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Influence of solution chemistry on heavy metals removal by bioadsorbent tea waste modified by poly (vinyl alcohol)

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ABSTRACT

In this study, the macroporous spherical composite biomaterials, Poly(vinyl alcohol)/teawaste (PVA/TW), were prepared and investigated for their potential to remove Pb^{2+}, Hg^{2+}, and Cu^{2+} from aqueous solution. Investigations showed that adsorption capacity of Hg^{2+} by PVA/TW bead was much higher than that of Pb^{2+} and Cu^{2+}, while adsorption rate of Pb^{2+} was fastest. The experimental data obtained for Pb^{2+}-PVA/TW, Hg^{2+}-PVA/TW, and Cu^{2+}-PVA/TW at different solution temperatures indicate a monolayer type biosorption, which explains why the Langmuir isotherm accurately represents the experimental data obtained in this study. The Langmuir maximum biosorption capacities of Pb^{2+}, Hg^{2+}, and Cu^{2+} onto PVA/TW were 81.56, 175.68, and 49.08 mg/g at 298 K, respectively, which is comparatively superior to most other low-cost biomaterials. Fourier transform infrared spectroscopic analysis of the metal-loaded biosorbents confirmed the participation of –COOH, $–NH_2$, and $O–CH_3$ groups in the complexation of Pb^{2+}, Hg^{2+}, and Cu^{2+}. Thermodynamic parameters demonstrated that the biosorption of Pb^{2+} onto PVA/TW was endothermic, spontaneous, and feasible at 288–318 K. The results evidently indicated that PVA/TW would be suitable biosorbents for Pb^{2+}, Hg^{2+}, and Cu^{2+} in wastewater under certain conditions.

Keywords: Tea waste; Polymer PVA; Adsorption mechanism; Heavy metals

1. Introduction

Heavy metals from a multitude of sources, such as metal plating, mining, tanneries, painting, batteries manufacturer [1], become a severe public health concern because of its persistent nature and negative effect on the environment. Lead and mercury as toxic priority pollutants which commonly interfere with the beneficial use of wastewater for irrigation and industrial applications would lead to kidney and blood diseases among other health disorders. Copper, as a trace element, is essential for nutrition but if it is taken in high doses it may became toxic. It was reported that an overdose of Cu^{2+} could lead to depression, lethargy, neurologic signs such as seizures and ataxia [2,3]. The allowable discharge of Pb^{2+}, Hg^{2+}, and Cu^{2+} in potable water is 0.01, 0.002, and 1 mg/L by the US EPA and Agency [4]. It is therefore mandatory to reduce their levels in water and wastewater.

Adsorption is an alternative technology because of its high effect, low cost and easy operation among

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other physicochemical treatment processes, such as filtration, reverse osmosis, chemical precipitation, and ion exchange. Biosorption is a passive non-metabolic, natural process based on the capability of biological materials to remove heavy metals from water by ion exchange, microprecipitation, adsorption, coordination, and complexation [5]. In recent years, as they are either inexpensive or highly available, the biomaterials have been reported widely as adsorbents, for instance: husk [6], sawdust [7], coffee residues [8], seaweed [9], and industrial bio-waste [10], including tea waste (TW). It is reported that approximately 1,350,000 ton (dry basis) of tea was manufactured in 2009 in China. Tea is popular drink, and postbrewing of this drink results in the production of wastes. Thus, the benefits from recycling and re-use of this waste biomass for the extraction of heavy metals would be significant in terms of energy-saving, low-cost, and environmental compatibility. As insoluble cell walls of tea leaves are largely made up of cellulose and hemicelluloses, lignin, condensed tannins and structural proteins, one-third of the total dry matter in tea leaves should have good potential as metal scavengers from solutions since the above constituents contain functional groups mainly including carboxylate, aromatic carboxylate, phenolic hydroxyl, and oxyl groups [10]. Amarasinghe and Williams have reported that the highest metal uptake of 65 and 48 mg/g by TW were observed for Pb^{2+} and Cu^{2+}, respectively, at solution pH range of 5–6 [11]. Wasewar et al. used the tea factory waste (TFW) as a low-cost adsorbent for the removal of zinc, and the maximum adsorption capacity of Zn^{2+} per gram of TFW was calculated as 8.9 ± 0.008 mg [12]. Basically, the contributions to heavy metals removal by tea waste include: (1) the function groups with complex and adsorptive characteristics; (2) the surface area of TW; (3) pores on the surface. However, due to low mechanical strength, which is unsuitable for severe conditions of factual effluents; the powder shape or shortage of desorption data these sorbents are limited for practical use in fluid system.

