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Metal ion free watermelon (*Citrullus lanatus*) rind as adsorbent for the removal of lead and copper ions from aqueous solution

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ABSTRACT

Chemically protonated watermelon rind (PWR) was evaluated as a low-cost and efficient adsorbent for the removal of Pb^{2+} and Cu^{2+} ions from aqueous solution. Protonation of watermelon rind (WR) was carried out with 0.1 M HCl as protonating agent. The adsorption process was found to be spontaneous and exothermic in nature. Kinetic investigations suggest that the present system follows pseudo-second-order kinetic model and rate-limiting step is not chemical reaction. The maximum loading capacity of PWR was found to be 116.2 and 39.2 mg g^{-1} for Pb^{2+} and Cu^{2+} ions, respectively. FTIR and energy dispersive X-ray analyses supported the sorption of metal ions onto PWR. The results suggested that WR can be an effective adsorbent for the removal of heavy metal ions from aqueous solution.

Keywords: Watermelon rind; Protonation; Adsorption; Desorption; Water treatment

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1. Introduction

Heavy metal ions are stable and persistent toxic environmental contaminants. The presence of heavy metals in the environment is of major concern. As a result, there has been a great deal of attention for safe and economical methods of eliminating these toxic heavy metal ions from contaminated water. Adsorption is found to be most effective and economical technique for the removal of contaminants from aqueous solution. Agricultural waste materials are economical, eco-friendly, nontoxic, and abundantly available substances. Wide range of agricultural wastes such as walnut waste [1], apple waste [2], maize cobs [3], peanut shell [4,5], cassava waste [6], jackfruit peels [7], fluted pumpkin waste [8], olive pomace [9], wheat bran [10], coconut shell [11], banana peel, and orange peel [12] are studied as adsorbents for the elimination of toxic metal ions.

Watermelon (*Citrullus lanatus*) rind, a common agricultural by-product, is a natural and rich source of the nonessential amino acid, citrulline, containing abundant carboxyl and amino groups, which has remarkable capability of binding heavy metal ions from aqueous solutions [13]. Watermelon rind (WR) consists of pectin, citrulline, cellulose, proteins, and caroteniods [14,15]. Only half of the fruit is considered to be edible leaving the other half like rind and peel as waste products. In order to manage the agro-waste, a novel adsorbent was prepared from WR and used to eliminate the Pb^{2+} and Cu^{2+} ions from aqueous solution.

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The stability and removal efficiency of raw biomass can be further improved by chemical modification and activation [16]. In view of this, several agricultural wastes have been chemically modified and proven to be better sorbents for the removal of heavy metal ions. Hence, in this study, WR was chemically protonated using hydrochloric acid as protonating agent and used as adsorbent toward sequestration of Pb^{2+} and Cu^{2+} ions from aqueous solution. Effect of pH, contact time, adsorbent dose, initial metal ion concentration, and temperature on adsorption was studied. In order to understand the nature of adsorption thermodynamics, equilibrium isotherms and kinetics have been evaluated for experimental data. Desorption and regeneration study was conducted to access the practical utility of protonated watermelon rind (PWR).

2. Materials and methods

2.1. Preparation of adsorbent

WR powder was prepared according to the procedure reported in literature [17]. Protonation was carried out by soaking 10 g of WR powder in 100 ml of 0.1 M HCl for 4 h. Later, it was rinsed with double distilled water repeatedly in order to remove the desorbed alkali and alkaline metals (e.g. K^+, Mg^{2+}). Thus, the WR is chemically modified where all weakly acidic sites are occupied by protons [18]. The oven-dried WR after protonation is named as PWR and sieved through 100 (BSS) mesh sieve and stored in airtight polyethylene bottles for further sorption experiments.

2.2. Sorption studies

The adsorption of Pb^{2+} and Cu^{2+} ions onto PWR was investigated in batch mode adsorption methods. All batch experiments were carried out in 100 ml conical flasks containing 20 ml of metal ions solution. Sorption capacity of PWR was determined by contacting 1.5 and 2.5 g l^{-1} of sorbent with 20 ml of known concentrations (50–300 ppm) of Pb^{2+} and Cu^{2+} metal ions, respectively, at room temperature. The solid phase was separated using Whatman filter paper and the residual concentration of supernatant metal ions solution was determined by atomic absorption spectrometer (Varian, AA240). The effect of pH on adsorption capacity of PWR was evaluated in the range of 2–8, initial pH of each metal solution was adjusted to desired value using 0.1 M HCl or 0.1 M NaOH. The effect of solid phase on adsorption was studied by varying the dose between 0.5 and 5 g l^{-1} and rate of metal sorption was determined by analyzing the residual concentration of metal ions at different time intervals (10–120 min). The amount of metal adsorbed onto PWR was determined by Eq. (1) and % removal was evaluated by Eq. (2).

$$q_e = (C_0 - C_1)\frac{V}{M} \tag{1}$$

$$\%\ \text{Removal} = \frac{C_0 - C_1}{C_0} \times 100 \tag{2}$$

where q_e is the metal uptake (mg g^{-1}) by PWR, C_0 and C_1 are the initial and final metal concentrations (mg L^{-1}),respectively, V is the solution volume (L), and M is the mass of the adsorbent (g).

