Preparation and characterization of green adsorbent from waste glass and its application for the removal of heavy metals from well water

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Abstract. Waste glass disposal causes environmental problems in the cities. To find a suitable green environmental solution for this problem low cost adsorbent in this study was prepared from waste glass. An effective new green adsorbent was synthesized by hydrothermal treatment of waste glass (WG), followed by acidic activation of its surface by HCl (WGP). The prepared adsorbent was characterized by scanning electron microscopy (SEM), X-ray fluorescence (XRF), X-ray diffraction (XRD), and BET surface measurement. The developed adsorbent was used for the removal of heavy metals (Cd, Cu, Fe, Pb and Zn) from well water. Batch experiments were conducted to test the ability of the prepared adsorbent for the removal of Cd, Cu, Fe, Pb and Zn from well water. The experiments of the heavy metals adsorption by adsorbent (WGP) were performed at different metal ion concentrations, solution pH, adsorbent dosage and contact time. The Langmuir and Freundlich adsorption isotherms and kinetic models were used to verify the adsorption performance. The results indicated high removal efficiencies (99-100%) for all the studied heavy metals at pH 7 at constant contact time of 2 h. The data obtained from adsorption isotherms of metal ions at different time fitted well to linear form of the Langmuir sorption equation, and pseudo-second-order kinetic model. Application of the resulted conditions on well water demonstrated that the modified waste glass adsorbent successfully adsorbed heavy metals (Cd, Cu, Fe, Pb and Zn) from well water.

Keywords: glass waste; adsorption; heavy metals; wastewater; pollution

1. Introduction

Pollution with toxic pollutants in the water body and wastewater has increased nowadays as the result of different activities (industrial, agricultural and mining) (Gardea *et al.* 2004).Water pollution by heavy metals is of great concern due to discharge of industrial wastewater to surface water, and to its difficulty of biodegradation (Gupta and Bhattacharyya 2006). Toxic heavy metals are hazardous for living organisms by being accumulated in their bodies and in turn they cause human health risks (Demirbas 2008).

The removal of heavy metals from wastewater, surface water, and ground drinking water has

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attracted considerable attention. In recent years, various heavy metals removal methods have been developed for wastewater treatment which includes flotation, chemical precipitation, reverse osmosis, biosorbtion, solvent extraction, ion exchange, membrane separation, and adsorption (Gupta and Ali 2004, Karapinar and Donat 2009, Inglezakis *et al.* 2007, Liu *et al.* 2010).

Adsorption is one of the widely used techniques for heavy metals removal from wastewater. It has been an economical and efficient treatment option for inorganic pollutants (includes heavy metals) and organic pollutants from polluted waters. Several adsorbents have been used for treatment of polluted water and wastewater (Immamuglu and Tekir 2008, Tangjuank *et al.* 2009, Rashed *et al.* 2013, 2017).

Recycling resources has been widely used today. Waste glasses have been recycled for several purposes. More than 2,500,000 tons of used glass bottles have been produced every year since 1995, while only around 60% of them were reused (Yanagisawa *et al.* 2006). As a result, researches have been carried out to develop low-cost adsorbents.

Recycled porous glass beads have been used to adsorb heavy metal ions from water. The porous glass beads showed good ion exchangeability (Shen and Wang 2012, Sun *et al.* 2008). It has been observed that the modifiers contained in the porous glass, namely Na^+, Ca^{2+}, and Mg^{2+}, could exchange with metal ions with higher electronegativities or hydrogen ions (Shen *et al.* 2012). In addition, ordered silica materials with some specific properties can be used for selective adsorption (Petrella *et al.* 2010).

Ibrahim *et al.* (2012) used recycled waste glass for the adsorption of Cd(II), Cu(II) and Pb(II). Ilkay *et al.* (2013) used glass beads-immobilized calixarenes derivative as a new sorbent in sorption study of removal heavy metal ions. Catalfamo *et al.* (2006) studied glass residue as adsorbent for the removal of heavy metals from wastewater. Nakazawa *et al.* (2006) studied the ability of porous glass material (PGM) to adsorb phosphate. Liying *et al.* (2015) studied the evaluation of lanthanum-doped mesoporous bioactive glass as adsorbents and its photocatalyst for removal of methylene blue from aqueous solution. Simultaneous removal of Cs and Sr using a photosynthetic bacterium, rhodobacter sphaeroides SSI immobilized on porous ceramic made from waste glass was studied by Ken *et al.* (2013). Bioremediation of heavy metal from polluted water using glass-ceramic materials was studied by García *et al.* (2003).

The aim of this study is converting waste glass residue to ecofriendly and green adsorbent, followed by its application for the removal of heavy metals from well drinking water.

2. Materials and methods

2.1 Sample collection

2.1.1 Waste glass sample

Waste glass bottles were collected from the house residue. The sample was washed with tap water, followed by deionized water, crushed and ground to powder with a laboratory agate mortar and pestle to size -63μm. The sample was oven dried at 105°C, and stored for subsequent use. The collected waste glass sample was made of silicate glass. Typically, the resulting glass (WG) composition is about 59.7 wt.% SiO_2, 25.1 wt.% Na_2O, 9.8 wt.% MgO, and 4.9 wt.% CaO.

2.1.2 Well water samples

Well water samples were collected from two different areas from the west and the east of the

River Nile at Qena governorate, upper Egypt, Egypt. One litter of the well water was collected in a clean glass bottle, and stored at -4°C until use.

All reagents used in the experiments were of analytical grade.