Poly(vinyl alcohol) (PVA) is a water-soluble material containing large amounts of hydroxide groups that has been developed for biomedical applications since it is biocompatible and nontoxic and exhibits minimal cell adhesion [13]. Recently, a new and economical way to prepare macroporous PVA beads has been developed in our laboratory [13]. However, there are currently no reported studies in literature on the removal of Pb^{2+}, Hg^{2+}, and Cu^{2+} using TW encapsulated by PVA (PVA/TW). Here, biodegradable polymer PVA was first introduced to make a composite bead of PVA/TW with good mechanical strength, chemical stability, and easy separation. The principal object of this investigation is to explore the ability of PVA/TW composite beads in removing Pb^{2+}, Hg^{2+}, and Cu^{2+} from aqueous solutions and to investigate the influence of process conditions on the removal of heavy metals. The bioadsorbents were analyzed using FT-IR spectroscopy before and after the biosorption, with the aim of detecting the main biomass functional groups involved in the biosorption process. In addition, the equilibrium data from the experiments were fitted with isotherm and kinetic models to determine the capacity of the biomass and identify the biosorption mechanisms.

2. Materials and methods

2.1. Preparation and characterization of PVA/TW composite beads

Tea leaves, from commercial tea bags, were boiled several times with water until a colorless solution was spectrometrically detected, i.e. the exit water ran clear. The washed material, TW, was dried in a conventional oven for 48 h at 75°C. Then, TW was crushed in an electric mixer and then sieved with vibratory sieves (Fritsch, Germany). Particle sizes of less than 1.00 mm were used. For the preparation of PVA/ATW composite beads, quantitative PVA with 1,700 degree of polymerization, $C_6H_7O_8Na$, and $CaCO_3$ were dissolved in distilled water with boiled water bath for 1 h. The PVA solution (8% w/w) was mixed with TW powders to yield a solution ratio of approximately 300 g/L. The resulting mixture was extruded into a gently stirred saturated 3% $CaCl_2$/boric acid solution by an injector with diameter approximately 2 mm and immersed for 24 h to form spherical beads. For forming porous, 10 mL HCl solution (1:10, v/v) was added into 500 mL water loaded with cleaned PVA/TW beads. After reaction of HCl with $CaCO_3$ in the PVA/TW beads, they became porous. The porous beads were washed with distilled water to remove residual reagents. The spherical PVA/TW beads exhibit an elastic property with an average diameter of 3 mm.

The FT-IR analysis was performed using a Perkin–Elmer Spectrum 100 spectrophotometer to identify the functional groups available on the PVA/TW surface before and after biosorption of Pb^{2+}, Hg^{2+}, and Cu^{2+} under different experimental conditions (KBr technique). Spectra within the range of 400–4,000 cm^{-1} were recorded. For the SEM analysis and energy dispersive X-ray analysis, frozen samples were coated with gold and vacuumed (5–10 min) for electron reflection prior to analysis on a JEOL-JSM 6400 scanning microscope.

2.2. Biosorption experiments and methods

All experimental equipment and glassware were soaked in an acid bath (HNO_3 (10% v/v)) for 24 h, rinsed thoroughly with tap water, then rinsed 3–4 times with deionized water. Pb^{2+}, Hg^{2+}, and Cu^{2+}, along with the acid and base utilized in this investigation were of analytical grade. Pb^{2+}, Hg^{2+}, and Cu^{2+} stock solution was prepared by dissolving quantitative $Pb(NO_3)_2$, $Cu(NO_3)_2$, and $HgCl_2$ in deionized water (Millipore apparatus, 18.2 $M\Omega\,cm^{-1}$ conductivity). Solutions of Pb^{2+}, Hg^{2+}, and Cu^{2+} with different initial concentrations containing PVA/TW were then placed in glass jars and shaken for the required contact time in a water-bath shaker (Clifton NE5-28) at 120 rpm with the temperature adjusted when required. The time needed for achieving the equilibrium condition was estimated by taking samples at time intervals until equilibrium was established. The sample was analyzed for Pb^{2+}, Hg^{2+}, and/or Cu^{2+} concentration. The experiments of competing ions in binary and ternary system, i.e. solution of Pb^{2+}/Hg^{2+}, Pb^{2+}/Cu^{2+}, Hg^{2+}/Cu^{2+}, and $Pb^{2+}+Hg^{2+}+Cu^{2+}$, were also conducted.

The concentration of mercury remnant in the solution was determined by a FIMS 400 Mercury Analysis System (Perkin–Elmer). Lead and copper concentrations were determined using flame-AAS with an Aanalyst 200 by Perkin–Elmer. Heavy metal ions in binary or ternary system were measured by inductively coupled plasma atomic emission spectroscopy (ICP, IRIS Advantage, Thermo Co. Ltd., USA). The adsorption capacity of the PVA/TW beads and the percentage removal of heavy metal ions are calculated using the following Eqs. (1) and (2), respectively:

$$Q_t = \frac{(C_i - C_e)V/1000}{W} \tag{1}$$

$$\%\ \text{Removal of } M^{2+} = \frac{C_i - C_o}{C_i} \times 100 \tag{2}$$

where Q_t is the adsorption capacity in mg/g at time t, C_i, C_o, and C_e are the initial, outlet and equilibrium concentration of metal ions in mg/L, V is the volume of solution in mL, M^{2+} is the heavy metal ions (Pb^{2+}, Hg^{2+}, or Cu^{2+}), and W is the total amount of PVA/TW in g.

