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Binary Adsorption Studies of Toxic Metal Ions of Lead and Copper from Aqueous Solution by Modified *Foeniculum vulgaris* Seeds (Fennel Seeds)

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Discharge of copper(II) and lead(II) ions into rivers and streams by industries and other human activities has gained serious consideration from regulatory bodies. These toxic metals are harmful to human beings and aquatic life when in high concentrations. Therefore, their removal from wastewater is very important. Hence, this work reports the binary adsorption of toxic metal ions of Cu(II) and Pb(II) from aqueous solution by pristine and modified fennel seeds. Pristine fennel seeds (PFS) were treated with acidic and alkaline solutions to develop modified adsorbents designated ATFS and BTFS, respectively. SEM images revealed that PFS had an amorphous surface with irregular cavities. However, upon acid and base treatment, the surface was more refined. The ATFS had interconnected pores while BTFS had somewhat honeycomb pores. The UV-Vis results confirmed that some of the components were removed from PFS during acid and base pre-treatment. FTIR spectra revealed that the adsorbents had functional groups such as (-OH) and (-C=O), which were involved in the uptake of the metal ions. It was observed that the uptake of Cu(II) and Pb(II) ions onto all adsorbents progressively increased when the initial concentration of the solution was increased. The maximum adsorption capacity was obtained when the initial concentration of the solution was 100 mg/L. The uptake of Cu(II) and Pb(II) on PFS was 3.345 and 11.524 mg/g. While for ATFS 3.78 and 13.07 mg/g and BTFS 8.143 and 14.85 mg/g, respectively. It was observed that the isotherm data fitted Freundlich better for the uptake of both metal ions onto all adsorbents. It was observed that there was a rapid uptake when contact time increased from 5 to 60 min. However, when time increased above 60 min the uptake stabilized and reached equilibrium this was due to the saturation of active sites on the surface for all adsorbents. The kinetics study revealed that PSO fitted the data better than PFO. IPD data revealed that the uptake of metal ions was controlled by the synergistic of ESA and EPA. The ΔHº values for Cu(II) and Pb(II) uptake onto all adsorbents were all negative. This suggested that the reactions were exothermic.

Keywords: Binary adsorption, Pristine fennel seeds, Isotherms, Kinetics, Thermodynamics.

INTRODUCTION

Due to the rapid increase in the population growth and industrial activities, there is an increase in environmental pollution [1-3]. This leads to the deposition of toxic metal ions such as copper(II) and lead(II) into water bodies from various industrial activities. These metal ions are carcinogenic, highly toxic and non-biodegradable causing a serious threat to the living organisms and ecosystem [4-7].

Copper(II) and lead(II) ions are amongst the common and frequently found water pollutants and thus they are selected for this study. Lead(II) is one of the priority pollutants due to its toxicity towards humans and the environment [8]. It is usually introduced into environment and water bodies by electroplating and painting industries, mining industries, smelting activities, aging infrastructure, petroleum refining, pigment production, battery manufacturing and printing [3,5,9-11]. It is exposed to humans through drinking contaminated water [12] and causes brain damage, infertility problem in men and women [13], impairs the central nervous system and kidney failure [1,14]. On the other hand, Cu(II) occurs naturally in nature as a mineral and is needed by the body to maintain healthy immune function, blood vessels, nerves and bones [15]. However, it is harmful to living organisms when found in high concentrations, it causes increased high blood pressure, neurological damage, lung cancer, liver and kidney failure [16-18]. Therefore, it is essential to remove these toxic metals ions from water.

Several methods such as ion-exchange, electro-dialysis, flocculation-coagulation and adsorption have been used to remove metal ions from aqueous solutions. However, there are drawbacks associated with these methods such as high operational cost and they produce secondary toxic metal sludge [19,20]. In contrast, adsorption is the most used and preferred method for the removal of heavy metal ions from wastewater or aqueous solutions [21]. This is due to its easy separation of an adsorbent, inexpensive and easy to perform [22-24].

Many agricultural waste materials such as orange peels [25,26], avocado seeds [27], coffee residue [28], peanut shells [29], have been used by researchers as a low-cost adsorbent for removal of metal ions [29,30]. This is due to agricultural waste materials have shown great potential in water treatment application. Therefore, in this study, modified fennel seeds were used as adsorbents for the removal of Cu(II) and Pb(II) ions from aqueous solutions. *Foeniculum Vulgaris is* also known as fennel is a herb that belongs to the Umbelliferae family. This plant is found in abundance in India with a production of 11×10^4 tons per year [31]. Fennel is primarily used for medicinal and cooking purposes because it poses a large variety of vitamins, essential oil compounds, fiber protein, antioxidants and minerals [32]. Fennel seeds also have hydroxyl (-OH) and carboxyl (-COOH) groups present on their surfaces, this makes the material to exhibit a strong affinity for pollutants in water leading to high adsorption capacity [33,34]. Moreover, fennel seeds are non-toxic, abundant in nature, accessible and inexpensive [35,36].