2.2 Preparation of waste glass adsorbent (WGP) by hydrothermal treatment

Hydrothermal treatment of waste glass was processed according to the methods shown in Wang *et al.* (2009). A mixture of waste glass powder WG (63μ) (20 g) distilled water (30 mL) were transferred into a Teflon container with 40% volume filled. The container was put into an oven for heating. Reaction was conducted at 180℃ for 2 h. The waste glass adsorbent was separated by filtration and washed several times with deionized water (Wang *et al.* 2009).

2.3 Surface activation of the prepared adsorbent

The obtained waste glass adsorbent (WGP) was treated with HCl to replace the metal ions contained in the shell part of porous glass with hydrogen ions (Shen *et al.* 2013). For this modification, WGP was dipped in 0.5 M HCl and was shaken for 12 h at 160 rpm in a temperature controlled shaker at 333 K. Then the modified WGP was filtered and washed with water until the pH of the washing water became neutral.

2.4 Characterization of the prepared adsorbent

The surface morphologies of the prepared WGP was examined by scanning electron microscopy (SEM, JSM-6460LV, JEOL, Japan), X-ray fluorescence (XRF), X-ray diffraction (XRD), and BET surface measurement. XPF measurements were performed using a Thermo Scientific ESCALAB250 spectrometer (Thermo VG, USA) equipped with an Al-Ka X-ray source (1486.6 eV). The specific surface area and pore diameter of the samples were determined by nitrogen adsorption-desorption experiments at a temperature of 77 K with an automated sorptometer (Quantachrome Autosorb NOVA2200e, USA). The X-ray diffraction (XRD, Brukeraxs D8, Germany) studies were performed using Cu Kα radiation (λ= 0.15405 nm) and a secondary monochromator in the 2θ range from 10 to 70° was used to appreciate the crystalline phase, the phase composition, relative crystallinity and crystallite diameter.

2.5 Batch experiments

The following batch adsorption experiments were carried out to determine the optimum conditions for the adsorption process of the selected heavy metals (Cu^{2+}, Cd^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+}). Batch adsorption experiments included: pH, contact time, adsorbent dose and initial metal concentration.

2.5.1 Effect of pH on metal adsorption

WGP was dipped in 50 ml of 50 mg/l single ion standard solution (Cu^{2+}, Cd^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+}) and was stirred for 30 min by electrical motor (500 rpm). Solution pH was varied at 2, 5, 7 and 9 using pH meter and HNO_3 and NaOH solutions. The solution was filtrated by filter paper (Whatman No 42) and the metal ions in the filtrate were measured by atomic absorption spectroscopy.

Heavy metal removal percentage (R%) was calculated using the following Eq. (1)

$$R = \frac{C_{Asb} - C_{Asa}}{C_{Asb}} \times 100\% \tag{1}$$

C_{Asa}, C_{Asb} are the metal concentration after and before the adsorption through the synthesized absorbent.

2.5.2 Effect of adsorbent dose

Different amounts (0.5, 1 and 1.5g) of WGP adsorbent were stirred with 50 mL of 50 mg/L metal standard solution (Cu^{2+}, Cd^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+}) at pH 7 for 30 min by electrical motor (500 rpm). The mixture was filtrated and the metal ions were measured by atomic absorption spectrophotometer.

2.5.3 Effect of contact time on metal adsorption

1.5 g of WGP adsorbent was stirred with 50 mL of 50 mg/L standard metal solution (Cu^{2+}, Cd^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+}) at pH7 for different contact times (15, 30 and 45 min). The mixture was filtered and the metal ion concentrations were measured by atomic absorption spectrophotometer.

2.5.4 Effect of initial metal concentration

Because the metal adsorption capacity was independent from initial concentration, results with different initial concentrations are comparable. The effect of initial metal ion concentration was investigated with 25, 50 and 100 mg/L metal standard solution (Cu^{2+}, Cd^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+}) at constant contact time of 45 min, and at pH7.
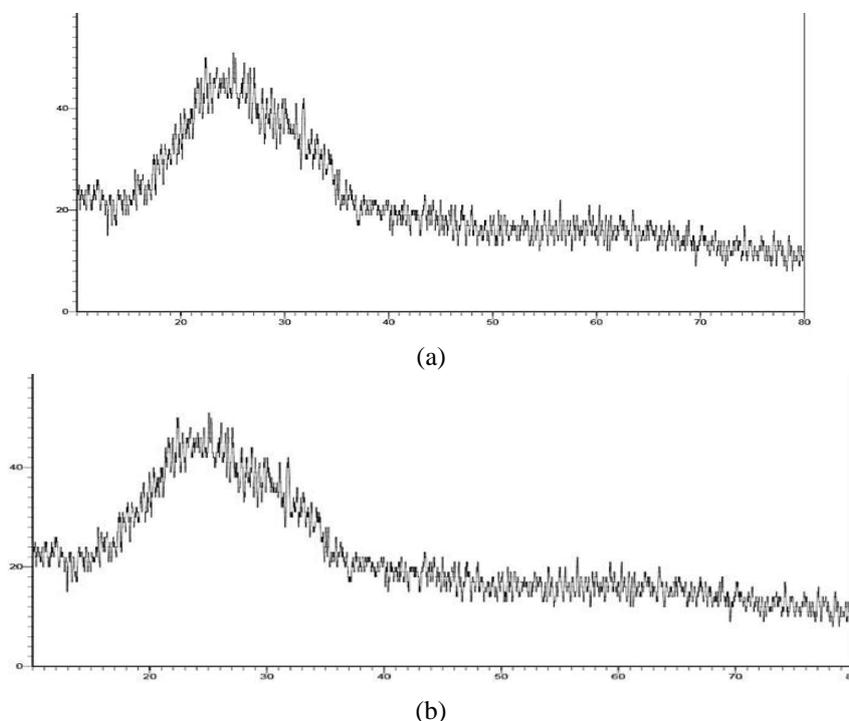