3. Results and discussion

3.1. Characterization of PVA/TW composite beads

The SEM image of the PVA/TW, as shown in Fig. 1, revealed that the TW was encapsulated by PVA homogeneously and the coarse surface with small pores (Fig. 1b) can be seen clearly from Fig. 1. These pores distributed randomly on the surface would provide the easy way for diffusion which facilitates the migration and adsorption of heavy metals into the inner sphere of PVA/TW beads.

The FT-IR spectra of PVA/TW beads before and after adsorption of Pb^{2+}, Hg^{2+}, and Cu^{2+} are shown in Fig. 2. The shift of functional group bands demonstrated the changes in surface characteristics and functional groups of the TW as a result of adsorption of metal ions, indicating the complex nature of TW. The cell wall of TW consists of carbohydrates, lignin, and cellulose which have hydroxyl groups in their structure. The troughs, due to bonded OH groups, are observed in the range of 3,340–3,380 cm^{-1} [14]. The FT-IR spectroscopic analysis indicated broad bands at 3432.5 cm^{-1}, representing bonded –OH groups which shift to 3430.4, 3426.6, and 3427.3 cm^{-1}, respectively, after the adsorption of Pb^{2+}, Hg^{2+}, and Cu^{2+}. The peak observed at 1636.6 and 1427.3 cm^{-1} corresponds to the C=O asymmetric and symmetric stretching vibration. In a number of investigations, this spectrum stands for a chelated form of carbonyl on the carboxyl group [14]. From the FT-IR spectra, the lignin structure can be confirmed by the C–O peak at around 1108.3 cm^{-1}. After adsorption of Pb^{2+}, Hg^{2+}, and Cu^{2+}, the peaks shift to 1081.7, 1072.6, and 1087.7 cm^{-1}, respectively. These bands were found to shift noticeably, indicating they are major functional groups involved in the biosorption.

EDX analysis of PVA/TW beads before Pb^{2+}, Hg^{2+}, and Cu^{2+} adsorption illustrates the presence of various element ions as shown in Table 1. The results of chemical analysis of the PVA/TW beads were: C, 59.71%; O, 38.12%; Na, 0.11%; Mg, 0.09%; K, 0.06%; Ca, 1.37%. It was evident that the concentration of Pb^{2+}, Hg^{2+}, or Cu^{2+} increased remarkably from ND to 9.64, 1.38, and 4.89%, respectively. Meantime, concentration of other elements, such as alkaline-earth metals Na, K, Mg, and Ca, reduced correspondingly. This indicates that ionic exchange between alkaline earth elements and heavy metal ions may play a role in the removal of Pb^{2+}, Hg^{2+}, and Cu^{2+} by PVA/TW.

3.2. Adsorption of Pb^{2+}, Hg^{2+}, and Cu^{2+} onto PVA/TW

3.2.1. Effect of pH

Solution pH affects adsorption process of heavy metals by affecting both aqueous chemistry and surface binding sites of the adsorbent. The effect of pH in the range 2.0–6.0 with a stirring time of 30 min on the removing of Pb^{2+}, Hg^{2+}, and Cu^{2+} was investigated. Fig. 3 shows the

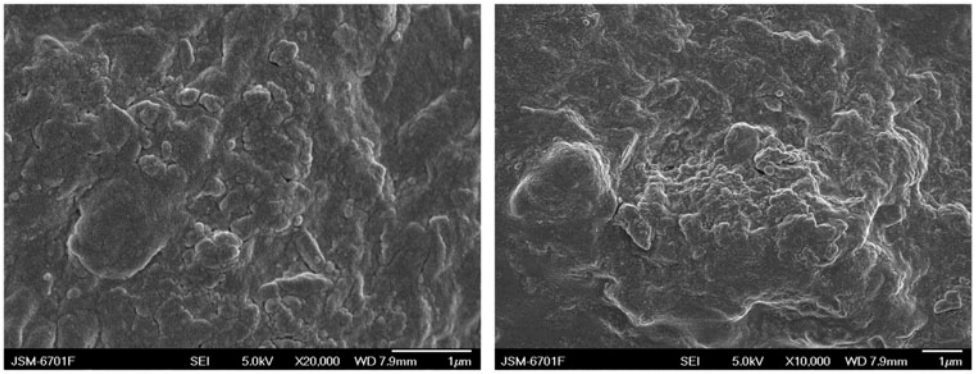

Fig. 1. SEM images of PVA/TW beads.

