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Adsorption and removal of mercury ions from aqueous solution using raw and chemically modified Egyptian mandarin peel

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ABSTRACT

In this study, the removal of mercury ions by Egyptian mandarin peel was investigated in aqueous solution. Three absorbents were derived from Egyptian mandarin peel, the first adsorbent was the raw peel (MP), the second one was pretreated mandarin peel with NaOH (MNa), and the third one was carbonized mandarin peel (MC). The extent of adsorption was studied as a function of pH, adsorbent dose, temperature, and contact time. Adsorption isotherms were modeled with Langnuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherms. The data fitted well with the Langmuir isotherm and the maximum monolayer adsorption capacities were found to be 19.01, 23.26, and 34.84 mg/g for MP, MNa, and MC, respectively. The kinetic data were analyzed using psudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models. The results indicated that Egyptian mandarin peel could be utilized as a low-cost adsorbent for mercury removal.

Keywords: Egyptian mandarin peel; Mercury removal; Biosorption

1. Introduction

Mercury is one of the most toxic pollutant in the environment. Annually, 5,500 tons are discharged into the atmosphere [1]. Mercury presents in a variety of waste products including contaminated soil, medical waste [2], fluorescent lamps, and contaminated water streams. Among the most important sources of mercury pollution is the effluent discharged from chlorine chlor-alkali manufacturing processes, pulp paper and oil refining, plastic, and battery manufacturing industries. The most toxic form of mercury is mercury(II) salts, which are often converted by bacteria into the neurotoxic substance methylmercury, which magnified pose a health risk to humans and wildlife through the aquatic food chain. The presence of mercury(II) in excess of 0.5 ng/mL could considerably increase alkylation of the element in water bodies and subsequently threaten all forms of sustainable development [3]. The inorganic mercury(II) constitutes the main pollutant of mercury present in natural waters. The maximum mercury uptake set by World Health Organization is 0.3 mg/week and 1 μg/L in drinking water [4]. It is reported that mercury exposure is more harmful for developing fetuses and children under the age of four because it interferes with development of normal brain [5].Thus, it is very important to decrease the residual mercury concentration below the permissible limit from industrial wastewater, especially from drinking water.

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A variety of mercury removal techniques have been investigated including adsorption, ion-exchange, precipitation, and photocatalytic removal. Adsorption as a technique for mercury removal achieved a great success [3,4,6]. In recent few years, there is a growing need to develop low-cost and locally abundant materials to act as efficient adsorbents. Different studies have investigated low cost sorbents that remove mercury with high efficiency such as marine brown algae [6], duckweed [7], palm shell [8], Indian almond [9], rubber waste [10], and rice husk [11]. For countries with low resources like Egypt, the biosorbents are an alternative to reduce the impact of pollution caused by local industries, besides being a biodegradable product.

Mandarin is recognized as one of the world's major fruit crops. The worldwide production of mandarin in 2006 was $2,566 \times 10^3$ tons and the Egyptian share was 665×10^3 tones [12]. In addition to large-scale consumption, the mandarin fruits are mainly processed to produce juice and the waste of this industry represents about 50% of the raw processed fruit [13]. Accordingly, there are a large amount of wastes which give rise to serious environmental pollution.

This study reports the use of Egyptian mandarin peel as an alternative natural adsorbent for mercury removal from aqueous solutions. For this sake, the adsorption efficiency of raw mandarin peel for mercury removal was investigated under different initial conditions (pH, temperature, adsorption concentration, and contact time). Meanwhile, treated mandarin with NaOH and activated carbon prepared from mandarin are also investigated to determine the possibility of mercury ion removal from water. To determine the kinetic parameters, various models (pseudo-first-order, pseudo-second-order, Elovich, and intraparticle-diffusion models) were used to correlate the experimental data. The experimental data have been analyzed using four isotherm models (Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich). Data analysis was performed to obtain the equilibrium and kinetic parameters and to find an appropriate model for the equilibrium and kinetics of removal of mercury ions by Egyptian mandarin adsorbents.

2. Methods

2.1. Adsorbents preparation

2.1.1. Raw Egyptian mandarin peel (MP)

Egyptian mandarin were extensively washed in running tap water for 30 min. to remove all the dirt particles, and then washed with distilled water several times. The washed peel was transferred to an oven set at 65°C for 48 h to reduce the water content. Then, it was ground and finally screened to obtain a particle size less than 500 μm. The obtained material was named MP for further adsorption study.