(a)

(b)

Fig. 1 (a) X-ray diffraction (XRD) patterns of the waste glass WG before treatment and (b) X-ray diffraction RD) patterns of hydrothermally treated waste glass WGP after treatment at 180 °C for 12 h
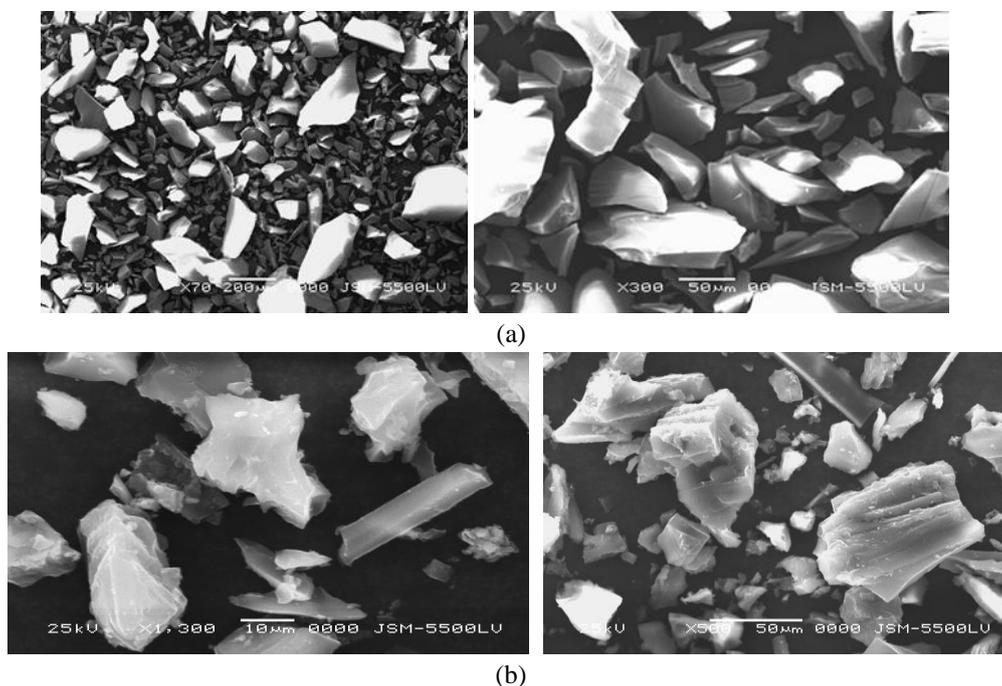
(a)

(b)

Fig. 2 (a) Micrographs of waste glass (WG) before treatment and (b) after hydrothermal treatment (WGP)

3. Results and Discussion

3.1 Characterization of the prepared acid activated adsorbent (WGP)

XRD is an important method to determine the phase of the prepared adsorbent. Fig. 1(a) and 1(b) shows XRD patterns of WG and WGP. No sharp peak is observed, and this indicates that both WG and WGP are in amorphous phase. A broad peak, ranging from $10°$ to $40°$, indicates WG and WGP are amorphous. It was conducted that WGP still remains as amorphous even after hydrothermal treatment.

Fig. 2 shows SEM micrographs of WG and WGP surfaces. WG raw waste glass particles are irregular and remain with sharp edges. After the hydrothermal treatment (WGP), the morphology of the WG surface changed greatly. The surface was exfoliated fragments stuck on the surface with corroded and rough with fine flaky bulges on WGP surface, which might be crystalline calcium silicate and sodium silicate. The change of WGP surface resulted in the variation of specific surface area of WG. Surface area of WG and WGP was checked by BET. The results showed that the specific surface areas for WG and WGP were 1.22 and 13.73 m^2/g, respectively.

3.2 Parameters affecting the adsorption potential of WGP

3.2.1 Effect of pH on metal adsorption

In using WGP adsorbent, pH is an important parameter affecting metal adsorption such as $Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+}$ and Zn^{2+}. The extent of the metal ion uptake from the single metal ion
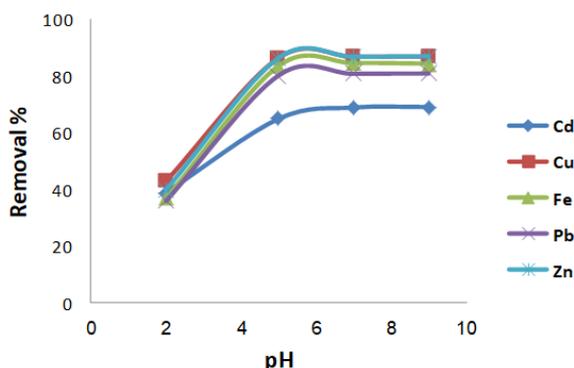
Fig. 3 Removal percentage of Cd^{+2}, Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} by WGP at different pH 2, 5, 7 and 9

solution was examined at different pH values (2, 5, 7 and 9) and the results are shown in Fig. 3 .