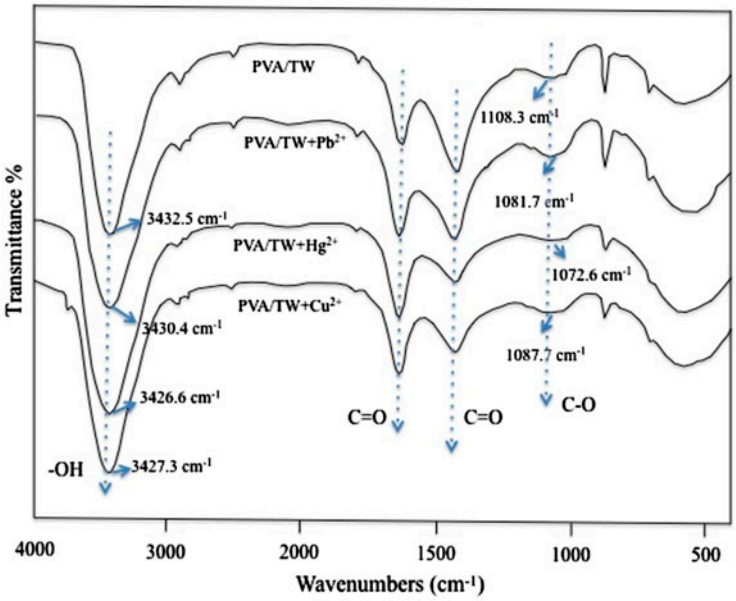

Fig. 2. FT-IR spectra of PVA/TW beads before and after Pb^{2+}, Hg^{2+}, and Cu^{2+} adsorption.

Q_e variations as a function of pH for each heavy metal ions. As Fig. 3 shows, the adsorption percentage in the case of Pb^{2+}, Hg^{2+}, and Cu^{2+} increased by increasing pH, reached a maximum at pH 5.0 and remained nearly constant up to pH 6.0. The generation of hydrolyzed species of Pb^{2+}, Hg^{2+}, and Cu^{2+} such as $Pb(OH)^+$, $Hg(OH)^+$, and $Cu(OH)^+$ at pH higher than 6.0 could promote a reduction of the adsorption capacity, due to the diminution of the formal charge of the metallic ion. Thus, solution pH tested was chosen in the range of 2.0–6.0 to prevent the formation of polynuclear hydroxo-bridged species or the precipitation of basic salts [15]. The low adsorption capacities of heavy metal ions observed at lower pH of the solution may be attributed to the partial protonation of the functional groups and the competition of H^+ with Pb^{2+}, Hg^{2+}, and Cu^{2+} ions for active sites on the adsorbents. In general, adsorption of Pb^{2+}, Hg^{2+}, and Cu^{2+} was affected significantly by pH values. Consequently, subsequent experiments were carried out at pH 6.0.

3.2.2. *Effect of initial concentration of Pb^{2+}, Hg^{2+}, and Cu^{2+}*

Initial Pb^{2+}, Hg^{2+}, and Cu^{2+} concentration was adjusted, respectively, in the ranges of 50–500 mg/L for adsorption on the chelating resin under pH 5.0 or so at 25℃ as shown in Fig. 4. The increasing initial metal ions concentration resulted in an increase in the metal ions on the PVA/TW. At the lower

Table 1
Element analysis of PVA/TW beads before and after Pb^{2+}, Hg^{2+}, and Cu^{2+} adsorption

	Atom ratio (%)								
Sample	C	O	Na	Mg	K	Ca	Pb	Cu	Hg
PVA/TW	59.71	38.12	0.11	0.09	0.06	1.37	–	–	–
PVA/TW-Pb	64.94	24.74	0.04	0.06	0.02	0.38	9.64		
PVA/TW-Cu	60.28	33.51	0.14	0.01	0.06	0.64		4.89	
PVA/TW-Hg	60.89	34.19	0.05	0.02	0.04	1.27			1.38

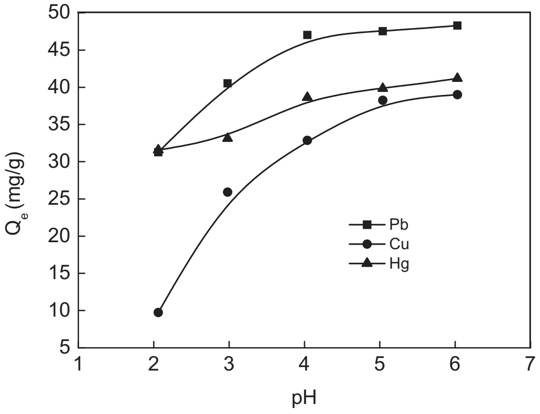

Fig. 3. Effect of initial pH on the adsorption of Pb^{2+}, Hg^{2+}, and Cu^{2+} onto PVA/TW beads.

concentrations, Pb^{2+}, Hg^{2+}, and Cu^{2+} in the solution would interact with the binding sites and thus facilitated its adsorption for the adsorbent. With increasing metal ion concentration, there is an increase in the amount of metal ion adsorbed due to increasing driving force of the metal ions towards the active sites on the adsorbents. For Hg^{2+}, adsorption capacity increases nearly linearly with the increase of initial concentration, and the maximum value obtained was 175.68 mg/g. For Pb^{2+} and Cu^{2+}, at low concentration, the adsorption capacity increased rapidly before it reached the adsorption equilibrium with the maximum adsorption capacity of 81.56 and 49.08 mg/g, respectively. It was observed that the adsorption capacity increased more slowly for Cu^{2+} than Pb^{2+}. Thus, it was concluded that PVA/TW shows the best affinity to Hg^{2+}, followed by Pb^{2+} and Cu^{2+}. It might be due to the different negative charge and ionic radius of Pb^{2+}, Hg^{2+}, and Cu^{2+}.