2.1.2. Chemically treated Egyptian mandarin peel (MNa)

About 50 g MP was soaked in 200 mL ethanol and 100 mL 0.1 N NaOH at room temperature for 24 h. After decantation and filtration, the residue was washed several times with deionized water to remove the remaining alkali until the filtrate solution reached a neutral pH value. The obtained product is dried in an oven at 65°C for 24 h; then crushed and sieved to obtain a particle size lower than 500 μm; and thereafter named as MNa.

2.1.3. Carbonized Egyptian mandarin peel (MC)

The carbonization of mandarin peel was achieved by adding 100 g of dried mandarin peel in small portion to 80 mL of 98% H_2SO_4 during 2 h followed by boiling for 2 h in an efficient fume hood. After cooling in ice bath, the reaction mixture was poured onto 0.5 L cold water and filtered. The carbonized material was heated in an oven at 180°C for 2 h and then immersed in 0.5 L 5% $NaHCO_3$ to remove any remaining acid. The obtained carbonized material was then washed with distilled water until pH reached 6, then it dried in an oven at 150°C for 12 h. After cooling to room temperature it was ground and sieved to the particle size less than 500 μm and named MC.

2.2. Chemicals and instrumentation

All the chemical and reagents used were of analytical reagent grade purchased from Sigma Aldrich. Stock solution of 1.0 g/L Hg(I) was prepared by dissolving Hg_2Cl_2 in deionized water and diluted to desired concentrations when being used. NaOH and HCl were used to adjust the pH value of experimental solutions. One hundred mmol/L solution of 2-[4-(2-hydroxyethyl)-1-piperazinyl] ethanesulphonic acid solution was used for the purpose of buffering.

The concentrations of mercury ions were determined by atomic absorption spectrophotometer (Varian Spectra AA 220, Australia) using a cold vapor atomic absorption method [14]. Measurements of pH value were performed using An Elico (LI-129) pH meter. Fourier transform infrared spectrometry (PerkinElmer, USA) was used to analyze the organic functional groups of the adsorbent using KBr pellets (the fraction of sample was about 0.1% in weight).

2.3. Adsorption studies

All of the adsorption tests were carried out in batch mode using 50 mL stoppered conical flasks at room temperature (20°C). The adsorbent (0.05–0.25 g) was taken into each conical flask which contained 20 mL of mercury ions solution with initial different concentration (50–200 mg/L). After predetermined time intervals, the sorption mixture was immediately filtered through a Whatman filter paper 40 and the mercury ion concentration in the filtrate was analyzed. The amount of mercury ion adsorbed by Egyptian mandarin peel q_e (mg/g) was calculated by using the following equation:

$$q_e = (C_0 - C_e)\ V/m \tag{1}$$

where C_0 and C_e are the initial and equilibrium mercury ions concentrations (mg/L), respectively; V is the volume of the mercury ions solution (mL); and m is the weight of adsorbent (mg).

For the calculation of the mercury percent adsorption (%) the following expression is used:

$$\%\ \text{Adsorption} = (C_0 - C_e)\ 100/C_e \tag{2}$$

To study the effect of each parameter, the values of other parameters must be fixed. The initial concentration of mercury ions used in adsorption isotherms, pH, and adsorbent dosage experiments was 100 mg/L while the mercury ions concentration used for kinetics study was 150 mg/L. Preliminary kinetic tests demonstrated that a contact time of 24 h was long enough to achieve equilibrium conditions for all the experiments and this equilibration time was therefore adopted for all tests. Each determination was replicated three times and the mean values were reported in the analysis. The mean deviation of the triplicate did not exceed 5%.

