces an excellent removal efficiency for Cu(II) ions compared with other reported adsorbents, with a distinguished regeneration process in dilute acid solution.

3.9. Feasibility study

The processes of wastewater and hard water treatment are essential worldwide from environmental, industrial, agricultural, etc. aspects. The efforts for developing cheaper, reproducible, and more efficient methods/procedures for the treatment of contaminated waters are harnessed everywhere. Most of the procedures relying on adsorbing species suffer from adsorbent irreproducibility/regeneration, short life time, high cost, and lack of domestic availability. In our study, we introduce low cost, natural, easily regenerated, and long life time activated adsorbents simply produced by the recycling of massive domestic bio-waste (camel bones). Table 5 introduces a cost-benefit analysis for our natural activated adsorbent, in comparison with two of the commercially available water adsorbents. The comparison includes the adsorbent source, production cost, removal efficiency, regeneration steps, and life time. As a result, the proposed adsorbent serve in cleaning the environment from accumulated biological camel bones wastes, through recycling, to produce efficient natural activated adsorbent that is used in the treatment of wastewater and hard water, saving the environment and providing the people of Aseer area with pure drinking water.

4. Conclusions

At the end of this article, we can conclude that a chemically activated natural hydroxyapatite adsorbent was successfully produced from camel bones collected from food waste in KSA. The activated sorbent was physically characterized, factors affecting its sorption efficiency were examined, and the thermodynamics of the sorption process were studied. HAP sorbent was efficiently used for the removal of Cu(II) ions contaminants from aqueous samples. The obtained HAP sorbent was used in the construction of an industrial semi-pilot column and was successfully applied to the treatment of contaminated well water sam-

Table 4
Comparison between current natural HAP and preceding metal-ion adsorbents

Adsorbing material	Sample type (natural/synthetic)	Removed metal ions	Removal efficiency (%) / adsorption capacity (mg/g)	Regeneration	Ref.
Iminodiacetic acid-modified kenaf fiber	Modified natural	Cu(II)	91.74 mg/g	97.59% (under 1 M HCl)	28
Banana peel, chestnut shell, and tea leaf	Natural	Cu(II)	1.94–3.36 mg/g	–	29
Fe ₂ O ₃ -TiO ₂ @activated carbon fiber membrane	Synthetic	Methyl orange, Cu(II) and As(V)	20 mg/g	> 90%	30
Orange biomass	Modified natural	Cd(II), Ni(II), Cu(II), and Zn(II)	30.7–6.9 mg/g	–	31
Raw and calcined seashell waste	Natural	Cu(II)	99% at pH = 7	–	32
Activated carbon/thiol functionalized graphene oxide composite	Synthetic	Pb(II) and Cu(II)	196.07–204.08 mg/g	–	33
Our HAP (Sample 2)	Natural	Cu(II)	200 mg/g at pH = 2	99.8% (under 0.05 M HNO ₃ for 30 min)	Current work

Table 5
Cost-benefit study

	Hydroxy-apatite from camel bones	Commercial charcoal	Commercial hydroxy-apatite
Source	Camel bones, local	Commercial, imported	Commercial, imported
Cost	~75 SR/Kg	~200–400 SR/Kg	~500–600 SR/Kg
Efficiency (removal of 50 ppm Cu ²⁺), %	98.1	36.15	79.8
Regeneration	0.05 M HNO ₃	0.05 M HNO ₃	0.05 M HNO ₃
Life time	95% efficiency after 5 cycles	81% efficiency after 5 cycles	84% efficiency after 5 cycles

ples in Aseer area, KSA. The authors succeeded to solve an important environmental issue associated with the accumulation of a major food waste in KSA, which is camel bones, via recycling the waste in order to produce a natural activated sorbent material that is used in turn to solve another important environmental issue, which is water treatment.