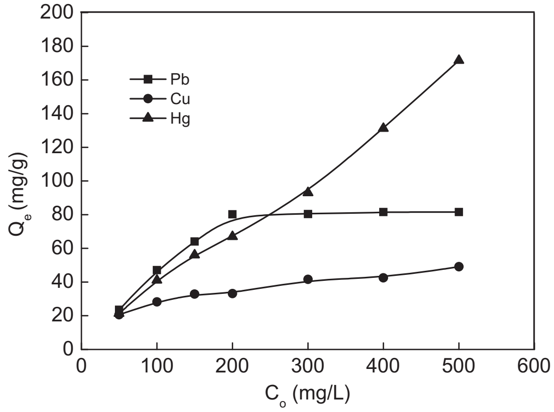

Fig. 4. Effect of initial metal concentration on the adsorption of Pb^{2+}, Hg^{2+}, and Cu^{2+} onto PVA/TW beads.

3.2.3. Effect of contact time and temperature

The effect of contact time to the adsorption capacity of the PVA/TW was investigated in the time ranges of 20–1,380 min under optimized pH at 25℃. The adsorption data for metal uptake vs. contact time for a fixed adsorbent amount are shown in Fig. 5. It can be seen that the adsorption of Pb^{2+}, Hg^{2+}, and Cu^{2+} increased with the contact time increased. When the initial concentration of heavy metal ion was 50 mg/L, adsorption equilibrium for Pb^{2+}, Hg^{2+}, and Cu^{2+} was achieved at 240, 480, and 540 min, respectively, while 480, 660, and 660 min was needed to reach adsorption equilibrium as the initial concentration was 100 mg/L. It was observed that the adsorption rate of PVA/TW for Pb^{2+} is much faster than that for Hg^{2+}, and Cu^{2+}. To be sure of the best adsorption conditions at higher concentration levels and to obtain equilibrium at the solid/liquid interface, all the experiments were carried out with 720 min of contact time.

Adsorption experiments to study the effect of temperature were carried out at 293, 303, 313, and 323 K, respectively, at optimum pH value of 5.0 and the contact time for the adsorption was maintained at 720 min as shown in Fig. 6. It can be clearly seen that amount adsorbed of Pb (II) is nearly constant with increase in the temperature. While the adsorption capacity of Hg^{2+} and Cu^{2+} increased evidently with temperature rising from 293 to 323 K. For example, equilibrium adsorption capacity for Cu^{2+} increased

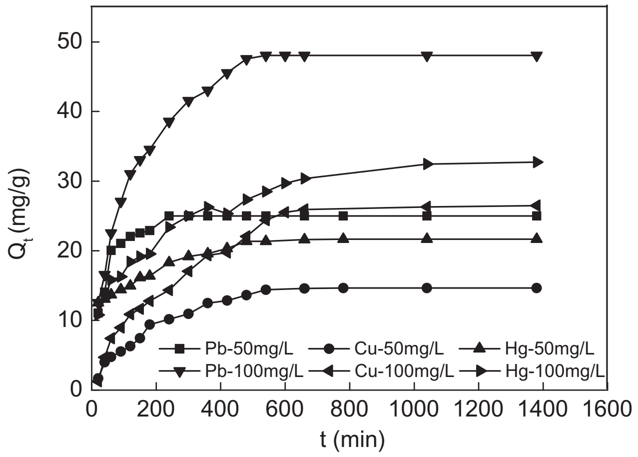

Fig. 5. Effect of contact time and initial metal concentration on the adsorption of Pb^{2+}, Hg^{2+}, and Cu^{2+} onto PVA/TW beads.

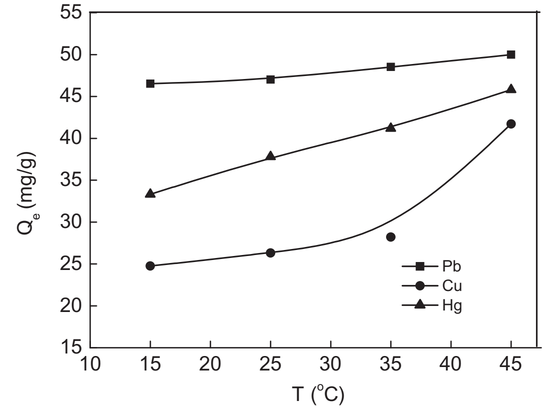

Fig. 6. Effect of temperature on the adsorption of Pb^{2+}, Hg^{2+}, and Cu^{2+} onto PVA/TW beads.

from 25.01 to 41.42 mg/g with temperature changing from 293 to 323 K. The result indicated the endothermic nature of the adsorption process and increasing temperature would favor the adsorption process.