3. Results and discussion

3.1. Characterization of adsorbents

FTIR analysis in solid phase was performed on the mandarin adsorbents (MP, MNa, and MC) in a KBr disk in order to determine which functional groups are responsible for mercury uptake. The FTIR spectra of adsorbents were measured in the range of 400–4000 cm^{-1}. The spectra reveal a number of absorption peaks indicating the complex nature of the studied biomass. The main characteristic bands for MP, MNa, and MC are reported in Table 1. In all spectra, the broad and intense absorption band at 3,416–3,432 cm^{-1} corresponds to the O–H stretching vibrations of alcohols, phenols and carboxylic acids, as in pectin, lignin, and cellulose, thus, showing the presence of free hydroxyl groups on the adsorbent surface. In the spectra of MP and MNa, the peak observed at 2,925 cm^{-1} is attributed to symmetric and asymmetric C–H stretching vibration of aliphatic acids. Such peak is almost disappeared in the MC spectrum due to carbonization. H_2SO_4 breaks many bonds in aliphatic and aromatic species present in precursor mandarin material causing elimination and liberation of various light and volatile substances leading to partial aromatization and thus carbonization. After the comparison between the spectrum of MNa and those of MP, it can been seen that the hydroxyl peaks in MNa shifted from 3424 to 3432 cm^{-1}, and carboxylic peak around 1740 cm^{-1} disappeared and new peaks at 1,645 and 1424 cm^{-1} were observed. This indicated that some functional groups (–COOH and –OH) have been successfully modified by chemical treatment. The peak observed at 1029 cm^{-1} for all spectra is assigned to C–O stretching vibration of carboxylic acids and alcohols. FTIR results indicate that the MC activated carbon does not completely destroy all the chemical functions of the original biomaterial (MP) without chemical treatment.

Table 1
Comparison of infrared bands in 4,000–400 cm^{-1} spectral region

Functional group of adsorbent	Wavenumber/cm^{-1}		
	MP	MNa	MC
O–H stretching vibration	3,424	3,432	3,416
Symmetric and asymmetric C–H stretching vibration	2,925	2,925	–
Non-ionic carboxyl groups (–COOH, –COOCH3)	1,740	–	1,704
Asymmetric vibrations of C=O	–	1,645	–
Symmetric vibrations of C=O	–	1,424	–
Stretching vibration of C–O–C	1,029	1,029	1,029

3.2. Effect of pH

The pH value has been suggested as one of the major parameters controlling the sorption process of metals with biosorbents. Fig. 1 shows the effect of pH on the removal of mercury ions from aqueous solution. When initial pH of the mercury solution was increased from 2.8 to 5.0, the percentage removal increased from 42.55 to 62.48%, 49.00 to 75.82% and 62.87 to 95.81% for MP, MNa and MC, respectively. With increase in pH from 5.0 to 6.0, the percent removal decreased from 62.48 to 56.79%, 75.82 to

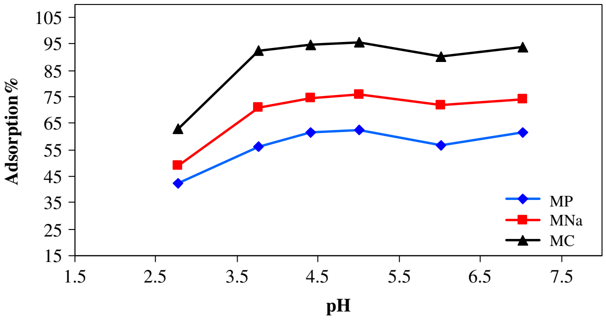

Fig. 1. Effect of pH on adsorption of mercury by MP, MNa and MC. Initial mercury concentrations 100 mg/L, S/L 5.0 g/L, time 24 h.

72.82%, and 95.81 to 90.69% for MP, MNa, and MC, respectively. With further increased in pH value to 7.0 there was a slight increase in percent removal from 56.79 to 61.54%, 72.62 to 73.97%, and 90.69 to 94.01% for MP, MNa, and MC, respectively. The lowest adsorption occurred at pH 2.8 and the greatest adsorption occurred at pH 5.0.

Mandarin peel consists of cellulose, hemicellulose, and lignin. Cellulose is a common constituent in plant materials and lignin is relatively hydrophobic and aromatic in nature. Raw, alkali-treated and activated carbon mandarin peel carry the same polar functional groups such as alcoholic, carbonylic, carboxylic, and phenolic groups which are potentially involved in binding with sorbed mercury ions. Lignocelluloses and the cell walls of sorbents mainly consist of polyphenolic compounds and hydroxyl groups such as lignin, which are believed to be the active sites for attachment of mercury ions. The pH value of the sorption solution affects the surface charge of adsorbent, the degree of ionization, and speciation of the surface function groups [15]. Furthermore, as hydrolysis degree of metal ions in aqueous solution is pH-dependent, the pH of solutions strongly influences the speciation of metal ions. The very low percentage removal of mercury ions can be explained by the competition of mercury with protons for the adsorption sites and by the electrostatic repulsion between protonated mandarin peel surface and mercury cations, since in this pH range mercury ions are present as cations [16]. At higher pH values, the lower number of H^+ and the greater number of surface ligands with negative charges resulted in greater metal adsorption. There is no precipitation at the pH lower than 5.0. The adsorption of mercury ions takes place on the surface of mandarin peel by replacing with H_3O^+ and above pH 5.0, several hydroxide species of mercury ions cause a decrease in the percentage of mercury removal.