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References

- [1] S. Kadouche, H. Zemouri, K. Benaoumeur, N. Drouiche, P. Sharrock, H. Lounici, Metal ion binding on hydroxyapatite (Hap) and study of the velocity of sedimentation, *Procedia Eng.*, 33 (2012) 377–338.
- [2] M.M. Rao, A. Ramesh, G.P.C. Rao, K. Seshiah, Removal of copper and cadmium from the aqueous solutions by activated carbon derived from Ceiba pentandra hulls, *J. Hazard. Mater.*, 129 (2006) 123–129.
- [3] M. Gutiérrez, K. Mickus, L.M. Camacho, Abandoned Pb-Zn mining wastes and their mobility as proxy to toxicity: A review, *Sci. Total Environ.*, 565 (2016) 392–400.
- [4] X. Lin, Y. Gu, Q. Zhou, G. Mao, B. Zou, J. Zhao, Combined toxicity of heavy metal mixtures in liver cells, *J. Appl. Toxicol.*, 36 (2016) 1163–1172.
- [5] D. Liao, W. Zheng, X. Li, Q. Yang, X. Yue, L. Guo, G. Zeng, Removal of lead(II) from aqueous solutions using carbonate hydroxyapatite extracted from eggshell waste, *J. Hazard. Mater.*, 177 (2010) 126–130.
- [6] G.J. Brewer, Risks of copper and iron toxicity during aging in humans, *Chem. Res. Toxicol.*, 23 (2010) 319–326.
- [7] K. Periasamy, C. Namasivayam, Adsorption of Pb(II) by peanut hull carbone from aqueous solution, *Sep. Sci. Technol.*, 30 (1995) 2223.
- [8] T. Goto, K. Sasaki, Synthesis of morphologically controlled hydroxyapatite from fish bone by urea-assisted hydrothermal treatment and its Sr²⁺ sorption capacity, *Powder Technol.*, 292 (2016) 314–322.
- [9] A. Ibrahim, W. Wei, D. Zhang, H. Wang, J. Li, Conversion of waste eggshells to mesoporous hydroxyapatite nanoparticles with high surface area, *Mater. Lett.*, 110 (2013) 195–197.
- [10] U. Anjaneyulu, D.K. Pattanayak, U. Vijayalakshmi, Snail shell derived natural hydroxyapatite: effects on NIH-3T3 cells for orthopedic applications, *Mater. Manuf. Processes*, 31 (2016) 206–216.
- [11] S.M. Wabaidur, M.A. Khan, M.R. Siddiqui, Z.A. Allothman, S. Vasudevan, M.S. Al-Gamdi, I.H. Al-Sohami, Dodecyl sulfate chain anchored bio-char to sequester triaryl methane dyes: equilibrium, kinetics, and adsorption mechanism, *Desal. Water Treat.*, 67 (2017) 357–370.
- [12] S.S. Rahavi, O. Ghaderi, S.A. Monshi, M.H. Fathi, A comparative study on physicochemical properties of hydroxyapatite powders derived from natural and synthetic sources, *Russ. J. Non-Ferrous Metals*, 58 (2017) 276–286.
- [13] A.A. Alqadami, M.A. Khan, M. Otero, M.R. Siddiqui, B-H. Jeon, K.M. Batoo, A magnetic nanocomposite produced from camel bones for an efficient adsorption of toxic metals from water, *J. Cleaner Prod.*, 178 (2018) 293–304.
- [14] M. Torab-Mostaedi, H. Ghassabzadeh, M. Ghannadi-Maraagheh, S.J. Ahmadi, H. Taheri, Removal of cadmium and nickel from aqueous solution using expanded perlite, *Braz. J. Chem. Eng.*, 27 (2010) 299–308.
- [15] R. Wahj, Z. Ngaini, V.U. Jok, Removal of mercury, lead and copper from aqueous solution by activated carbon of palm oil empty fruit bunch, *World Appl. Sci. J.*, 5 (2009) 84–91.
- [16] H.M.H. Gad, N.S. Awwad, Factors affecting on the sorption/desorption of Eu (III) using activated carbon, *Sep. Sci. Technol.*, 42 (2007) 3657–3680.
- [17] N.S. Awwad, A.A.M. Daifullah, Preconcentration of U(VI) from aqueous solutions after sorption using Sorel's cement in dynamic mode, *J. Radioanal. Nucl. Chem.*, 264 (2005) 623–628.
- [18] W.J. Weber, In: C.B. Beck, *Physicochemical Processes for Water Quality Control*, John Wiley, New York 1972, pp. 1–640.
- [19] E. Musapatika, M. Onyango, O. Aoyi, Cobalt(II) removal from synthetic wastewater by adsorption on South African coal fly ash, *S. Afr. J. Sci.*, 106 (2010) 1–7.
- [20] U. Kumar, Thermodynamics of the adsorption of Cd(II) from aqueous solution on NCRH, *Int. J. Environ. Sci. Dev.*, 2 (2011) 334–336.
- [21] H. Nadaroglu, E. Kalkan, Removal of cobalt (II) ions from aqueous solution by using alternative adsorbent industrial red mud waste material, *Int. J. Phys. Sci.*, 7 (2012) 1386–1394.
- [22] Z.A. Al Othman, A. Hashem, M.A. Habila, Kinetic, equilibrium and thermodynamic studies of cadmium (II) adsorption by modified agricultural wastes, *Molecules*, 16 (2011) 10443–10456.
- [23] Q.Y. Yue, Q. Li, B.Y. Gao, A.J. Yuan, Y. Wang, Formation and characteristics of cationic-polymer/bentonite complexes as adsorbents for dyes, *Appl. Clay Sci.*, 35 (2007) 268–275.
- [24] Y.S. Ho, Isotherms for the sorption of lead onto peat: comparison of linear and non-linear methods, *Pol. J. Environ. Stud.*, 15 (2006) 81–86.
- [25] M. Appell, M.A. Jackson, Sorption of Ochratoxin A from aqueous solutions using β -cyclodextrin-polyurethane polymer, *Toxins*, 4 (2012) 98–109.
- [26] C.H. Xiong, Y.J. Feng, C.P. Yao, C. Chen, Removal of Co(II) from aqueous solutions by NKC-90 strong acid resin, *J. Trans. Non-ferrous Metals Soc. China*, 20 (2010) 1141–1147.
- [27] G. Alagumuthu, V. Veeraputhiran, R. Venkataraman, Adsorption isotherms on fluoride removal: batch techniques, *Arch. Appl. Sci. Res.*, 2 (2010) 170–185.
- [28] M.R. Razak, N.A. Yusof, M.J. Haron, N. Ibrahim, F. Mohamed, S. Kamaruzaman, H.A. Al-Lohedan, Iminodiacetic acid modified kenaf fiber for waste water treatment, *Int. J. Biol. Macromol.*, 112 (2018) 754–760.
- [29] M. Ince, O.K. Ince, E. Asam, A. Onal, Using food waste biomass as effective adsorbents in water and wastewater treatment for Cu(II) removal, *At. Spectrosc.*, 38 (2017) 142–148.