2.3. Desorption and regeneration studies

In order to determine the re-usability potential of the adsorbent, metal ion-loaded PWR sorbent (0.1 g) was shaken with 50 ml of desorbing agent (0.1 M HCl) for 30 min at room temperature. The suspension was separated using 0.45 μm filter paper and the residual concentration of supernatant metal solution was determined by atomic absorption spectrometer. The metal-desorbed PWR was used as the regenerated sorbent for three cycles.

2.4. Instrumentation analysis

Flame atomic absorption spectrophotometer (Varian AA240) equipped with air/acetylene burner was used to determine the concentration of Pb^{2+} and Cu^{2+} ions. FTIR spectroscopy (Thermo Nicolet, AVATAR 330) was used to identify the surface functional groups present in WR and PWR. FTIR analysis of original, protonated, and PWR after metal binding were recorded in the range of 4,000–400 cm^{-1} by KBr pellet method. Scanning electron microscope (Phillips XL30, Netherlands) equipped with electron dispersive X-ray analysis was used for elemental analysis.

3. Results and discussion

WRs are known to be rich in alkali and alkaline earth metals such as K^+, Na^+, Mg^{2+}, and Ca^{2+} and trace amount of Zn^{2+} and Fe^{2+}. The total cation content of WR was found to be 2.102 meq g^{-1}. In order to remove excess cations, such as K^+, Na^+, and Mg^{2+} ions that could interfere with metal sorption, WR was chemically protonated using 0.1 M HCl solution. The protonation step enhances binding of heavy metal ions by decreasing the competition between different ions like K^+ and Mg^{2+} with heavy metal ions like Pb^{2+} and Cu^{2+} ions. Protonation of WR was found to be a promising sorbent for removal of basic cationic dyes from aqueous solution with enhanced loading capacity [19]. The present study reports the potential use of PWR for the removal of Pb^{2+} and Cu^{2+} ions from aqueous solution.

3.1. Characterization of biosorbent

3.1.1. FTIR analysis

The pattern of sorption of metal ions onto plant materials is attributable to the active groups and bonds present on them [20]. Therefore, FTIR spectra were recorded for native, protonated, and metal ion-loaded PWR. FTIR spectra of WR displayed a number of peaks pertaining to different functional groups. The broad and intense peak around 3,371 cm^{-1} corresponds to –OH stretching vibrations of cellulose, pectin and peaks at 2,917 cm^{-1} attributes to –CH stretching vibrations of methyl groups. A peak at 1,734 cm^{-1} corresponds to –C=O stretching of carboxylic acid or esters and asymmetric and symmetric vibrations of ionic carboxylic groups ($–COO^-$), respectively, appeared at 1,633, and 1,423 cm^{-1}. The comparisons of FTIR spectra of native, protonated, metal-loaded WR are presented in Table 1.

As seen from Table 1, a slender change in wave numbers of hydroxyl and carbonyl groups of PWR are due to desorption of naturally present K^+ and Mg^{2+} ions and protonation at vacant sites. The shift in wave numbers of metal-loaded PWR corresponds to change in counter ions associated with carboxylate and hydroxylate anions suggesting that acidic groups, carboxyl, and hydroxyl groups are predominant contributors in metal uptake. Strong shift in the hydroxyl peak confirms the binding of metal ions. The peak shifts observed for carbonyl peak of native WR and metal-loaded WR was found to be same compared to PWR. This may be because carbonyl groups of native WR were already at a similar energy level due to naturally present K^+, Mg^{2+} bound to carboxylic acid groups. The mechanism of sorption is accomplished by deprotonation of hydroxyl groups followed by metal chelating or complexation with deprotonated functional groups and ion exchange with carboxylic groups.