In this work, we present binary adsorption studies of Cu(II) and Pb(II) by PFS, ATFS and BTFS. However, to the best of our knowledge, there is very little literature available on fennel seeds as adsorbents. A study by Laskar *et al.* [35] reported that 98% of the sorption capacity was observed after three regeneration cycles when fennel seeds were used for adsorption of Zn(II). Taqui *et al.* [31] reported that maximum adsorption capacity of 50 mg/g at a pH range of 2-4 and optimum temperature of 30 ºC, when using nutraceutical industrial fennel seeds spent on Congo red dye removal. Hussein & Jasim [37], also reported the use of fennel seeds for removal of methylene blue and crystal violet dyes and reported 97% and 86% for crystal violet and methylene blue at optimum conditions of pH 4 and 6, the particle size of 75 µm, 60 min of contact time, 5 mg L^{-1} dye concentration and adsorption dosage of 5 g L^{-1}. Fennel seeds exhibited good adsorption capacity and have shown great potential in wastewater remediation. Therefore, it is fair to further exploit the fennel seeds to remove other toxic metal ions from water. After an extensive literature search, no work has been found where fennel seeds were used for binary adsorption of Cu(II) and Pb(II).

EXPERIMENTAL

Pristine fennel seeds were purchased from Dischem in Vanderbijlpark, South Africa. Sodium hydroxide, hydrochloric acid, copper nitrate, lead nitrate and potassium nitrate were procured from Sigma-Aldrich,USA.

Preparation of adsorbents

Preparation of untreated pristine fennel seeds adsorbent (PFS) : Pristine fennel seeds were ground using a blender then labelled (PFS). The PFS was used to prepare other adsorbents and as an adsorbent for the adsorption of Cu(II) and Pb(II) from an aqueous solution.

Preparation of acid treated adsorbent (ATFS): Untreated pristine fennel seeds (500 g) were ground using a blender and placed into a 1000 mL of 0.1 M HCl solution. The solution was then stirred magnetically for 120 min and then after, it was allowed to settle down for another 120 min to separate the HCl solution from PFS. The resulting PFS was dried in an oven for 3 days at 50 ºC. It was labelled ATFS and used as an adsorbent for removal of Cu(II) and Pb(II) ions in aqueous solutions.

Preparation of base treated adsorbent (BTFS): Untreated pristine fennel seeds (500 g) were ground using a blender and placed into a 1000 mL of 0.1 M NaOH solution. The solution was then stirred magnetically for 120 min and then allowed to settle down for another 120 min to separate the NaOH solution from PFS. The resulting PFS was dried in an oven for 3 days at 50 ºC. It was labelled BTFS and used as an adsorbent for the removal of Cu(II) and Pb(II) ions in aqueous solutions.

Adsorption preparation methods

Adsorbate solution preparation: A binary metal stock solution containing 1000 mg/L of Pb(II) and Cu(II) was prepared by dissolving 0.1 g of their nitrate salts in 1 L of deionized water. The experimental metal solutions of desired concentrations were prepared by diluting the stock solution.

Adsorption procedure: The evaluation of PFS, ATFS and BTFS to remove Pb(II) and Cu(II) aqueous solution was conducted. Parameters such as the effect of time at different time intervals (5, 10, 15, 20, 30, 45, 60 and 120 min), temperature (25, 30, 40, 60 and 80 ºC), concentration (20, 40, 60, 80 and 100 mL/g, pH (1, 3, 5, 7 and 8) were studied. This was done by transferring 20 mL of stock solution into capped bottles containing 0.1 g of an adsorbent. The shaker was used for each parameter to equilibrate the working standard and adsorbent at 200 rpm. When one parameter was investigated, the other parameters were kept constant. Thereafter, the bottles were removed and filtered after each experiment to separate the adsorbents from the adsorbate. The concentration of Pb(II) and Cu(II) before and after adsorption were determined using AAS.

Point zero charge procedure: Each adsorbent (PFS, ATFS and BTFS) (0.1 g) was placed separately in a centrifuge flask. KNO_3 solution (20 mL of 0.1 M) was added and then agitated using a shaker for 24 h. The pH was evaluated from the range of 1-12 and pH before and after the agitation was measured.

Adsorption data management: The percentage removal (%A) and adsorption capacity (q_e) of Pb(II) and Cu(II) ions at equilibrium were calculated using the equations below:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

$$\%A = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

where C_o is the initial concentration, C_e is the equilibrium Pb/Cu concentration at a specific time, V is the volume of Cu/Pb solution in L and m is the adsorbent dosage in mg.

Isotherms models Langmuir and Freundlich models were estimated using non-linear equation (eqns. 3 & 4) subjected to KyPlot software.

$$q_e = \frac{Q_o b C_e}{1 + bC_e} \tag{3}$$

where Q_o (mg/g) represents the maximum adsorption capacities for Pb(II) and Cu(II) per unit weight, b stands for the solute surface interaction energy constant. The Freundlich model was estimated using the following equation:

$$q_m = k_f C_e^{1/n} \tag{4}$$

where k_f stands for capacity factor constant and 1/n represents linearity factor.