3.2.4. *Effect of ionic strength*

The presence of salts in wastewaters is one of the important factors that may affect the adsorption performance of the adsorbent. The ionic strengths of 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, and 1.0 mol/L were used to test their effects on Pb^{2+}, Hg^{2+}, and Cu^{2+} adsorption by PVA/TW at initial heavy metal concentration of 100 mg/L. In Fig. 7, it can be seen that the amount of Pb^{2+}, Hg^{2+}, and Cu^{2+} ions adsorbed onto PVA/TW was affected observably by the variations of the ionic strength. Adsorption capacity of Pb^{2+}, Hg^{2+}, and Cu^{2+} deceased by 70.06, 26.55, and 38.53%, respectively, when ionic strength increased from 0.01 to 1.0 mol/L. It is reported that chemical-binding reaction between the metal ions and the surface functional groups may be specific that it forms inner-sphere surface complexes and electrostatic-binding reaction may be non-specific with less selectivity forming outer-sphere adsorption [16]. The fact that the metal ions removal from solution by adsorbents is dependent on ionic strength may indicate the adsorption mechanism of Pb^{2+}, Hg^{2+}, and Cu^{2+} onto PVA/TW would include complexing, ionic exchange, and/or electrostatic binding. On the other hand, increasing ionic strength could affect the activity coefficient of heavy metal ions so that their transfer to the surface of PVA/TW would be interfered.

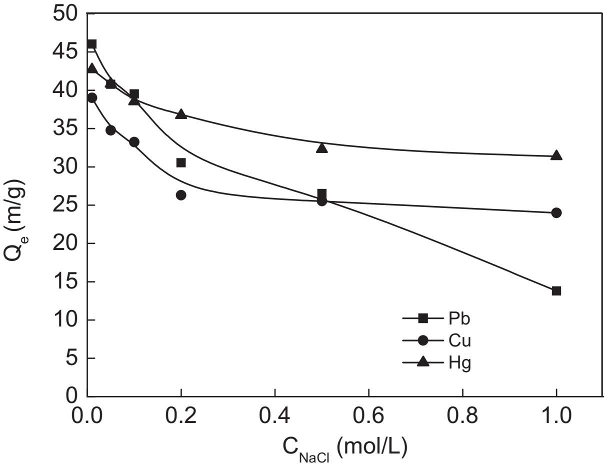

Fig. 7. Effect of ionic strength on the adsorption of Pb^{2+}, Hg^{2+}, and Cu^{2+} onto PVA/TW beads.

3.2.5. *Competing adsorption*

Generally, many heavy metal ions present in industrial wastewaters may interfere with the adsorption of desired ions. Therefore, competitive adsorption was conducted in binary mixtures (Pb^{2+}/Cu^{2+}, Pb^{2+}/Hg^{2+}, and Cu^{2+}/Hg^{2+}) and ternary mixture ($Pb^{2+} + Cu^{2+} + Hg^{2+}$) at pH 5.0 and other conditions similar to those in batch adsorption experiments. The result was shown in Table 2. It can be seen that in binary system, existing of Pb^{2+} has a significant effect on the Cu^{2+} and Hg^{2+} adsorption. While in contrast, few Pb^{2+} adsorption was affected by Cu^{2+} and Hg^{2+}, even in ternary system, adsorption removal of Pb^{2+} could reach 73.48%. In ternary system of $Pb^{2+} + Cu^{2+} + Hg^{2+}$,

Table 2
Competitive adsorption in binary and ternary systems

Metal ions solution		Q_e (mg/g)		
		Cu^{2+}	Hg^{2+}	Pb^{2+}
Single system	Pb^{2+}, Hg^{2+} or Cu^{2+}	20.57	21.40	23.53
Binary system	Cu^{2+}–Hg^{2+}	12.27	11.40	–
	Cu^{2+}–Pb^{2+}	11.88	–	19.46
	Pb^{2+}–Hg^{2+}	–	18.69	23.01
Ternary system	Pb^{2+}–Hg^{2+}–Cu^{2+}	9.19	11.20	17.29

heavy metal ions adsorbed by PVA/TW was in the following order: $Pb^{2+} > Hg^{2+} > Cu^{2+}$.

3.3. Adsorption isotherms

Analysis of sorption equilibrium data is important for optimizing the design of adsorption systems. Adsorption isotherm expresses the relationship between metal ions adsorbed onto the adsorbent and metal ions in the solution and provides important design parameters for adsorption systems. In this study, linear Langmuir, Freundlich isotherms were used to describe the equilibrium of Pb^{2+}, Cu^{2+}, and Hg^{2+} adsorption onto PVA/TW. The Langmuir isotherm model assumes a monolayer adsorption with a homogeneous distribution of the sorption sites and sorption energies, and that once the adsorption site is occupied no further adsorption can take place at that site [17,18]. The linear form of Langmuir isotherm equation is given as:

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_{max}} + \frac{C_e}{Q_{max}} \tag{3}$$

where Q_e (mg/g) and C_e (mg/L) are the equilibrium heavy metal concentrations in the solid and liquid phase, respectively. Q_{max} (mg/g) and K_L (L/mg) are the Langmuir constants related to saturated monolayer adsorption capacity and the binding energy of the sorption system, respectively.