The results show that the removal percent of Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+}, and Zn^{2+} ions by WGP adsorbent increased as pH increases from 2 to 9. At pH 2, metal ion uptake was and it was probably due to the competition effect with ion H_3O^+. A small adsorption appears at low pH and it is often attributed to a competition between H+ and metal ion on the same sites (Kouakou *et al.* 2013). Hence the lowest removal efficiency of metal ions is due to the electrostatic repulsion between positively charged H_3O^+ (sorbent surface) and metal ions. At pH 5 metal ion adsorption sharply increased and reached to a plateau value at pH 5 to 7. The increase of pH causes the increase of negative charge density on the surface due to the deprotonation of positively charged groups on the surface (sorbent surface). So, the most suitable pH values for the maximum adsorption of all metal ions were found at pH (5-7), while after that pH values it increased slowly at pH 9 as the result of precipitation.

Oshima *et al.* (2006) investigated the adsorption behavior of the metal ions using mesoporous silicate, MCM-41, and found that the optimum pH for the adsorption was at 6.2. Givianrad (2011) studied the use of activated carbon and silica aerogel for removal of cadmium ions from aqueous solutions, where Cd^{2+} adsorption by adsorbents was performed at pH 6.0. The adsorption of heavy metals Cd(II), Cu(II) and pb(II) by recycled waste glass powder was investigated and found that the adsorption was the maximum at pH 5.6 (Hanan *et al.* 2012). Removal of heavy metals Cd(II) and Fe(II) ions from aqueous solutions by snail shell powder as adsorbent revealed that the optimum adsorption value was at pH 7 (Orodu *et al.* 2014).

The maximum adsorption of Cu^{2+} ion by glass containing the ligand at pH 5.5 was studied by Zaitoun *et al.* (2014). Harry *et al.* (2008) reported that the optimum value of pH is 5 which give the best removal of Cr ions onto silica modified with 2-Mercaptoimidazol. Ibrahim *et al.* (2012) studied used recycled waste glass powder as adsorbent for the removal of Cd(II), Cu(II) and Pb (II) ions. The maximum sorption capacity was observed at pH 6. Darvishi *et al.* (2013) reported that the optimum value of pH 5 was the best for removal of lead(II) ion by entrapped silica nanopowders within calcium alginate.

These previous literature results were agreed with the pH effect observed in this study.

3.2.2 Effect of contact time on metal adsorption

Contact time is an important parameter for the effectiveness of removing pollutants in the treatment process. The adsorption data for the removal of Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} by

Table 1 The adsorption data for the removal of Cd, Cu, Fe, Pb, and Zn on WGP adsorbent at different contact time 15, and 3, 45 min

Tim (min)	Removal, %									
	Cd		Cu		Fe		Pb		Zn	
	Ce	%	Ce	%	Ce	%	Ce	%	Ce	%
15	17.11	66%	9.826	80.3	9.275	81.4	11.60	77	10.25	79.5
30	16.63	67%	9.537	80.9	9.021	81.9	11.01	78	9.172	81.6
45	15.54	69%	8.429	83.1	8.247	83.5	9.63	80	8.507	83
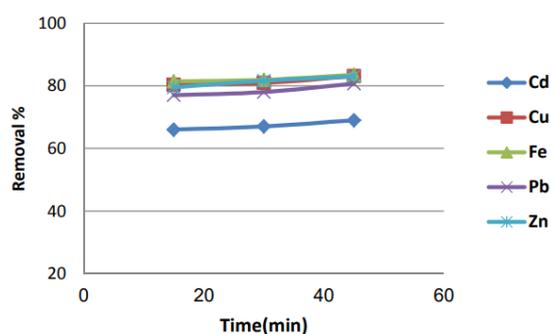
Fig. 4 Removal percentage of Cd^{+2}, Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} by WGP adsorbent at different contact time 15, 30 and 45 min
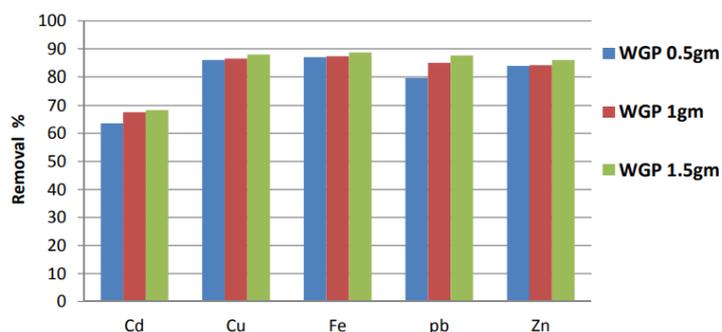
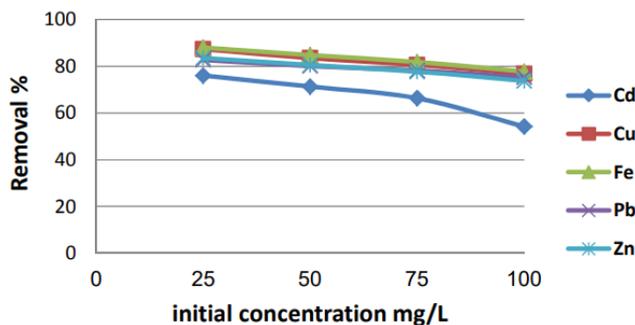Fig. 5 Effect of WGP adsorbent dose on the removal of the studied metals

Fig. 6 Removal percentage of Cd^{+2}, Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} by WGP adsorbent at different initial concentration 25, 50, 75 and 100 mg/L

WGP adsorbent at different contact times (15, 30 and 45 min) under the same experimental conditions (metal initial concentration 50 mg/L, adsorbent dose 1.5 g, and pH 7) were studied and represented in Fig. 4. The results are from Table 1.

The results revealed that the adsorption of Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} increased slowly from 15 min to 30 min, and gave a maximum percentage of metal adsorption at 45 min. So, 45 min as a contact time was enough to achieve maximum adsorption for metal ion on the surface of WGP. This might due to the nature of the sorbent and its available sorption sites that affect the time needed to reach equilibrium (Bhattacharya *et al.* 2008).