Kinetics studies were estimated to better understand the adsorption mechanism using pseudo-first order (PFO), pseudo-second order (PSO) and intraparticle diffusion (IPD) models. The kinetic models were estimated using non-linear equations subject to KyPlot software.

$$q_e = q_t(1 - e^{-k_1 t}) \tag{5}$$

where, q_e (mg/g) is the amount adsorbed at equilibrium, q_t (mg/g) is the amount adsorbed at interval t, k_1 (min^{-1}) stands for the rate constant for the first order and (t) is the time:

$$q_e = \frac{1 + k_2 q_e t}{k_2 q_e^2 t} \tag{6}$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant for the second order reaction.

$$q_t = k_i(t^{1/2}) + C \tag{7}$$

where k_i (g g^{-1} $min^{1/2}$) is the IPD rate constant and C stands for the concentration of Pb(II) or Cu(II) on the adsorbent surface. Enthalpy change (ΔHº), Gibbs free energy (ΔGº) and entropy change (ΔSº) were estimated at 288, 298 and 308 K using the following the equations:

$$\ln K_c = -\frac{\Delta H^\circ}{RT} - \frac{\Delta S^\circ}{R} \tag{8}$$

$$\Delta G^\circ = -RT \ln K_c \tag{9}$$

Characterization: The PFS, ATFS and BTFS were characterized using FTIR, SEM and UV-Vis instruments to determine the functional groups, morphology and phase purity of all adsorbents. Nicolet iS50 FTIR spectrometer was used for functional groups determination. SEM images were taken using Joel-JSM-IT 500. EVOLUTION 220 UV-visible spectrometer was used for phase purity. AAS Shimdzu SAC 7000 autosampler was to measure the concentration of the sample.

RESULTS AND DISCUSSION

Adsorbents characterization

FTIR studies: The IR spectra of PFS, ATFS and BTFS before adsorption are shown in Fig. 1. Adsorption peak at 3287 cm^{-1} was attributed to the presence of stretching hydroxyl groups (-OH) of lignin, cellulose and hemicellulose in fennel seeds [32], showing both hydrophilic and hydrophobic properties of fennel seeds [31]. The (-OH) was present in all the adsorbent but the peak intensity on ATFS and BTFS was reduced and shifted to 3288 and 3312 cm^{-1} after modification. The strong band at 2920 and 2850 cm^{-1} was observed in all adsorbents and represented the (-C-H) carboxyl stretch vibrations. The peak at 1742 cm^{-1} was attributed to (-C=O) of the ketonic group present in all adsorbents and it shifted to 1736 and 1737 cm^{-1} on ATFS and BTFS, respectively. The peak at 1597 cm^{-1} observed in all adsorbents was due to the presence of (-C=C) and its intensity decreased on ATFS and BTFS. The strong peak at 1027 cm^{-1} represents the presence of cellulose and it was observed in all adsorbent. The reduction in intensity and shift the peaks indicated that some components were removed during modification [37]. The presence of functional groups such as (-OH) and (-C=O) was anticipated to enhance the uptake of metal ions.

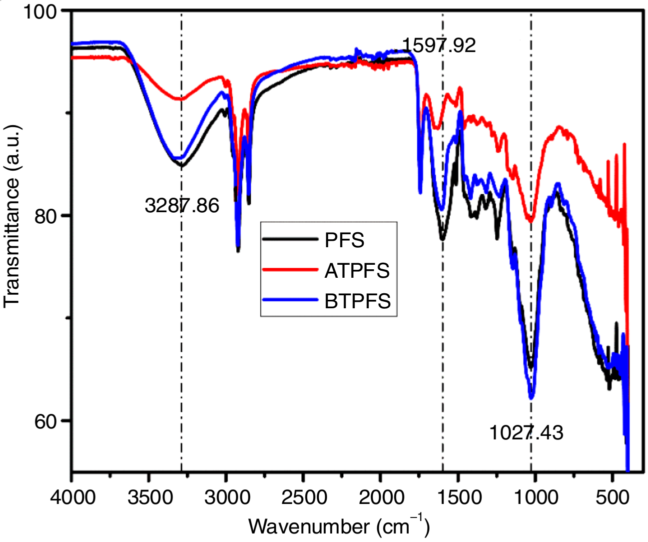

Fig. 1. FTIR spectra for PFS, ATFS and BTFS

UV-visible studies: Fig. 2 below represents the UV-Vis results for PFS, ATFS and BTFS. The results show there was a

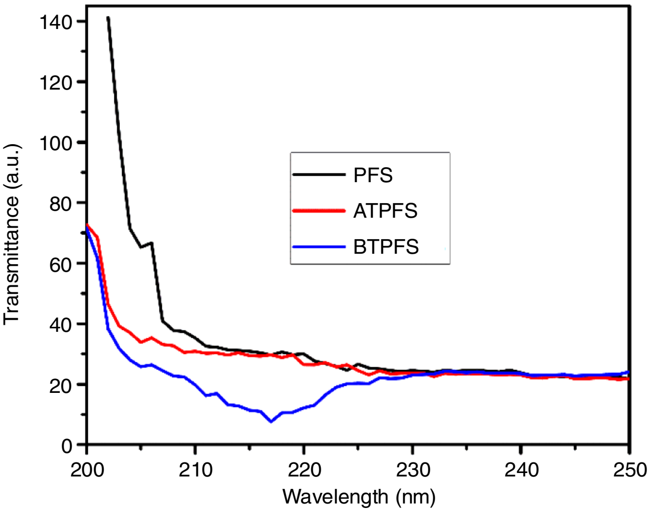

Fig. 2. UV-Vis results for PFS, ATFS and BTFS

decrease in reflectance when the fennel seeds were modified with acid and base. This suggested that some of the lignocellulose materials were hydrolyzed from the seeds during acid and base pre-treatment and this was in agreement with the FTIR results which showed the disappearance of the peaks due to hydrolysis.