The Freundlich isotherm is an empirical equation based on adsorption on a heterogeneous surface. It is assumed that the stronger binding sites are occupied first and the binding strength decreases with the increasing degree of site occupation [19]. The linear form of Freundlich equation is given as:

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{4}$$

where K_f and n are the Freundlich constants, indicating the relative adsorption capacity of the adsorbent related to the bonding energy and the adsorption intensity, respectively.

The parameters of Langmuir and Freundlich isotherms for Pb^{2+}, Cu^{2+}, and Hg^{2+} adsorption by PVA/TW were listed in Table 3. It can be seen that Langmuir isotherm model is much better to describe the equilibrium data of Pb^{2+} and Cu^{2+} than Freundlich isotherms indicating that adsorption of Pb^{2+} and Cu^{2+} onto PVA/TW was primarily monolayer adsorption. Furthermore, Q_{max} values calculated from Langmuir isotherm model were very close to the experimental Q_e value. It is noted that the maximum adsorption capacity of this PVA/TW composite bead was larger than other TW-based adsorbent such as Turkish TW, activated TW, and acid-washed TW (Table 4). On the other hand, high R^2 value indicates that Freundlich isotherm model fits the equilibrium adsorption of Hg^{2+} onto PVA/TW well.

Table 3
Isotherm constants for adsorption of Pb^{2+}, Hg^{2+}, and Cu^{2+} onto PVA/TW beads

Isotherm parameters	Metal ions		
	Pb^{2+}	Hg^{2+}	Cu^{2+}
Q_{exp} (mg/g)	81.56	175.68	49.08
Langmuir isotherm			
Q_{max} (mg/g)	82.64	217.39	50.25
K_L (L/g)	0.20	0.01	0.03
R^2	0.9998	0.7079	0.9775
Freundlich isotherm			
K_f (mg/g)	26.87	6.56	12.47
n	4.53	1.58	4.59
R^2	0.7529	0.9703	0.9715

Table 4
Comparison of adsorption capacity of Pb^{2+}, Hg^{2+}, and Cu^{2+} by PVA/TW beads with other tea-based biosorbents

Name of adsorbent	Adsorption capacity (mg/g)			References
	Cu^{2+}	Pb^{2+}	Hg^{2+}	
Sri Lankan tea	48	65	–	[11]
Turkish TW	8.64 ± 0.51	–	–	[10]
Activated TW	–	81	–	[26]
Acid washed TW	–	79	–	[27]
Waste tea leaves	–	73		[28]
PVA/TW beads	49.08	81.56	175.68	In this study

The constant $n > 1$ suggests that it is a favorable adsorption process and heterogeneous reaction prevails in Hg^{2+} adsorption by PVA/TW. This may be due to that PVA/TW was a composite bead and the two parts PVA and TW both could adsorb the heavy metal ions. Additionally, physical adsorption is another possible adsorption mechanism because of the pore structures of PVA/TW beads.

3.4. Adsorption kinetics

In order to investigate the kinetic mechanism that controls the adsorption of Pb^{2+}, Hg^{2+}, and Cu^{2+} on PVA/TW bead, the pseudo-first-order and the pseudo-second-order models are used to analyze the equilibrium data. The linear form of the pseudo-first-order kinetic model [20] is expressed as:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \tag{5}$$

where Q_e and Q_t (mg/g) are the amounts of heavy metal ions adsorbed at equilibrium and at time t (min), respectively, and K_1 (1/min) is the adsorption rate constant.

The pseudo-second-order equation [21] is expressed as:

$$\frac{t}{Q_t} = \frac{1}{K_2 {Q_e}^2} + \frac{t}{Q_e} \tag{6}$$

where K_2 (g/(mg min)) is the rate constant of second order. The second-order rate constant is used to calculate the initial adsorption rate, h (mg/(g min)), which is given by:

$$h = K_2 Q_e^2 \tag{7}$$

Kinetic parameters for the adsorption of Pb^{2+}, Hg^{2+}, and Cu^{2+} onto PVA/TW beads based on the pseudo-first- and pseudo-second-order equations were shown in Table 5. It can be seen that the R^2 value for pseudo-first-order model was low indicating that the pseudo-first-order model did not fit the adsorption data of Pb^{2+}, Hg^{2+}, and Cu^{2+} onto PVA/TW beads. While the R^2 value for pseudo-second-order model was larger than 0.98 and the calculated Q_e value was close to the experimental one suggesting that pseudo-second-order model could describe the adsorption of Pb^{2+}, Hg^{2+}, and Cu^{2+} onto PVA/TW beads well. Thus, it is concluded that the chemical adsorption is the rate-limiting process. Binding between Pb^{2+}, Hg^{2+}, and Cu^{2+} onto PVA/TW beads may be mainly through exchanging or sharing the electron [22]. The values of h and K_2 for Pb^{2+} adsorption were larger than that for Hg^{2+} and Cu^{2+} adsorption indicating the adsorption rate of Pb^{2+} by PVA/TW beads was faster than Hg^{2+} and Cu^{2+} which is agreement with the adsorption process in the batch experiments.