Ibrahim *et al.* (2012) reported that 60 min contact time was enough for maximum adsorption of Cd(II), Cu(II) and Pb(II) using recycled waste glass as adsorbent. The removal of Cu (II) increases with time and attains saturation in 60 to 120 min by using Zeolite NaX as adsorbent (Pandey *et al.* 2009). The removal of Cu^{2+} increases rapidly until it reached an equilibrium state after 45 min by using bentonite treated with ammonium chloride (Boukerroui *et al.* 2012). Karthikeyan and Sivaillango (2008) studied the effect of time on the adsorption of metals iron(III), copper(II) and cobalt(II) ions using activated carbon prepared from recinius communis and found that the adsorption increases with increasing contact time.

3.2.3 Effect of adsorbent dose on metal adsorption

The adsorption data for the removal of Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} by WGP adsorbent at different dose (0.5, 1 and 1.5 g) under the same experimental conditions (initial concentration; 50 mg/L; at pH 7) were studied and represented in Fig. 5. The percentage removal of Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} after treatment at WGP dose (0.5, 1, 1.5 g) was shown in Fig (1). It was observed that WGP dose of 1.5 g higher removal percentage was observed for Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{+} (68%, 88%, 88.7%, 87.6%, 86%, respectively). The amount adsorbent dose for the removal of Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} follows in the order of WGP 1.5 gm>WGP 1 gm>WGP 0.5 gm. Thus WGP 1.5g was selected for the adsorption experiments in which it had higher removal of Cd^{2+}, Cu^{2+}, Fe^{2+}, pb^{2+} and Zn^{2+} than with the other adsorbent doses. An increased metals ions removal was noted with increase in the amount of adsorbent; because of the greater availability of the adsorbent surface area. High adsorbent dosage enhances the removal of metal ions until it reaches the optimum level.

Givianrad *et al.* (2011) used silica aerogel and activated carbon for removal of cadmium ion from polluted water, and found that the removal percentage of cadmium increases with increasing the amount of adsorbent from 0.02-0.10 g and fixed at greater amount than 0.10 g. Meena *et al.* (2010) reported that the removal percentage of Cd, Pb, Hg, Mn, Ni and Zn ions increases rapidly with increase in the amount of chemically (Na_2S) treated granular activated carbon. Moyo *et al.* (2013) studied that the effect of biomass dosage on the biosorption of Pb(II) ions, and found that the removal increases with increasing in amount of dose from 0.1 to 1.2 g, respectively.

3.2.4 Effect of initial concentration on metal adsorption

Fig. 6 represents the effect of initial metal concentrations (Fe, Cu, Zn, Pb and Cd) on its adsorption. It was revealed that at low heavy metal concentration, the removal percentage was high and gradually decreased with the increase of heavy metal concentration. At 25 ppm of heavy metals, the removal percentages were 88, 87.3, 83.5, 82.7 and 76% for Fe, Cu, Zn, Pb and Cd, respectively. At 25 ppm, iron was the metal with the highest removal percentage at all concentrations, followed by Cu, Zn, Pb then Cd, which had the lowest removal percentages. On the other hand, the highest heavy metal concentration (100 ppm) led to the lowest removal
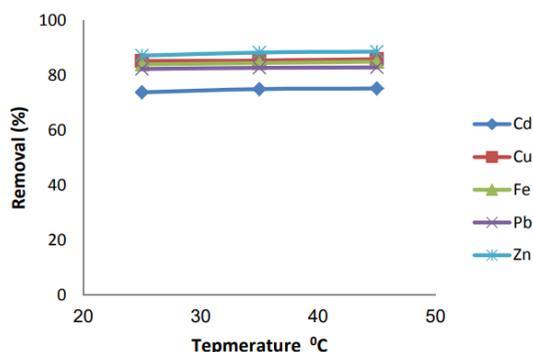
Fig. 7 Removal percentage of Cd^{+2}, Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} by WGP adsorbent at different Temperature 25, 35 and 45 ^0C

percentage of the studied heavy metals (54.2, 73.7, 75.3, 76.8 and 77.7% for Cd, Zn, Pb, Cu and Fe, respectively). The removal percentage for all the tested metals was the highest at 25 ppm and decreased with the increase in metal concentration. El-Ashtoukhy *et al.* (2008) explained that at low concentrations, metals are adsorbed by specific sites, while with increasing metal concentrations the specific sites are saturated and the exchange sites are filled leading to less adsorption efficiency.

Salim and Munekage (2009) reported that the maximum adsorption of Pb^{2+} by silica ceramic adsorbent was at 50 mg/L.

3.2.5 Effect of temperature on metal adsorption

The effect of solution temperature on the adsorption efficiency of the studied heavy metals is presented in Fig. 7. The results show that with increasing solution temperature from 25℃ , the adsorption percentage of Cd^{2+}, $Cu^{2+,}$ Fe^{2+}, Pb^{2+} and Zn^{2+} ions increased until it reached high adsoption at 45℃ (75.2%, 85.9%, 85%, 82.9% and 88.6% for Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} ions, respectively). Therefore, it is revealed that the adsorption process is endothermic.

The increase of heavy metal adsorption with temperature may be attributed to increase in the number of active sites available in the adsorbent surface, or the desolvation of the adsorbing species and the decrease in the thickness of the boundary layer surrounding the adsorbent with temperature, so that the mass transfer resistance of adsorbate in the boundary layer decreases (Meena *et al.* 2005). Effect of temperature on removal of Pb ion using silica ceramic was studied by Salim and Munekage (2009), where results revealed that Pb uptake increases when temperature of the solution increases from 20 to 30℃, and the adsorption is highest at 40℃.