3.3. Effect of adsorbent dose

The study of adsorbent dosages for the mercury removal from aqueous solution was carried out using quantities of adsorbents ranging from 0.025 to 0.25 g and fixing the volume and initial mercury ions concentration at 20.0 mL and 100.0 mg/L, respectively. The effect of adsorbent dose or solid/liquid ratio (S/L ratio) is an important parameter affecting metal ion removal. As shown in Fig. 2, the adsorption efficiency increased as the S/L ratio increased till S/L ratio reaches 7.50. For adsorbent dose higher than this ratio, the adsorption efficiency increased less (see Fig. 2). Increases in the percentage of the mercury removal with S/L ratio could be attributed to increases in the adsorbent surface areas, augmenting the number of adsorption sites available for adsorption, as already reported in several papers [17]. When S/L ratio is small, the binding sites on the adsorbent surface are small hence the adsorption efficiency is low. Increasing in S/L ratio leads to increase in active sites of metal binding which means more metal ions are adsorbed. Thus, the adsorption efficiency increases till saturation. Any further addition of the adsorbent beyond 7.5 as S/L ratio did not cause any significant change in the adsorption.

3.4. Adsorption isotherms

Adsorption isotherms play an important role to determine the maximum capacity of adsorption. It can be used to relate the concentration of the pollutant in the bulk and the adsorbed amount at the interface at equilibrium. In this regard, the adsorption data were analyzed by fitting them to different isotherm equations of Langmuir, Freundlich, Tempkin, and Dubinin–Radushkevich (D-R). The Langmuir model is the most widely used isotherm equation and represented by the following linear equation [18]:

$$C_e/q_e = (1/q_L K_L) + (1/q_L)\,C_e \tag{3}$$

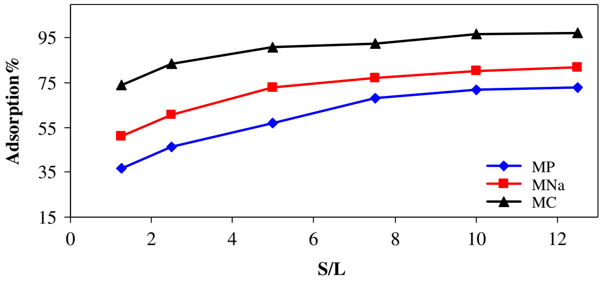

Fig. 2. Effect of adsorbent dose on adsorption of mercury ions by MP, MNa and MC. Initial mercury concentrations 100 mg/L, pH 6.02, time 6 h, temperature 293 K.

where C_e is the equilibrium concentration, mg/L; q_L is the monolayer adsorption capacity of adsorbent, mg/g; and K_L is the Langmuir adsorption constant, L/mg. The plot of C_e/q_e vs. C_e gives a straight line with intercept $1/(q_L K_L)$ and slope $1/q_L$.

The linear form of the Freundlich equation is given by [19]:

$$\mathrm{Log}\ q_e = \log K_F + (1/n)\log C_e \tag{4}$$

where K_F and n are Freundlich constants, n giving an indication of how favorable the adsorption process is, and K_F is the adsorption capacity of the adsorbent. The slope $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or heterogeneity of the surface, becoming more heterogeneous as its value gets closer to 0. When log q_e was plotted against log C_e a straight line with a slope of $1/n$ and an intercept of log K_F are obtained.

Temkin model is represented by the following equation [20]:

$$q_e = B\ln A + B\ln C_e \tag{5}$$

where

$$B = RT/b \tag{6}$$

where R is the gas constant and T is the absolute temperature. The plot of q_e vs. ln C_e, gives a straight line that enables the determination of the Temkin constants A and B. A is the equilibrium binding constant, L/mg and is related to the maximum binding energy, whereas constant B is related to the adsorption heat.