3.5. Adsorption thermodynamics

Thermodynamics parameters can be determined using the equilibrium constant K_d (Q_e/C_e) which depends on temperature. The change in free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) associated to the adsorption process was calculated using following equations [23]:

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

$$\Delta G^o = -RT \ln K_d \tag{9}$$

where R is the universal gas constant (8.314 J/(mol K)), and T is the absolute temperature (K).

Table 5
Kinetic parameters for the adsorption of Pb^{2+}, Hg^{2+}, and Cu^{2+} onto PVA/TW beads based on the pseudo-first- and pseudo-second-order equations

Metal ions (mg/L)	Q_{exp} mg/g	Pseudo-first-order kinetics			Pseudo-second-order kinetics			
		Q_e (mg/g)	K_1	R^2	Q_e (mg/g)	K_2	h	R^2
Pb-50	25.00	14.07	1.18×10^{-2}	0.8980	25.97	1.85×10^{-3}	1.25	0.9992
Hg-50	21.67	15.32	0.72×10^{-2}	0.9389	22.93	0.88×10^{-3}	0.46	0.9960
Cu-50	14.63	21.42	0.77×10^{-2}	0.8982	18.83	0.27×10^{-3}	0.09	0.9892
Pb-100	48.05	46.40	0.76×10^{-2}	0.9183	51.54	0.28×10^{-3}	0.73	0.9976
Hg-100	32.71	25.45	0.38×10^{-2}	0.9588	34.84	0.27×10^{-3}	0.33	0.9941
Cu-100	26.49	31.78	0.50×10^{-2}	0.9486	32.25	0.13×10^{-3}	0.14	0.9861

Table 6
Thermodynamic parameters for Pb^{2+}, Hg^{2+}, and Cu^{2+} adsorption onto PVA/TW beads

Metal ions	ΔG° (kJ/mol)				ΔH° (kJ/mol)	ΔS° (J/(mol K))
	288 K	298 K	308 K	318 K		
Pb^{2+}	−4.55	−5.12	−7.17	−8.52	35.65	138.59
Hg^{2+}	0.03	−1.09	−2.16	−4.05	37.99	131.43
Cu^{2+}	1.70	1.46	0.11	−4.59	41.07	134.86

Table 6 shows the thermodynamic parameters for Pb^{2+}, Hg^{2+}, and Cu^{2+} adsorption onto PVA/TW beads. It is reported that the negative values of ΔG° indicated the feasibility of the process and spontaneous nature of the adsorption [24]. As can be seen from Table 6 that, all ΔG° values for Pb^{2+} adsorption were negative, while ΔG° values for Hg^{2+} and Cu^{2+} adsorption were negative only when the temperature was above 25 and 45℃, respectively. It indicates that spontaneous nature of the adsorption was direct proportional to the temperature. The positive values of ΔH° further confirmed the endothermic nature of adsorption process whereas the positive values of ΔS° suggested that the degrees of freedom increased at the solid–liquid interface during the adsorption and it might be due to the substitution of water hydration molecules of metal ion by different binding sites [25]. The observed positive value of ΔS° for PVA/TW bead may be due to the stronger interaction between Pb^{2+}, Hg^{2+}, and Cu^{2+} ions and functional groups of PVA/TW. In addition, the heat of adsorption value (35.65–41.07 kJ/mol) between 20.9 and 418.4 kJ/mol indicates the chemisorption process. Hence Pb^{2+}, Hg^{2+}, and Cu^{2+} ions adsorption on PVA/TW bead was chemical and endothermic in nature.

4. Conclusions

Removal of Pb^{2+}, Hg^{2+}, and Cu^{2+} from aqueous solutions onto polymer PVA encapsulated TW (PVA/TW) was carried out. The experimental conditions of maximum adsorption of the Pb^{2+}, Hg^{2+}, and Cu^{2+} were optimized in terms of solution pH, initial concentration, contact time, temperature, ionic strength, and competing ions. It was observed that adsorption capacity of Hg^{2+} by PVA/TW bead was much higher than that of Pb^{2+} and Cu^{2+}, while adsorption rate of Pb^{2+} was fastest. Moreover, adsorption capacity of Pb^{2+}, Hg^{2+}, and Cu^{2+} decreased gradually with the increase of ionic strength indicating that PVA/TW beads could treat effectively the polluted water with low salt concentration. The competing adsorption experiments showed that PVA/TW bead has a good selectivity towards Pb^{2+} ions. Based on the thermodynamic parameters, adsorption of Pb^{2+}, Hg^{2+}, and Cu^{2+} was endothermic in nature. According to the above results, it is concluded that PVA/TW could be an effective and environmental friendly potential alternative adsorbent for the Pb^{2+}, Hg^{2+}, and Cu^{2+} removal from aqueous solutions.

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