3.3 Adsorption equilibrium study of Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^2 on WGP

The adsorption isotherms are fundamentally important in the design of adsorption system. The adsorption isotherms, usually the ratio between the quantity adsorbed and the quantity remaining in the solution at fixed temperature on the equilibrium (Han *et al.* 2005). The most commonly used adsorption models are Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms.

3.3.1 Langmuir isotherm

The Langmuir isotherm represented by the following equation

$$C_e/q_e = C_e/Q_0 + 1/Q_0\, b \qquad (2)$$

where C_e is the equilibrium concentration (mgL^{-1}), q_e is the amount of adsorbed at equilibrium (mg/g), b is the sorption constant (mgL^{-1}) (at a given temperature) related to energy of sorption, Q_0 is the maximum sorption capacity (mgg^{-1}). The linear plots of C_e/q_e versus C_e suggest the applicability of the Langmuir isotherms. Values of Q_0 and b were determined from slope and intercepts of the plots.

Table 2 Langmuir and Freundlish parameter for the adsorption of Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} by WGP adsorbent

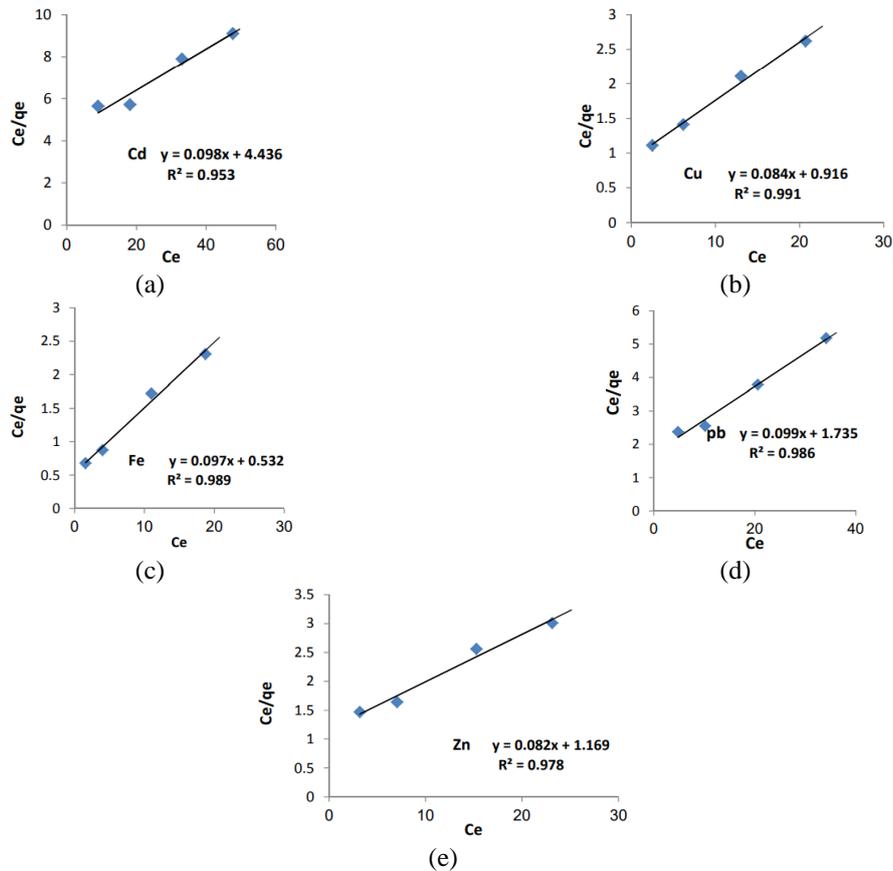| Solute	Langmuir Constant			Freundlich Constant		
	Q_o	b	R^2	1/n	K_f	R^2
Cd^{2+}	10.204	0.022	0.953	0.69	2.686	0.970
Cu^{2+}	11.904	0.091	0.991	0.58	1.381	0.987
Fe^{2+}	10.309	0.182	0.989	0.48	2.028	0.967
Pb^{2+}	10.101	0.057	0.986	0.59	1.143	0.956
Zn^{2+}	12.195	0.070	0.978	0.61	1.137	0.976