The D-R model can be represented as [21],

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \tag{7}$$

where β is a coefficient related to the mean free energy of adsorption E (kJ/mol) where:

$$E = (-2\beta)^{-1/2} \tag{8}$$

q_m is the maximum adsorption capacity and ε is the Polanyi potential that can be given as:

$$\varepsilon = RT\ (1 + 1/C_e) \tag{9}$$

The plotting of mercury ions adsorbed (q_e) by Egyptian mandarin peel against the equilibrium concentration of mercury ions (C_e) in solution gives the equilibrium adsorption isotherms (Fig. 3). One can see that the adsorption ability of MC was the highest and MNa are much higher than that of MP, which indicates that the chemical modification was effective.

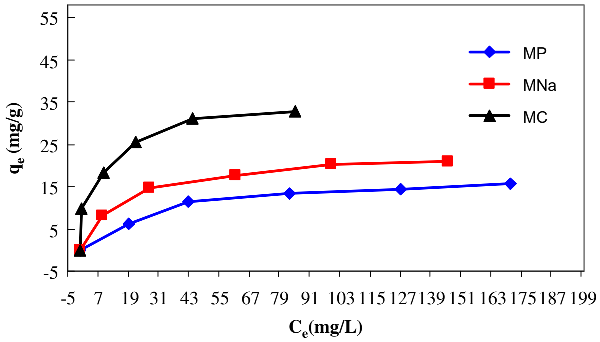

Fig. 3. Adsorption isotherms of mercury ions by MP, MNa and MC. S/L 5.0 g/L, pH 6.02, contact time 24 h, temperature 293 K.

The applicability of different isotherms was compared and the correlation coefficients conducted that the Langmuir model shows a better fit to the adsorption isotherm data. Langmuir isotherm assumes monolayer adsorption; the correlation coefficient (R^2) values were very close to 1, which revealed the extremely good applicability of the Langmuir model to these adsorptions (Fig. 4). The value of different parameters and correlation coefficients of different isotherms were listed in Table 2. The adsorption capacity of MP, MNa, and MC were 19.01, 23.26, and 34.84 mg/g; respectively. MC was the most efficient absorbent for mercury removal.

The Langmuir adsorption constant K_L represents the affinity between the adsorbent and adsorbate. The magnitude of K_L has small values (0.028–0.176 L/mg), which indicates a low heat of adsorption capacity [22]. The essential characteristics of Langmuir isotherm can be configured by a dimensionless constant known as equilibrium parameter (R_L), it can be written as:

$$R_L = 1/(1 + K_L C_{max}) \tag{10}$$

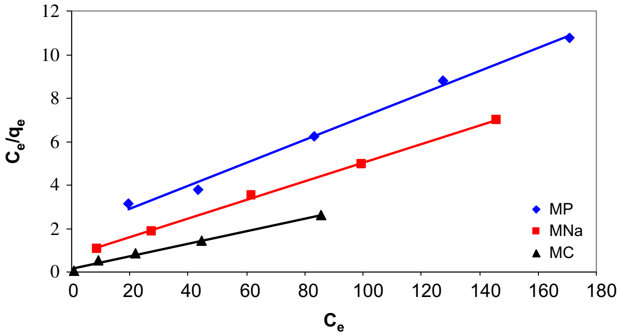

Fig. 4. Plot of C_e/q_e vs. C_e for estimation of correlation coefficient R^2 of Langmuir model.

Table 2
Values of parameters of each isotherm model used

Isotherm model	Adsorbents	Parameter	R^2
Langmuir	MP	$q_L = 19.01$ $K_L = 0.028$	0.994
	MNa	$q_L = 23.26$ $K_L = 0.059$	0.999
	MC	$q_L = 34.84$ $K_L = 0.176$	0.993
Freundlich	MP	$K_F = 2.028$ $n = 2.420$	0.911
	MNa	$K_F = 4.298$ $n = 3.000$	0.952
	MC	$K_F = 11.046$ $n = 3.906$	0.986
Temkin	MP	$A = 0.259$ $B = 4.252$	0.965
	MNa	$A = 0.749$ $B = 4.581$	0.988
	MC	$A = 9.345$ $B = 4.846$	0.951
D-R	MP	$q_m = 14.663$ $E = 0.091$	0.902
	MNa	$q_m = 18.775$ $E = 0.224$	0.922
	MC	$q_m = 26.361$ $E = 1.581$	0.787

where C_{max} is the highest initial metal concentration in the solution (mg/L). When the value of $R_L < 1$, then the Langmuir adsorption process is favorable, and if $R_L > 1$, this indicates unfavorable process. The Langmuir adsorption process will be linear when $R_L = 1$ and irreversible when $R_L = 0$. The value of equilibrium parameter (R_L) of the adsorption of mercury ions on MP, MNa, and MC adsorbents were 0.126, 0.054, and 0.019; respectively; which indicate that adsorption process is favorable.