SEM studies: The surface morphologies of the PFS, ATFS and BTFS before adsorption were evaluated by SEM images shown in Fig. 3a-f. The images of PFS are shown in Figs. 3a-b and it was observed that pristine material had an amorphous surface with irregular cavities. However, upon acid and base treatment, the surface became more refined. ATFS had interconnected pores as shown in Fig. 3c-d while BTFS had somewhat honeycomb pores (Fig. 3e-f). It was anticipated that the porosity of the adsorbents will play a vital role in the metal uptake processes [38].

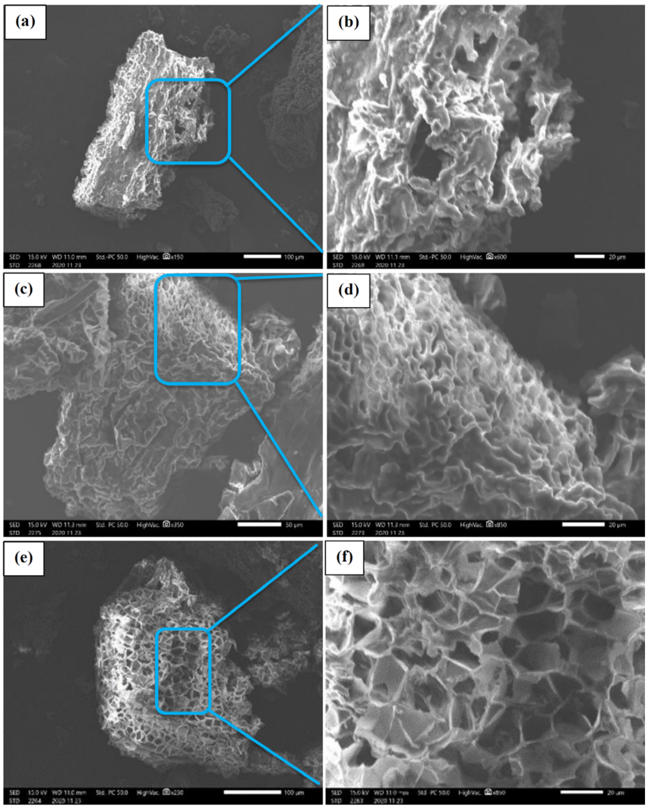

Fig. 3. SEM images of (a-b) PFS, (c-d) ATFS & (e-f) BTFS

Adsorption studies

Effect of concentration: The plots of the effect of initial concentration of Cu(II) and Pb(II) ions in solution are shown in Fig. 4. It was observed that the uptake of both cations onto all adsorbents progressively increased when the initial concentration of solution was increased. However, low uptake was recorded on standard solutions (20, 40, 60 and 80 mg/L) this was attributed to high hindering forces [8,39]. However, when the initial concentration of the solution was increased to 100 mg/L it resulted in higher uptake of both metal ions. This might be attributed to high chances of collision between the Cu(II) and Pb(II) metal ions and the adsorbent surface [24,40, 41]. It was also observed that both metal ions followed the same adsorption trends and the uptake of Pb(II) ions was greater than that of Cu(II) onto all adsorbents. The maximum adsorption capacity for Cu(II) and Pb(II) on PFS were 3.345 and 11.524 mg/g. While for ATFS, it was 3.78 and 13.07 mg/g and for BTFS 8.143 and 14.85 mg/g, respectively.

Isotherms studies: Langmuir and Freundlich isotherms were determined in order to understand the adsorption mechanisms for the uptake of Pb(II) and Cu(II) metal ions on PFS, ATFS and BTFS adsorbents. The isotherm data is shown in Table-1. It was observed that the data fitted Freundlich better for the uptake of both metal ions onto all adsorbents with correlation coefficient (r^2) ranging from 0.989-0.996. The good fit for Freundlich suggests that the uptake of Cu(II) and Pb(II) ions occurred on the surface of the adsorbents and the processes involved multi-layer adsorption on the heterogeneous surfaces of the adsorbents at equilibrium [42,43].

Effect of time: The effect of time was investigated at time intervals of 5, 10, 15, 20, 30, 45, 60 and 120 min to evaluate the rate at which Cu(II) and Pb(II) were adsorbed from aqueous solution and the plots are shown in Fig. 5a-c. It was observed that there was a rapid uptake onto all adsorbents when contact time increased from 5 to 60 min. The increase was attributed to the abundant available active sites and pores on the adsorbent surface [44]. When contact time increased above 60 min the uptake stabilized and reached equilibrium. This was due to the saturation of the active sites on the adsorbents surface [45]. BTFS had a higher adsorption capacity for Pb(II) ions compared to PFS and ATFS the trend was PFS < ATFS < BTFS with adsorption capacities of 9.26, 13.17 and 14.77 mg/g, respectively. ATFS had higher adsorption for Cu(II) ions compared