- [30] C. Han, M.X. Jing, X.Q. Shen, G.J. Qiao, Preparation and characterization of 3D nano $\text{Fe}_2\text{O}_3\text{-TiO}_2$ @activated carbon fiber membrane for wastewater treatment, *J. Nanosci. Nanotechnol.* 17 (2017) 5327–5334.
- [31] G. Sandoval-Flores, S. Alvarado-Reyna, L.G. Elvir-Padilla, D.I. Mendoza-Castillo, H.E. Reynel-Avila, A. Bonilla-Petriciolet, Kinetics, thermodynamics, and competitive adsorption of heavy metals from water using orange biomass, *Water Environ. Res.*, 90 (2018) 2114–2125.
- [32] M. Egeric, I. Smiciklas, A. Markivic, M. Jovic, M. Slijvic-Ivanovic, J. Sokolovic, M. Ristic, Separation of Cu(II) ions from synthetic solutions and wastewater by raw and calcined seashell waste, *Desal. Water Treat.*, 132 (2018) 205–214.
- [33] F. Mojoudi, A.H. Hamidian, N. Goodarzian, S. Eagderi, Effective removal of heavy metals from aqueous solution by porous activated carbon/thiol functionalized grapheme oxide composite, *Desal. Water Treat.*, 124 (2018) 106–116.