Fig. 8 Langmuir isotherm plots for the adsorption of heavy metals by WGP adsorbent
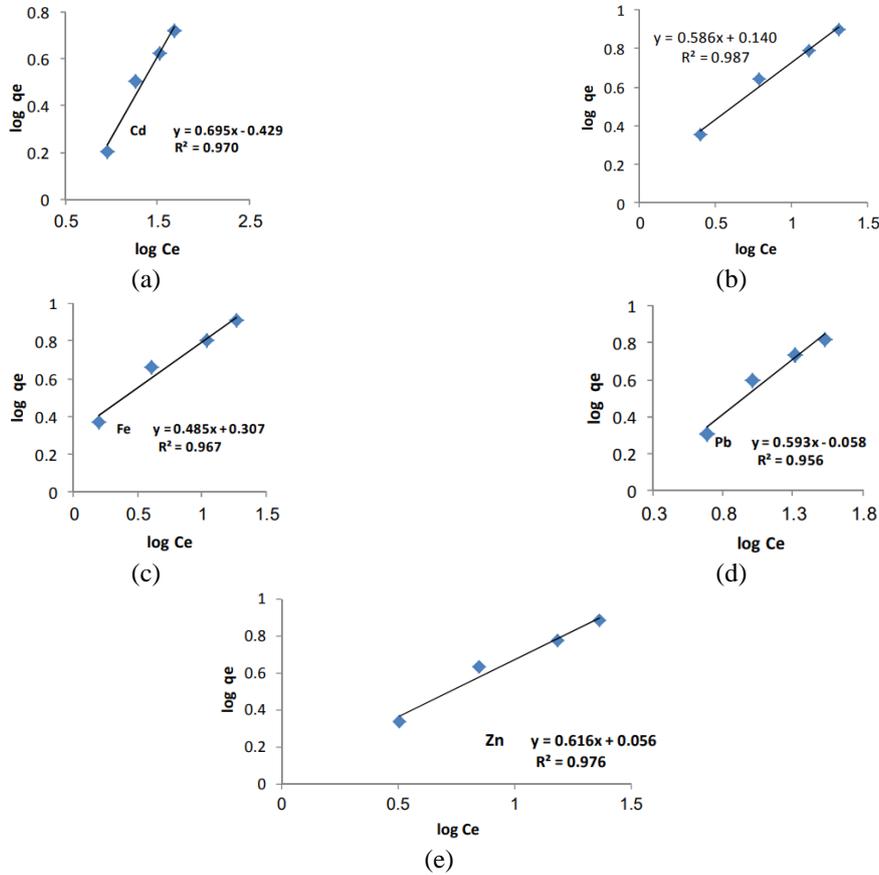
Fig. 9 Freundlich Isotherm plots for the adsorption of metals by WGP adsorbent

The resulting data are represented in the Fig. 8 and are listed in Table 2. The maximum adsorption for Cd^{2+} on WGP was 10.204 mg/g, for Cu^{2+} 11.904 mg/g, for Fe^{2+} 10.309 mg/g, for Pb^{2+} 10.101 mg/g, and for Zn^{2+} 12.195 mg/g. These values indicated that the order of metal ions according to their affinity to adsorption on WGP were $Zn^{2+}>Cu2^{2+}>Fe^{2+}>Cd^{2+}>Pb^{2+}$. The correlation coefficient for the adsorption of Cd^{2+} onto WGP was 0.953, Cu^{2+} 0.991, Fe^{2+} 0.989, Pb^{2+} 0.986, and Zn^{2+} 0.978. The fit to the linear form models was examined by calculation of the linearity coefficient (R^2). Regression values (R^2) were presented in the Table 2, and indicates that the adsorption data for Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} fits better the Langmuir model than the Freundlich model for all adsorbents.

3.3.2 Freundlich isotherm

Freundlih model can be applied for non-ideal sorption on heterogeneous surfaces and multilayer sorption. The Freundlih model linear form is

$$q_e = K_f \cdot C_e^{1/n} \tag{3}$$

Eq.(3) can also be expressed in the linearized logarithmic form

$$Log \ q_e = logK_f + 1/n \ logC_e \tag{4}$$

where q_e is the amount of metal ions adsorbed per unit weight (mgg^{-1} adsorbent), C_e is the equilibrium concentration (mgL^{-1}) of adsorbate, and K_f and n are Freundlich constants. When log q_e is plotted against log C_e a straight line with slope $1/n$ and intercept log K_f is obtained. The intercept of line log K_f is roughly an indicator of the adsorption capacity, whether the slope, $1/n$ is an indicator of adsorption intensity. The Freundlich parameters for the adsorption of metal ions are given Fig. 9 and listed in Table 2.

From Freundlich constant, the values of $1/n$ for adsorption on WGP adsorbent were 0.69, 0.58, 0.48, 0.59 and 0.61 for Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+}, respectively. The previous values of $1/n$ less than 1 indicate that the metal ions are favorably adsorbed by WGP.

3.3.3 Dubinin-Radushkevich isotherm

The Dubinin-Radushkevich (D-R) isotherm model was applied to the data in order to deduce the heterogeneity of the surface energies of adsorption and the characteristic porosity of the adsorbent. The linear form of the D-R isotherm is given in Eq. (5).

$$Ln\ qe = \ln qm - B\mathcal{E}^2 \tag{5}$$

where B a constant related to the adsorption energy (mol^2/kJ^2), qm is a constant that indicates the sorption degree characterizing the sorbent (mg/g), $\mathcal{E}$ is the polany potential, which can be obtained by the following equation

$$\mathcal{E} = RT \ln (1+1/Ce) \tag{6}$$

where R is the ideal gas constant (R=8.314 J/mol K) and T is absolute temperature (K). By plotting ln qe vs $\mathcal{E}^2$, it is possible to determine the value of B from the slope and the value of qm from the intercept, which is ln qm. The mean free energy E (KJ/mol) of sorption can be estimated by using B values as expressed in the following equation

$$E = 1/ (2B)^{1/2} \tag{7}$$

If the value of E lies between 8 and 16 kJ/mol, the sorption process is a chemisorptions one, while values of below 8kJ/mol indicates a physical adsorption process (Sivakumar and Palanisamy 2009).

The Dubinin-Radushkevich (D-R) parameters for the adsorption of metal ions are given in Fig.10 and listed in Table 3. From Dubinin constant, the values of E for adsorption on WGP adsorbent were 0.158, 0.5, 0.79, 0.316 and 0.408 for Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+}, respectively). The values of E below 8kJ/mol indicate a physical adsorption process between WGP adsorbents and Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} ions (adsorbate), respectively.