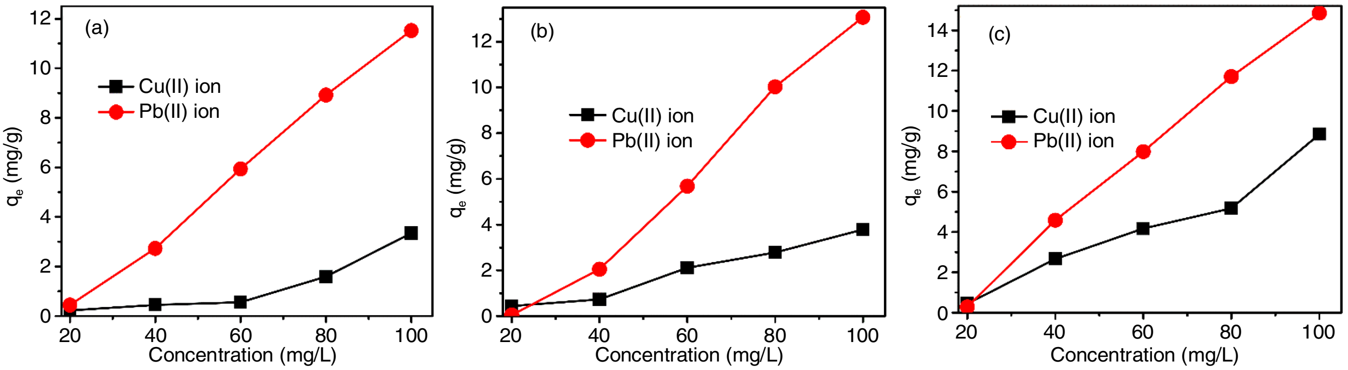

Fig. 4. Effect of initial concentration of Cu(II) and Pb(II) on (a) PFS, (b) ATFS and (c) BTFS

TABLE-1
ISOTHERMS STUDIES OF Cu(II) AND Pb(II) ON PFS, ATFS AND BTFS

Model		PFS		ATFS		BTFS	
		Cu(II)	Pb(II)	Cu(II)	Pb(II)	Cu(II)	Pb(II)
Langmuir	Q_m	11.87	36.68	9.38	44.41	16.02	34.14
	B	0.198	0.290	0.372	0.259	0.469	0.412
	R^2	0.827	0.960	0.961	0.928	0.974	0.967
Freundlich	K	1.579	0.012	1.969	0.04	4.254	0.027
	1/n	0.316	0.670	0.168	0,562	0.963	0.726
	R^2	0.989	0.994	0.994	0.991	0.996	0.990
Experimental	q_e	3.345	11.52	3.787	13.07	8.173	14.857

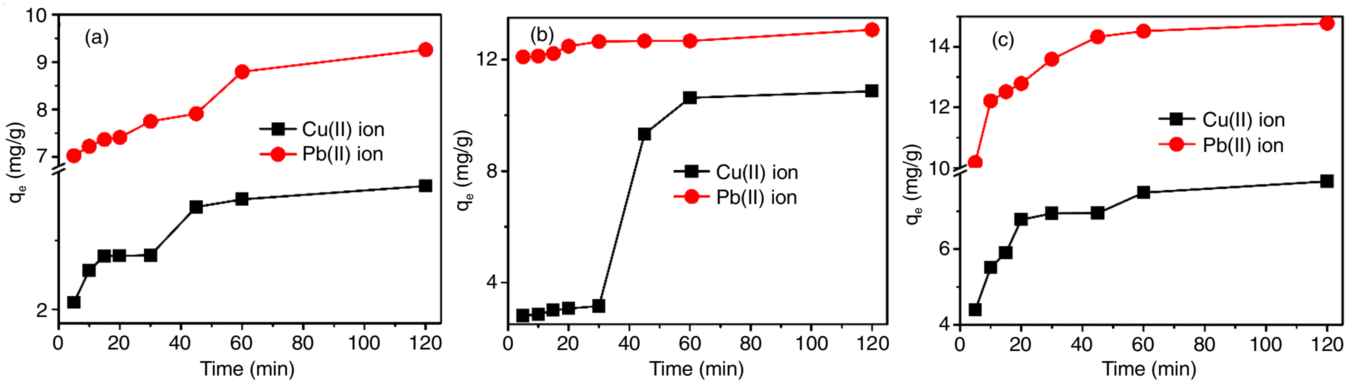

Fig. 5. Effect of time of Cu(II) and Pb(II) ions on (a) PFS, (b) ATFS and (c) BTFS

to PFS and BTFS and the trend was PFS < BTFS < ATFS with adsorption capacities of 2.896, 7.787 and 10.865 mg/g, respectively.

Kinetic studies: The kinetic studies of PFS, ATFS and BTFS on Cu(II) and Pb(II) were investigated using pseudo-first order (PFO), pseudo-second order (PSO) and intraparticle diffusion (IDP) and the data is shown in Table-2. To determine whether the data had a good fit for PFO, PSO, or IDP, it required that the value of (r^2) be close to unity and the calculated adsorption capacity to be close to the experimental value. It was observed that the (r^2) values for PSO were closer to 1. Also, PSO gave experimental (q_e) values closer to the calculated (q_e). The kinetics study revealed that PSO fitted the data better than PFO. PSO suggested that the adsorption mechanism involved electrostatic interaction between adsorbate and adsorbents active sites [46,47].

Intraparticle diffusion (IPD) was also studied to determine the nature of adsorption either it occurred through the pores (EPA) or surface (ESA) on the adsorbents. It was observed that the uptake dominated on the surface thus ESA was favoured more than EPA. Analysis of IPD data suggested that the uptake of metal ions was controlled by the synergistic of ESA and EPA. However, ESA was dominant than EPA [48].