3.1.2. EDX analysis

Elemental analysis was carried out for native WR and PWR by energy dispersive X-ray analysis (EDX) to confirm the protonation. The EDX pattern of native WR (Fig. 1(a)) shows the distinct peaks of K^+ and Mg^{2+} ions present in WR. While for PWR (Fig. 1(b)) these peaks are found missing which indicates that during acid wash with 0.1 M HCl, desorption of K^+ and Mg^{2+} ions takes place from native WR and the vacant sites created are occupied by protons. In order to confirm the binding of Pb^{2+} and Cu^{2+} ions onto PWR, elemental analysis was carried out for different metal-loaded PWR samples. EDX pattern of Pb-loaded PWR (Fig. 1(c)) clearly shows the presence of Pb^{2+} ion peak which confirms the binding of Pb^{2+} ions onto PWR. Similar patterns have been observed for binding of Cu^{2+} ions onto PWR (not shown here). From these findings, the mechanism of removal of Pb^{2+} and Cu^{2+}

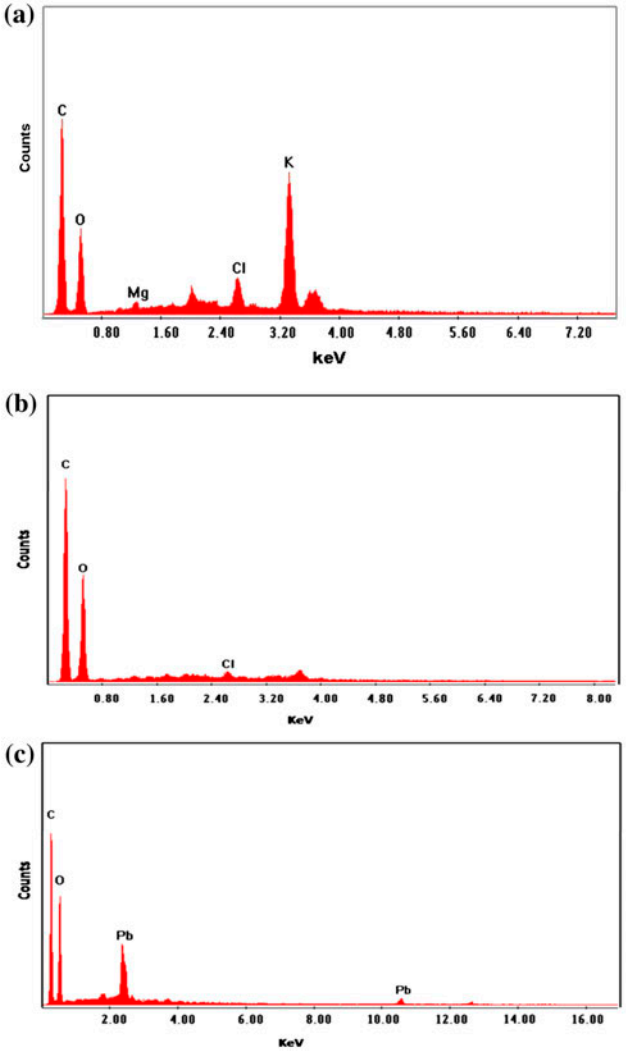

Fig. 1. EDX patterns of (a) native WR without any pretreatment, (b) WR after protonation with 0.1 M HCl, and (c) PWR after biosorption of Pb^{2+} ions.

ions onto PWR might be due to involvement of ion exchange process with protons. The high percentage of desorption supports the involvement of ion exchange mechanism.

3.2. Effect of pH on metal ion sorption

It is well known and extensively reported that pH is an important variable governing the adsorption of metal ions by adsorbent [21]. The solution pH influences metal ion sorption on to active sites of adsorbent due to the competition between the metal and H^+ ions. The FTIR spectroscopic analysis show that the PWR has variety of functional groups such as carbonyl, carboxyl, and hydroxyl groups which are involved in almost all the potential binding mechanism. Moreover, depending on the solution pH, the functional groups precipitate in metal ions’ bindings. Thus, the batch equilibrium studies were conducted at different initial pH values in the range of 2–8 (Fig. 2). It was observed that very little sorption took place at pH 2. A continuous increase in the sorption capacity of PWR occurred in the pH range of 2–5 and maximum removal was found at pH 5. At pH 2, the low metal sorption may be explained on the basis of protonation of active sites by H^+ ions. The increase in metal sorption with increase in pH can be explained in terms of pH_{pzc} (point of zero charge) of the adsorbent and metal speciation occurring in the solution.