Different parameters values for each isotherm model are recorded in Table 2. The values of K_F from the Freundlich model are an indicator of the adsorption capacity of a given adsorbent. From the Table 2, the sorption capacity, K_F increased in the order: MC > MNa > MP. The n should have values lying in the range of 1–10 for classification as favorable adsorption. A smaller values of n (Table 2) indicate a weaker bond between mercury ions and Egyptian mandarin peel [22].

The D-R parameter predicting the type of adsorption E, was found to be 0.091, 0.224, and 1.581 kJ/mol for MP, MNa, and MC, respectively. These values showed that the adsorption process was physical in nature [23]. Since the D-R model is not being followed by this system, the E values provide only an estimation of the nature of the biosorption process (as shown in Table 2).

Table 3
Comparison of mercury adsorption capacity of Egyptian mandarin peel with other reported low-cost adsorbents

Adsorbent	q_{max} (mg/g)	Reference
Fly ash with aluminosilicate	20.65	[24]
Ceiba pentandra hulls	25.88	[5]
Fern tree	26.50	[25]
Camel bone	28.24	[26]
Egyptian mandarin peel	34.84	Present study
Sugarcane bagasse	35.71	[27]
Leaves of castor tree	37.20	[28]
Malt spent rootlets	50.00	[29]
Lichen biomass	82.80	[30]

Table 3 summarizes the comparison of the maximum mercury adsorption capacities of various adsorbents including Egyptian mandarin peel. The comparison shows that Egyptian mandarin peel has similar adsorption capacity of mercury as like as other reported adsorbents, reflecting a promising utility for Egyptian mandarin peel utilization in mercury removal from contaminated water.

3.5. Kinetic studies

Kinetics studies were carried out by leaving the sorption mixture at various predetermined intervals and analyzing the mercury content at the end of contact time. Each time, a different sample was used to ensure that the solid/liquid (S/L) ratio did not change after sampling. The kinetic profiles of mercury adsorption onto MP, MNa, and MC at different times are shown in Fig. 5. One can see a very fast increase in the adsorption rate of mercury ions on Egyptian mandarin peel in the first 30 minutes for all the three adsorbents, MP, MNa, and MC, followed by a less rapid increase and a practically constant plateau after 60 min. At time 0–20 min, the uptake increased sharply due to the availability of free active sites on the adsorbent surface and the high concentration of the solution. After that period, a very few free active sites on the adsorbent surface are available, hence a low increase in mercury removal is observed. The observed rapid kinetics has significant practical and economical importance, as it facilitated smaller reactor volumes, ensuring high efficiency and economy [31].

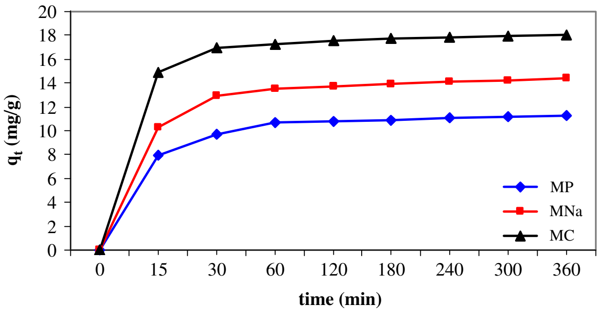

Fig. 5. Effect of time on mercury ions adsorption by MP, MNa and MC. Initial concentration 100 mg/L, S/L 5.0 g/L, pH 6.02 and temperature 293 K.

The obtained kinetic data were analyzed using various kinetic models in order to understand the dynamics of adsorption of mercury on Egyptian mandarin peel. The pseudo-first-order model is given by Lagergren as [32]:

$$\text{Log}\ (q_e - q_t) = \log q_e - (k_1/2.303)\ t \tag{11}$$

where q_e and q_t are the amounts of mercury adsorbed at equilibrium and time t (mg/g), respectively, and k_1 is the rate constant of pseudo-first-order adsorption process (min^{-1}). The values of the first-order rate constant k_1 and equilibrium adsorption capacity q_e were calculated from the slope and intercept of plotting log ($q_e - q_t$) against t (Table 4). It can be seen that the adsorption data were not represented by Lagergren's model with correlation coefficients R^2 <0.92 for the adsorbents under investigation; MP, MNa, and MC.