Effect of temperature: The uptake of Cu(II) and Pb(II) on PFS, ATFS and BTFS was investigated at different temperatures of 288, 298 and 308 K as shown in Fig. 6a-c. It was observed that the adsorption of both metal ions increased when the temperature of the system was increased. The same trend was observed for all the adsorbents. This was because metal ions gained more energy as the temperature was increased, thus resulted in hindering forces been overcame [49]. Maximum adsorption capacities of Cu(II) at 288, 298 and 308 K were

TABLE-2
KINETIC STUDIES OF Cu(II) AND Pb(II) ON PFS, ATFS AND BTFS

Model		PFS		ATFS		BTFS	
		Cu(II)	Pb(II)	Cu(II)	Pb(II)	Cu(II)	Pb(II)
PFO	q_e	2.605	8.025	12.79	12.58	7.139	13.67
	K_1	0.022	0.067	0.107	0.105	0.059	0.114
	R^2	0.710	0.475	0.909	0.484	0.944	0.867
PSO	q_e	2.807	8.550	12.35	12.81	7.799	14.63
	K_2	0.023	0.071	0.103	0.107	0.065	0.122
	R^2	0.897	0.760	0.902	0.797	0.986	0.967
IDP	C	1.955	6.318	9.46	11.82	4.631	10.44
	K_1	0.016	0,053	0.079	0.099	0.039	0.087
	R^2	0.939	0,974	0.888	0.968	0.845	0.888
EPA	%	32.50	31.80	12.93	10.29	38.18	29.33
ESA	%	67.50	68.20	87.07	89.71	61.82	70.67
Experimental	q_e	2.896	9.264	10.86	13.178	7.490	14.78

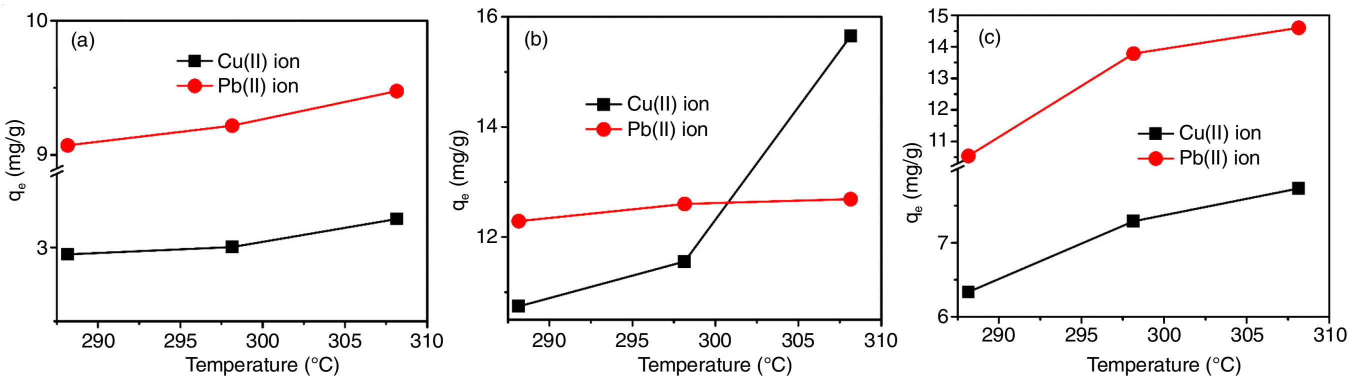

Fig. 6. Effect of temperature of Cu(II) and Pb(II) on (a) PFS, (b) ATFS and (c) BTFS

2.953, 3.003 and 3.193 mg/g whereas for Pb(II) maximum adsorption capacities were 9.072, 7.219 and 9.477 mg/g, respectively for PFS. While maximum adsorption capacities for Cu(II) were 10.74, 11.55 and 15.65 mg/g whereas Pb(II) maximum adsorption capacities were 12.28, 12.60 and 12.69 mg/g, respectively for ATFS. For BTFS, maximum adsorption capacities of Cu(II) were 6.33, 7.29 and 7.73 mg/g and for Pb(II) maximum adsorption capacities were 10.54, 13.78 and, 14.60 mg/g, respectively. Therefore, this suggests that the adsorption processes in this work favoured high temperatures, this revealed the exothermic nature of the uptake reactions. The results obtained in this study were in agreement with the previous study based on similar adsorbent fennel herb biomass for the adsorption of Cd(II) ions [50].

Thermodynamic studies: The calculated thermodynamic parameters *i.e.* enthalpy change (ΔH°), Gibbs free energy (ΔG°) and entropy change (ΔS°) are shown in Table-3. The ΔS° values were positive for Cu(II) and Pb(II) adsorbed on all the adsorbents and negative for Pb(II) adsorbed on PFS. The positive values suggested increased randomness at a solid-liquid phase at equilibrium and degree of freedom of Cu(II) and Pb(II) in the solution, whereas negative value indicated reduced randomness. The ΔH° values for Cu(II) and Pb(II) uptake onto all adsorbents were all negative. This suggested that the reactions were exothermic. ΔG° values were all negative for all the adsorbents. This indicates that the reaction was a spontaneous and feasible process.