The point of zero charge (pH_{pzc}) which is referred to as the point at which the charge of the solid surface is zero was experimentally found to be at pH 4.9 for PWR. At $pH > pH_{pzc}$, the surface charge of the adsorbent is negative and hence positively charged Pb^{2+} and Cu^{2+} ions are adsorbed onto PWR by electrostatic attraction. At low pH values, H^+ ions occupy most of the adsorption sites on the PWR surface and less Pb^{2+} and Cu^{2+} ions could be adsorbed because of electrostatic repulsion with H^+ ions on PWR surface. When the pH value increases, the surface charge of PWR is more negatively charged and adsorption of Pb^{2+} and Cu^{2+} ions increased and reached equilibrium at pH 5. At higher pH (>5), adsorption of ions decreases which might be due to the formation of soluble hydroxyl complexes of Pb^{2+} and Cu^{2+} ions. The metal speciation occurring in the solution is also pH dependent which affects the adsorption process. It is extensively reported that Pb^{2+} and Cu^{2+} ions exist as predominant species till pH 7 and at higher pH several hydroxides starts precipitating. For this reason, further metal sorption studies were carried out at pH 5.

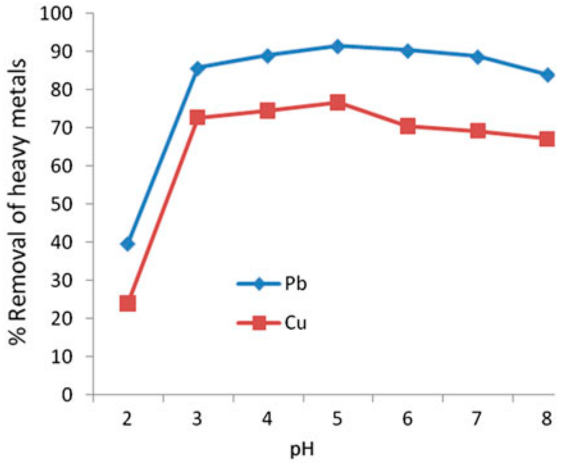

Fig. 2. Effect of pH on sorption of Pb^{2+} and Cu^{2+} ions from aqueous solution by PWR.

3.3. Effect of initial metal ion concentration and fitting to adsorption isotherms

In order to evaluate the maximum metal ion loading capacity of PWR, the adsorbent was contacted with different initial metal ion concentration (50–300 mg L^{-1}) of Pb^{2+} and Cu^{2+} ions at equilibrium. It was observed that metal ion loading capacity of PWR increased with an increase in initial metal ion concentration and reached a maximum capacity of 115.1 and 37.7 for Pb^{2+} and Cu^{2+}, respectively. To examine the relationship between metal ion concentration at equilibrium (C_e) and metal loading capacity (q_e), equilibrium sorption data of both the metals fit to Langmuir, Freundlich, and Temkin isotherm models. Langmuir and Freundlich isotherm models are two classical models, widely used for adsorption data analysis and for describing equilibrium between metal ions adsorbed onto the sorbent and metal ions remaining in solution at equilibrium.

Freundlich isotherm is an empirical equation that is based on the sorption of an adsorbate on a heterogeneous surface of an adsorbent. The linear form of Freundlich isotherm is given as:

$$\log\ q_e = \log\ K_F + \frac{1}{n} \log C_e \tag{3}$$

where K_F and n are the Freundlich constants indicating the adsorption capacity and intensity, respectively. By applying Eq. (3), a plot of log q_e vs. log C_e gives a straight line.

The Langmuir isotherm assumes monolayer adsorption process and linear form of Langmuir isotherm after rearrangement is given as:

$$\frac{C_e}{q_e} = \frac{1}{bV_m} + \frac{C_e}{V_m} \tag{4}$$

where C_e is the concentration of metal solution at equilibrium (mg^{-1}), q_e is the amount of metal adsorbed per unit mass of adsorbent (mg g^{-1}), V_m is the amount of adsorbate at complete monolayer coverage (mg g^{-1}), and b is a constant that relates to the heat of adsorption (L mg^{-1}). If the biosorption follows Langmuir isotherm, then a plot of C_e/q_e vs. C_e should be a straight line with slope $1/V_m$ and intercept $1/bV_m$.

The Temkin isotherm considers the effect of the adsorbate interaction on adsorption at active sites. The linear form of equation is given as:

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

where A is the equilibrium binding constant (L mg^{-1}) and B is related to the heat of adsorption. A plot of q_e vs. $\ln C_e$ enables the determination of isotherm constants.