The pseudo-second-order kinetic model by McKay and Ho [33] expressed as:

$$t/q_t = 1/(k_2 q_e^2) + (1/q_e)\ t \tag{12}$$

where k_2 is the pseudo-second-order rate constant of pseudo-second-order adsorption (g/mg min) and can be determined experimentally from the slope and intercept of plot t/q_t vs. t (Fig. 6). This model fits the kinetic data very well with $R^2 = 1$ for the three concerned adsorbents, MP, MNa, and MC. These results suggest that the adsorption of mercury ions on Egyptian mandarin peel may be best described by the pseudo-second-order kinetic model with excellent correlation coefficients and such kinetic model provides the best agreement between the calculated values of q_e and the experimental q_e data. The calculated q_e values were 11.36, 14.52, and 18.14 mg/g for MP, MNa and MC; while the experimental values were 11.43, 14.53, and 18.15 mg/g for the same order.

Table 4
Values of parameters of each kinetic model used

Kinetic model	Adsorbents	Parameter	R^2
Pseudo-first-order	MP	$q_e = 2.40$ $k_1 = 0.010$	0.895
	MNa	$q_e = 2.46$ $k_1 = 0.008$	0.905
	MC	$q_e = 1.93$ $k_1 = 0.008$	0.915
Pseudo-second-order	MP	$q_e = 11.43$ $k_2 = 0.014$	1
	MNa	$q_e = 14.53$ $k_2 = 0.012$	1
	MC	$q_e = 18.15$ $k_2 = 0.017$	1
Elovich	MP	$\alpha = 0.985 \times 10^3$ $\beta = 1.12$	0.841
	MNa	$\alpha = 4.314 \times 10^3$ $\beta = 0.97$	0.789
	MC	$\alpha = 13.94 \times 10^6$ $\beta = 1.23$	0.808
Intraparticle-diffusion	MP	$k_{\text{int}} = 0.168$	0.695
	MNa	$k_{\text{int}} = 0.193$	0.645
	MC	$k_{\text{int}} = 0.152$	0.665

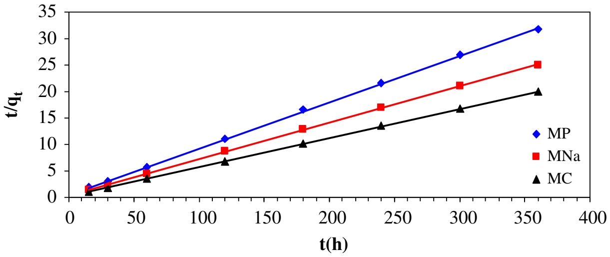

Fig. 6. Pseudo-second order kinetics for mercury ions removal by MP, MNa and MC. Initial concentration 100 mg/L, S/L 5.0 g/L, pH 6.02 and temperature 293 K.

The adsorption data were also further analyzed using the Elovich model [34] which defined as:

$$q_t = 1/\beta \ln\ (\alpha\beta) + (1/\beta) \ln\ t \tag{13}$$

where β is a constant related to the extent of surface coverage and activation energy for chemisorptions (g/mg) and α is the initial sorption rate constant (mg/g min). The constants, β and α can be obtained from the slope and intercept of plotting q_t vs. ln t. The determined values of correlation coefficients R^2 related to this model were lower than 0.841which conducted that Elovich model does not fit the kinetic data of mercury removal by MP, MNa, and MC adsorbents.

Weber and Moris model was used to investigate intraparticle diffusion mechanism [35]. The model is:

$$q_e = C + k_{int}\, t^{1/2} \tag{14}$$

where k_{int} is the intraparticle rate constant (mg/g min$^{1/2}$). If the intraparticle diffusion is rate-limited, then plot of mercury removal q_t against the square root of time ($t^{1/2}$) would result in a linear relationship and k_{int} value can be obtained from the slope of this plot. If the linear plot passes through the origin, then intraparticle diffusion is the sole rate-limiting step [36]. However, the regression of q_t vs. $t^{1/2}$ is linear but did not passes through the origin which indicates that the intraparticle diffusion was not only rate-controlling step.