Effect of pH: The effect of pH is one of the important parameters; it influences the ionization of functional groups and the oxidation state of metal ions in solution. Fig. 7a-c shows the pH effect plots at pH values ranging from 1-8. It was observed that when pH increases there was an increase in uptake of both metal ions. At low pH values below 3, there was low adsorption capacity due to the protonation of functional groups at the surface of the adsorbent leading to the electrostatic repulsion between the metal ions and adsorbents. This inhibited the attraction between the adsorbent's surface and metal ions [51]. When the pH was increased from 5 to 8, there was an

TABLE-3
THERMODYNAMIC STUDIES OF Cu(II) AND Pb(II) ON PFS, ATFS AND BTFS

Parameters		PFS		ATFS		BTFS	
		Cu(II)	Pb(II)	Cu(II)	Pb(II)	Cu(II)	Pb(II)
ΔH° (KJ mol^{-1})		-1.162	0.009	-4.979	-0.145	-1.371	-3.962
ΔS° (KJ mol^{-1} K^{-1})		0.633	-0.549	15.692	0.188	2.398	12.33
ΔG° (KJ mol^{-1})	288 K	-8.05	-4.30	-3.50	-2.74	-5.70	-3.59
	298 K	-8.28	-4.38	-3.21	-2.67	-5.37	-2.01
	308 K	-7.93	-4.39	-0.84	-2.71	-5.30	-1.57

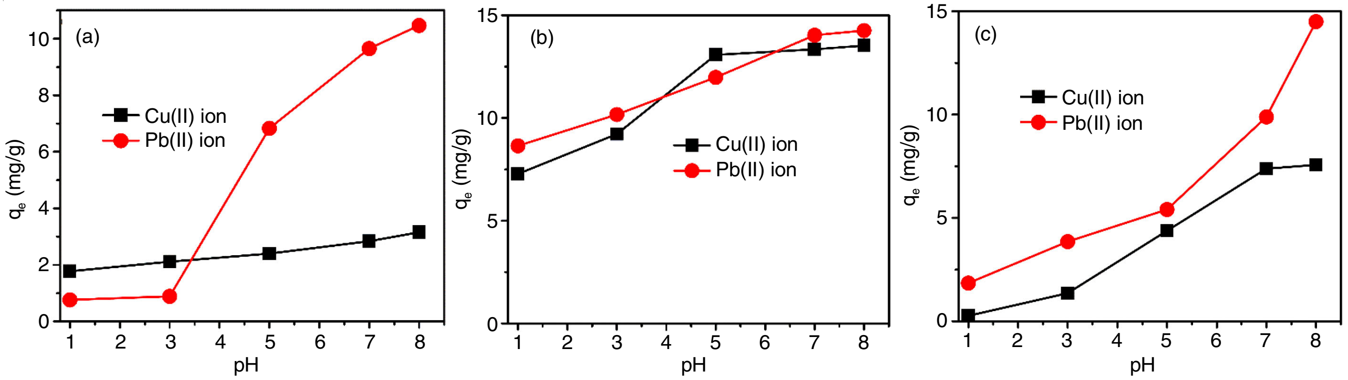

Fig. 7. Effect of pH of Cu(II) and Pb(II) ions on (a)PFS, (b) ATFS and BTFS

increase in adsorption capacity. Maximum adsorption capacities at pH 8 of Cu(II) and Pb(II) were 3.15 and 10.47 mg/g, respectively for PFS. While for ATFS the maximum adsorption capacities were 13.52 and 14.25 mg/g for Cu(II) and Pb(II). For BTFS the maximum adsorption capacities were 7.568 and 14.50 mg/g for Cu(II) and Pb(II). This could be explained by the fact that the surface of the adsorbents became more deprotonated, enhancing the electrostatic attraction between adsorbent surface and metal ions and thus resulted in high adsorption capacity [10,52]. Speciation of metal ions is also one of the important aspects of pH. Previous studies revealed that at pH > 8 and, Cu(II) and Pb(II) are the main species in the solution.

Point zero charge: Point zero charge is an important parameter as it determines the charge of the adsorbent's surface. Fig. 8 shows the plots for ΔpH *vs.* pH*i* of the adsorbents. $pH_{(pzc)}$ of PFS, ATFS and BTFS is 7.5, 3.5 and 8.7, respectively. This revealed that $pH_{(pzc)}$ of PFS is near neutrality, BTFS is slightly alkaline and ATFS is acidic.

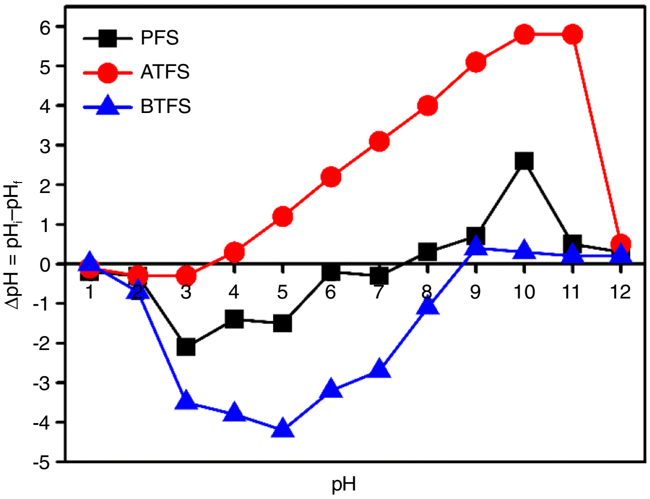

Fig. 8. Results of point zero charge for PFS, ATFS and BTFS

Post adsorption

FTIR results: The FTIR spectra of PFS, ATFS before and after adsorption are shown in Fig. 9. This was done to evaluate the changes in the wavelength of functional groups present on the surface of the adsorbent before and after the adsorption of metal ions. It was observed that peaks for (-OH, -C=O-, -C=C-) shifted positions and their intensities were reduced after adsorption. The apparent changes suggested that the functional groups might have been involved in the adsorption processes. Therefore, there was a possibility of electrostatic attraction and π-π interaction between metal ions and the functional groups. There was a new peak observed at 1143.46 cm^{-1} after adsorption and this suggested that there was a chemical interaction between the adsorbent and adsorbate.