The experimental data obtained for both the metal ions were fit to Langmuir, Freundlich, and Temkin isotherms. The respective constants and correlation coefficients (R^2) are summarized in Table 2. It is found that adsorption of Pb^{2+} and Cu^{2+} onto PWR fits better with the Langmuir isotherm than the Freundlich and Temkin isotherms. The better fit to Langmuir isotherm is further supported by its respective correlation coefficients (Fig. 3), which is a measure of how well-predicted values from a forecast model match with the experimental data. The theoretical complete monolayer coverage (V_m) of Pb^{2+} and Cu^{2+} onto PWR was calculated to 116.2 and 39.2 mg g^{-1}, respectively, against 115.1 and 37.7 mg g^{-1} found experimentally. Based on the Langmuir isotherm model, the metal ion loading capacities of Pb^{2+} and Cu^{2+} ions for PWR was found to be greater than native WR as reported in the literature (Table 3). Hence, simple acid wash of WR using hydrochloric acid has enhanced the metal loading capacity of Pb^{2+} ions and sixfold for Cu^{2+} ions. The sixfold increase in sorption capacity of Cu^{2+} ions can be attributed to availability of more vacant sites due to desorption of alkali and alkaline metals which are of similar atomic radius and electronegativity. However, the metal ion loading capacity of PWR was found to be high for Pb^{2+} ions than Cu^{2+} ions. This may be attributed to high electronegativity and smaller atomic radius of Pb^{2+} ions compared to Cu^{2+} ions. Sorption of metal ions having a smaller ionic radius has been reported as superior to those with larger ionic radius [24].

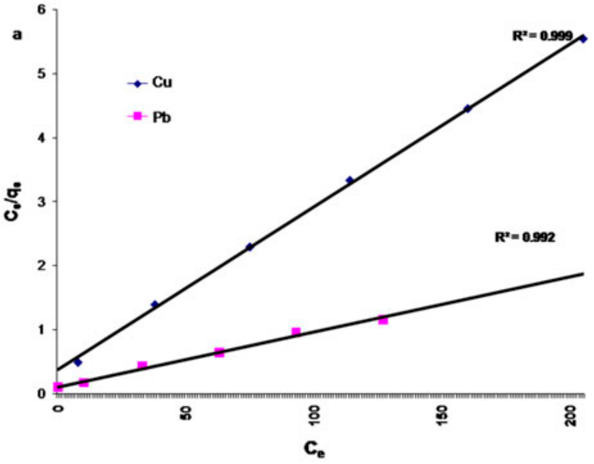

Fig. 3. Plots of Langmuir isotherm for Pb^{2+} and Cu^{2+} ions removal by PWR from aqueous solution (pH 5, 30 min, 303 K).

The essential characteristics of Langmuir equation can be expressed in terms of dimensionless separation factor, R_L, is given as:

$$R_L = \frac{1}{1 + bC_e} \tag{6}$$

where C_e (mg L^{-1}) is the equilibrium concentration of dyes and b (mL mg^{-1}) is the Langmuir isotherm constant. The adsorption process as a function of R_L may be described as $R_L > 1$; unfavorable, and $0 < R_L < 1$; favorable, linear and irreversible for $R_L = 1$ and 0, respectively. Table 4 represents the R_L values of Pb^{2+} and Cu^{2+} ions obtained for different initial concentrations. It can be seen that all the R_L values obtained are between 0 and 1, showing that the adsorption of Pb^{2+} and Cu^{2+} ions is favorable onto PWR.

3.4. Metal sorption kinetics

The rate of metal sorption is an important parameter for selecting a wastewater treatment system. In order to optimize the contact time for the maximum uptake of metal ions, contact time was varied between 10 and 120 min. The sorption of Pb^{2+} and Cu^{2+} ions onto PWR was rapid in first 10 min and equilibrium reached within 30 min. Results show that adsorption of Pb^{2+} and Cu^{2+} onto PWR is two-phase process. The first phase involved rapid adsorption of metal ions by PWR and second phase of sorption was on slower phase with longer contact time. The rapid uptake of metal ions is due to the availability of ample active

Table 1
Wave numbers of FTIR peaks of different WR samples

Functional groups	WR	PWR	Pb loaded PWR	Cu loaded PWR
–OH stretching vibrations of cellulose	3,371	3,378	3,397	3,401
–CH stretching vibrations of methyl groups	2,917	2,916	2,919	2,918
–C=O stretching of carboxylic acid or esters	1,734	1,728	1,736	1,736
–COO$^-$ asymmetric vibrations of ionic carboxylic groups	1,633	1,621	1,627	1,629
–COO$^-$ asymmetric vibrations of ionic carboxylic groups	1,423	1,421	1,420	1,421

sites for sorption and slower phase is due to gradual occupancy of active sites on biosorbent. So, a contact time of 30 min was fixed for further experiments.

To analyze the mechanism of adsorption of Pb^{2+} and Cu^{2+} ions onto PWR, the experimental data were fit to kinetic models such as pseudo-first-order, pseudo-second-order model, Elovich equation, and intraparticle diffusion model.