3.6. Thermodynamic studies

In order to fully understand the nature of adsorption and evaluate its feasibility, experiments were carried out at different temperature in the range of 20–41 ℃ (Fig. 7). The thermodynamic parameters such as free energy change (ΔG°, J/mol), enthalpy change (ΔH°, J/mol) and entropy change (ΔS°, J/mol K) were obtained from analysis of experimental data at different temperatures using the following equations:

$$\Delta G^{\circ} = -RT \ln K_c \tag{15}$$

$$\ln K_C = -\Delta G^{\circ}/RT = -(\Delta H^{\circ}/RT) + (\Delta S^{\circ}/R) \tag{16}$$

where R is the gas constant (8.314 J/mol K), and T is the absolute temperature (K). K_C is the thermodynamic equilibrium constant and can be obtained as follows [31]:

$$K_C = C_{\partial}/C_e \tag{17}$$

where C_{∂} is mg of adsorbate adsorbed per liter and C_e is the equilibrium concentration of solution (mg/L).

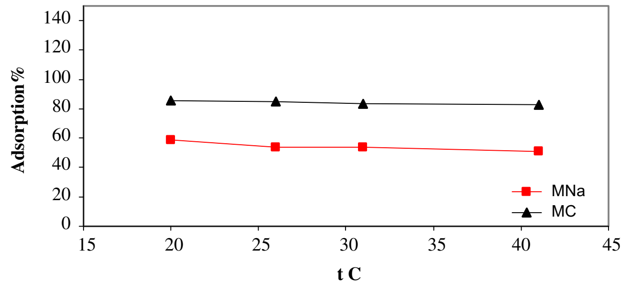

Fig. 7. Effect of temperature on adsorption of mercury ions by MNa and MC. Initial concentration 150 mg/L, S/L 5 g/L, pH 6.02, contact time 24 h.

Table 5
Values of thermodynamic parameters for the adsorption of mercury ions by MNa and MC

Adsorbent	T (K)	K_C	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
MNa	293	1.43	−0.87	−11.05	−35.90
	299	1.18	−0.41		
	304	1.16	−0.39		
	314	1.03	−0.08		
MC	293	5.83	−4.29	−7.76	−11.84
	299	5.60	−4.28		
	304	5.03	−4.08		
	314	4.77	−4.08		

The plot of ln K_C vs. $1/T$ gives a straight line from which ΔH° and ΔS° were calculated from its slope and intercept. Table 5 shows the obtained thermodynamic parameters of mercury adsorption on MNa and MC adsorbents. The negative value of ΔH° indicates the exothermic nature of the adsorption. The magnitude of ΔH° gives an idea about the type of adsorption process. There are two main types of adsorption, physical and chemical. Generally, the heat evolved during physical adsorption is of the same order of magnitude as the heats of condensation, i.e. 2.1–20.9 kJ/mol, while the heats of chemisorption generally fall into a higher range of 80–200 kJ/mol [31]. As shown in Table 5, the values of ΔH° for MNa and MC were −11.05 and −7.76 kJ/mol, respectively. These results indicate that mercury adsorption onto MNa and MC is a pure physical process and confirmed by the mean free energy of biosorption E. Physisorption is also called nonspecific adsorption which occurs as a result of long-range weak Van der Waals forces between adsorbates and adsorbents [23]. The energy released when a particle is physisorbed is of the same magnitude of the enthalpy of consideration. The negative value of ΔS° interprets increased randomness at the solid/solution interface. The negative value of ΔG° indicates a decrease in Gibbs free energy which verifies the feasibility and spontaneity of the adsorption process.

4. Conclusion

This study proved that Egyptian mandarin peel could be an alternative for more costly adsorbents used for mercury removal from aqueous solutions. The equilibrium data of mercury ions could be described by the Langmuir isotherm equations with regression coefficient $R^2 > 0.993$ for all adsorbents. The maximum monolayer adsorption capacities were found to be 19.01, 23.26, and 34.84 mg/g for MP, MNa, and MC, respectively. Kinetic modeling results showed that the pseudo-second-order equation was appropriate for the description of adsorption and removal of mercury ions. Depending on the negative value of ΔG° and ΔH°, the adsorption of mercury ions on Egyptian mandarin surfaces was spontaneous and the adsorption was exothermic process. The comparison of the maximum mercury adsorption capacities of Egyptian mandarin peel with various low-cost adsorbents shows that Egyptian mandarin peel has a promising utility for mercury removal from contaminated water.

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