SEM images of PFS, ATFS and BTFS after adsorption are shown in Fig. 10a-c. It was observed that the surface of PFS and ATFS became amorphous. It was also observed that there were pores especially for BTFS, cavities and smooth surfaces filled and coated with the metal ion solution [31].

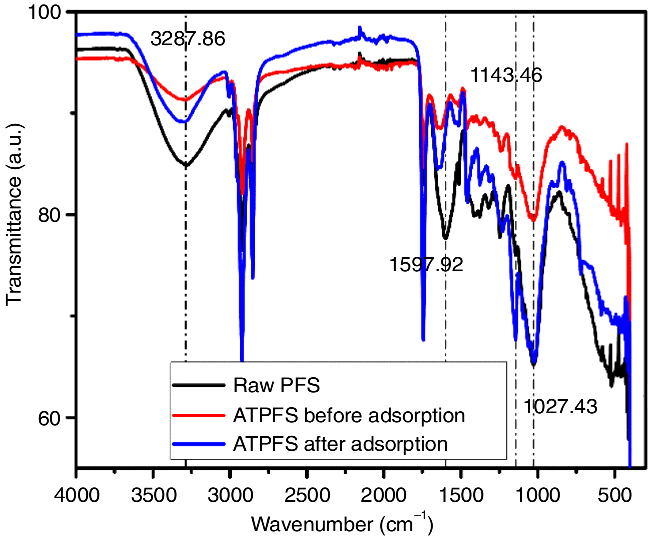

Fig. 9. FTIR spectrum for PFS and ATFS before and after adsorption

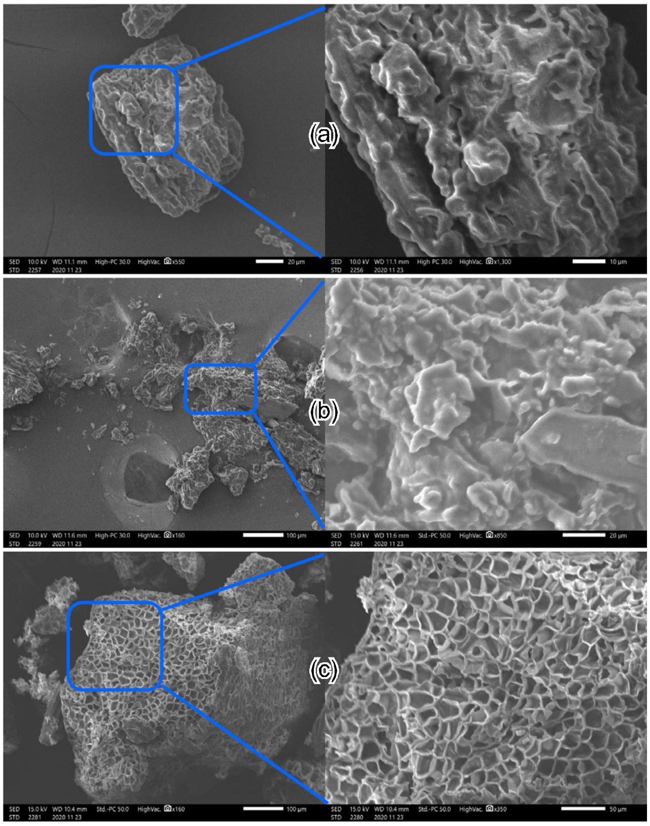

Fig. 10. SEM images for (a) PFS, (b) ATFS and (c) BTFS after adsorption

Conclusion

The pristine fennel seeds were treated with HCl and NaOH solution to modify their surface for improved removal of Cu(II) and Pb(II) ions from aqueous solution. The acid and base treatment improved the active sites responsible for metal ion adsorption. The acid and basic treated fennel seeds (ATFS and BTFS) exhibited high adsorption capacity compared to the untreated fennel seeds (PFS) for both Cu(II) and Pb(II). The FTIR spectra exhibited shifts in –O-H, -C=O-, -C-O and –C=C- peaks to new wavenumbers after modification and after adsorption showing that there were an electrostatic attraction and π-π interaction involved during adsorption. It was observed that high concentrations of Cu(II) and Pb(II) resulted in high adsorption capacity and the equilibrium data fitted Freundlich model. Kinetics studies that the adsorption of Cu(II) and Pb(II) fitted the PSO model, suggesting that the adsorption occurred on the adsorption sites and based on electrostatic attraction between the adsorbate and the adsorbents. Thermodynamic studies suggested that the adsorption reaction was exothermic, spontaneous and feasible for both metal ions on all adsorbents.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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