The pseudo-first-order rate equation of Lagergren is represented as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{7}$$

where q_e is the amount of metal ions adsorbed at equilibrium (mg g^{-1}), q_t is the amount of metal ions adsorbed at time t, and k_1 is the first-order reaction rate constant. A straight line of $\ln(q_e - q_t)$ vs. t suggests the applicability of this kinetic model and values of k_1 and q_e were determined from the plot.

Based on the sorption equilibrium capacity, pseudo-second-order equation can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo-second-order adsorption. The plot of t/q_t vs. t is shown in Fig. 4(a) and values of k_2 and q$_e$ can be calculated from the plot.

The kinetic data may also be analyzed using the Elovich equation, which has the linear form:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{9}$$

where α is the initial sorption rate constant (mg g^{-1} min^{-1}) and the parameter β is related to the extent of surface coverage and activation energy for chemisorption (mg g^{-1}). The constant can be obtained from the slope and intercept of the plot of q_t vs. $\ln t$. The values and correlation coefficients calculated from pseudo-first-order and pseudo-second-order and Elovich models at different initial concentrations are represented in Table 5.

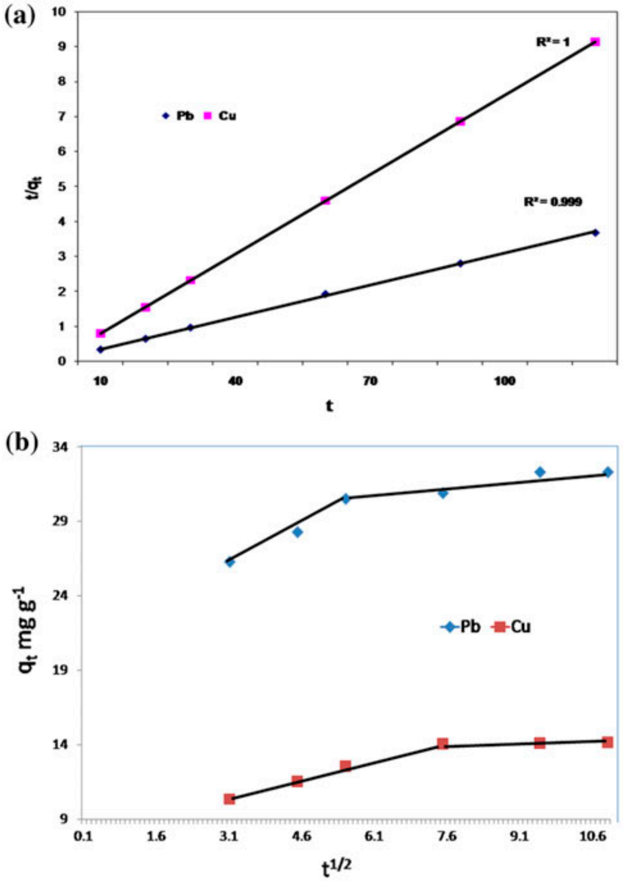

Fig. 4. Plots of (a) pseudo-second-order kinetic model and (b) Weber and Morris plot for intraparticle diffusion.

It is observed from Table 5 that the first-order kinetic model failed to provide a realistic estimate of q_e of adsorbed Pb^{2+} and Cu^{2+} ions onto PWR at different initial concentrations. The low correlation coefficients indicate that pseudo-first-order and Elovich equations might not be sufficient to describe the adsorption of Pb^{2+} and Cu^{2+} onto PWR. The

Table 2
Freundlich, Langmuir, and Temkin constants calculated for adsorption of Pb^{2+} and Cu^{2+} ions onto PWR from aqueous solution

		Metal ions	
Isotherms	Parameters	Pb	Cu
Freundlich	K_F	30.19	5.02
	$1/n$	0.016	0.026
	R^2	0.961	0.988
Langmuir	q_{max} (mg g^{-1})	116.2	39.2
	b (L mg^{-1})	0.103	0.077
	R^2	0.992	0.999
Temkin	A	25.96	15.20
	B	1.31	1.48
	R^2	0.809	0.986

linearized second-order plot resulted in straight lines for Pb^{2+} and Cu^{2+} ions with correlation coefficients being closer to one. The theoretical q_e values were also very close to the experimental values which show appropriateness of this model. These observations suggest that sorption by PWR followed pseudo-second-order reaction and our results are in good agreement with earlier reports of protonated pectin [25] and orange peels [26] which followed pseudo-second-order model. In general, the experimental data that fit to pseudo-second-order model indicate that the rate-limiting step for the process involves chemical reaction, that is, chemisorption. A number of conditions must be met if the rate of removal of heavy metals from solution is controlled by chemical reactions. These conditions are [27]:

(1) The rate constant should be constant for all values of initial concentration of counter-ions,
(2) The rate constant should not change with adsorbent particle size, and
(3) The rate constant is sometimes independent of the degree of agitation (stirring rate).

If any of these conditions is not satisfied, chemical reaction kinetics is not rate controlling even if the rate data are successfully fitted to pseudo-second-order model [28]. To test whether the rate of removal of Pb^{2+} and Cu^{2+} ions is controlled by reactions, kinetic experiments were conducted at two different initial metal ion concentrations. From Table 5, it is seen that rate constant k, for removal of Pb^{2+} and Cu^{2+} ions was not constant for different initial metal ion concentrations. This lack of consistency is the proof that even though the results give a good fit to the kinetic model, the rate-limiting step is not chemisorptions.

Kinetic data were further analyzed using intraparticle diffusion model in order to study the steps of diffusion mechanisms. The intraparticle diffusion equation can be written as:

$$q_t = k_{\mathrm{int}} t^{1/2} + C \tag{10}$$

where k_{int} is the intraparticle diffusion rate constant and C is the intercept related to the thickness of the boundary layer. According to Eq. (10), a plot of q_t vs. $t^{1/2}$ should give a straight line if the adsorption mechanism follows intraparticle diffusion process only if the plots show multilinear plots, such plots indicate that two or more steps take place. It is clear from the figure (Fig. 4(b)) that there are two separate zones present. The first linear plot is due to the immediate utilization of ample active sites on the adsorbent surface and the second linear plot attributed to very slow diffusion of the adsorbate from the surface site into the inner pores [29]. Thus, initial adsorption of Pb^{2+} and Cu^{2+} by PWR may be governed by intraparticle transport of surface diffusion and later part controlled by pore diffusion. However, the intercept of the line fails to pass through the origin which may attribute to the difference in the rate of mass transfer in the initial and final stages of adsorption [30].

3.5. Biosorption thermodynamics

The adsorption of metal ions onto PWR was studied at three different temperatures in the range of 30–50˚C. The experimental results showed that adsorption capacity decreased with an increase in solution temperature. The decrease in the rate of adsorption with the increase in temperature may be attributed to weakening of adsorptive forces between actives sites of adsorbent and adsorbate species [31].

Table 3
Comparative studies for maximum sorption uptake of native and PWR

Metals	q_e (mg g^{-1})	Refs.
Pb^{2+}	98.06	[22]
	116.2	This study
Cu^{2+}	6.28	[22]
	5.73	[23]
	39.2	This study

Table 4
R_L values for adsorption of Pb^{2+} and Cu^{2+} ions onto PWR based on Langmuir model

	Separation factor (R_L)	
Initial metal ions concentration (mg L^{-1})	Pb^{2+} ions	Cu^{2+} ions
50	0.99	0.63
100	0.49	0.27
150	0.22	0.16
200	0.13	0.11
250	0.09	0.08
300	0.07	0.06

Table 5
Kinetic parameters of pseudo-first-order, pseudo-second-order and Elovich expressions for removal of Pb^{2+} and Cu^{2+} ions from aqueous solution

		Pb (mg L^{-1})		Cu (mg L^{-1})	
Kinetic model	Parameters	50	100	50	100
Experimental	q_e (mg g^{-1})	33.32	61.31	12.84	20.76
Pseudo-first-order	q_e (mg g^{-1})	6.04	10.65	3.89	5.26
	k_1 (min^{-1})	0.031	0.104	0.0008	0.007
	R^2	0.9023	0.9165	0.6937	0.7423
Pseudo-second-order	q_e (mg g^{-1})	31.25	62.56	13.10	20.13
	k_2 (g mg^{-1} min^{-1})	0.025	0.009	0.118	0.075
	R^2	0.999	0.999	0.999	0.999
Elovich	α	2.1×10^{-27}	3.8×10^{-24}	4.5×10^{-36}	1.7×10^{-32}
	β	3.74	3.25	5.64	4.97
	R^2	0.856	0.885	0.912	0.943

Table 6
Thermodynamic parameters for the biosorption of Pb^{2+} and Cu^{2+} ions onto PWR at different temperatures

Metal	T (K)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
Pb^{2+}	303	−8.489	−1.035	−9.408
	313	−7.104		
	323	−6.418		
Cu^{2+}	303	−1.737	−0.117	−1.860
	313	−1.638		
	323	−1.503		

From these results, thermodynamic parameters including the change in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were used to describe the thermodynamic behavior of biosoprtion of Pb^{2+} and Cu^{2+} ions onto PWR.

Thermodynamic parameters can be evaluated from the following equations:

$$K_D = \frac{q_e}{C_e} \tag{11}$$

Table 7
Competitive sorption of Pb^{2+} and Cu^{2+} ions in binary and multi-metal sorption systems (pH 5, 30 min, 303 K, 50 mg L^{-1})

Sorption system	Sorption capacity, q_e (mg g^{-1})	Sorption system	Sorption capacity, q_e (mg g^{-1})
Pb	33.3	Cu	16.6
Pb–Cu	32.2	Cu–Pb	10.5
Pb–Cd	30.7	Cu–Cd	11.8
Pb–Co	32.9	Cu–Co	15.4
Pb–Ni	32.6	Cu–Ni	14.2
Pb–Zn	32.9	Cu–Zn	16.4
Pb–Cu–Cd–Cu–Ni–Zn	29.6	Cu–Pb–Cd–Co–Ni–Zn	7.1

$$\Delta G^\circ = -RT \ln K_D \tag{12}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{13}$$

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{14}$$

where K_D is the equilibrium constant, q_e is the amount of metal ions adsorbed at the surface of the adsorbent, C_e is the equilibrium concentration in solution (mg L^{-1}), R is the gas constant (8.314 J Mol^{-1} K^{-1}), and T is the temperature (K). The enthalpy (ΔH°) and entropy (ΔS°) of biosorption were estimated from the slope and intercept of the plot ln K_D vs. $1/T$, respectively. The values of the above-said parameters are summarized in Table 6.

The negative values of change in free energy (ΔG°) at different temperature (Table 6) indicate that the biosorption of Pb^{2+} and Cu^{2+} ions onto PWR is thermodynamically feasible and is a spontaneous process. The decrease in ΔG° values with an increase in temperature shows a decrease in feasibility of biosorption at higher temperature. The negative values of ΔH° confirm the exothermic process and the negative ΔS° values suggest a decrease in the randomness of the solid/solution interface during the biosorption.

3.6. Desorption and regeneration studies

Stability is important when same sorbent is used for multiple adsorptions and desorption cycles. In order to investigate the reusability potential and stability of PWR, adsorption–desorption cycle was repeated three times using 0.1 M HCl as desorbing agent. For desorption study, 0.1 g of Pb-loaded PWR (Pb^{2+} ions was preferential due to high loading capacity than Cu^{2+} ions) was contacted with 20 ml of 0.1 M HCl for 30 min and later desorbed acidic solution was subjected to atomic absorption spectrometer to determine the metal concentration. Desorption for the first cycle resulted in 98.1% recovery of Pb^{2+} ions and efficiency remained almost unchanged during three repeated cycles. These observations suggest that PWR can be a better sorbent for removal of heavy metal ions from aqueous solution.

3.7. Effect of co-cations in solution

Wastewater or industrial effluents contain a broad range of different cations as well as other organic and inorganic contaminants that could interfere in the sorption mechanisms including competitive sorption among metal ions. Therefore, a study was executed to evaluate the effect of the presence of co-ions on the sorption process. The results of the study are presented in Table 7. It can be observed from Table 7 that the presence of co-cations has no effect on sorption of Pb^{2+} ions onto PWR. But in the case of Cu^{2+} ions, sorption was been greatly influenced by presence of co-cations such as Pb^{2+} and Cd^{2+} ions in binary and multi-metal ion system. The high competitive preferential uptake of Pb^{2+} ions can be attributed to high electro negativity and smaller ionic radius compared to that of other co-cations. Similarly, the low competitive preference for Cu^{2+} ions in presence of Pb^{2+} and Cu^{2+} ions is due to less electronegativity and larger ionic radius compared to that of Pb^{2+} and Cd^{2+} ions. In general, it is believed that sorption of metal ions is superior for small ionic radius ions than larger ionic radius ions. These results conclude that PWR has high preferential uptake of Pb^{2+} ions in presence of other co-cations in the aqueous solution.

4. Conclusion

A simple acid wash of WR has enhanced the removal efficiency of heavy metals from aqueous solution. The total cation content of WR released during protonation was found to be 2.102 meq g^{-1}. FTIR and

EDX analyses confirm the protonation of WR and involvement of ion exchange mechanism for metal ion uptake. Experimental data tend to fit better with Langmuir isotherm and consistent with pseudo-second-order kinetic model. The loading capacity of PWR toward Cu^{2+} ions was found to increase sixfold compared to native WR. Successive regeneration of PWR for three sorption cycles implies the practical utility of the material in real-time process. The competitive sorption of Pb^{2+} ions in presence of other heavy metal ions suggest that PWR is an efficient sorbent for the removal of Pb^{2+} ions from aqueous solution. These results suggest that WR, a low-cost biosorbent, can be used as a non-hazardous material for removal of heavy metal ions from aqueous solution.

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