Table 3 Dubinin-Radushkevich (D-R) and Temkin parameters for the adsorption of Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} by WGP adsorbent

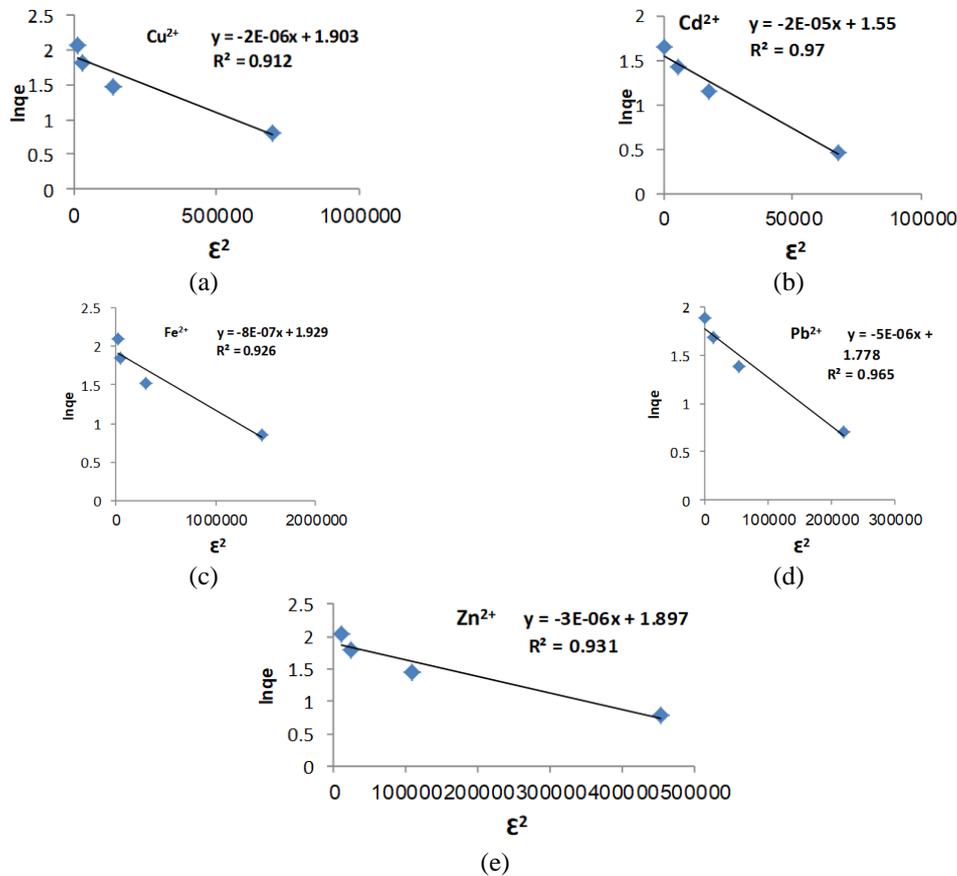| Solute	Dobinin-Radushkevich constant				Temkin constant		
	$B(mol^2/kJ^2)$	lnqm(mg/g)	E(KJ/mol)	R^2	(L/mg) k_t	b_t (J/mol)	R^2
Cd^{2+}	2×10^{-5}	4.711	0.158	0.97	0.238	1171.982	0.993
Cu^{2+}	2×10^{-6}	6.706	0.5	0.912	0.901	945.638	0.991
Fe^{2+}	8×10^{-7}	6.882	0.790	0.926	1.7923	1099.188	0.990
Pb^{2+}	5×10^{-6}	5.918	0.316	0.965	0.518	1073.471	0.997
Zn^{2+}	3×10^{-6}	6.665	0.408	0.931	0.694	925.849	0.998

Fig. 10 Dobinin-Radushkevich Isothermal plots for the adsorption of Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} by WGP adsorbent

3.3.4 The Temkin isotherm

Temkin isotherm model contains a factor that describes adsorbing species-adsorbate interactions (Temkinand 1940). This model assumes the following:

(i) The heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate-adsorbent interactions, and (ii) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm has commonly been applied in the following form Eq. (8)

$$q_e = RT/b_t \ln (K_t \, C_e)$$
$$B = RT/b_t \tag{8}$$

Eq. (2) can be linearized as

$$q_e = B \ln K_t + B \ln Ce \tag{9}$$

where constant $BT = RT/bT$, which is related to the adsorption heat, R is the gas constant (8.314

J/mol K), T (K) is absolute temperature in Kelvin, bT (J/mol) is the Temkin isotherm constant, which is the variation of adsorption energy and K_t (L/mg) is the equilibrium binding constant corresponding to the maximum binding energy. Both B_t and K_t can be calculated from the slope and the intercept of the linear plot based on q_e versus $\ln C_e$, respectively. The Temkin parameters for the adsorption of metal ions are given Fig. 11 and listed in Table 3. From Temkin constant, the value of K_t for the adsorption on WGP were 0.238, 0.901, 1.792, 0.518 and 0.694 for $Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+}$ and Zn^{2+} respectively. The value of B_t for the adsorption on WGP were 2.114, 2.62, 2.524, 2.308 and 2.676 for $Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+}$ and Zn^{2+}, respectively. Low values of Bt and Kt indicate a weak interaction between adsorbent and adsorbate supporting a mechanism of ion exchange. The parameters and the regression coefficients of Temkin model are presented in Table 3. Higher values of the coefficient of correlation show a good linearity regardless of the maximum capacity of adsorption used to calculate the coverage area. The value of b_t, which is the variation of the adsorption energy (J/mol) is positive for all compounds studied. This indicates that the reaction of the adsorption is exothermic.

3.4 Kinetic models

Kinetic models are helpful to understand the mechanisms of metal adsorption, and so it
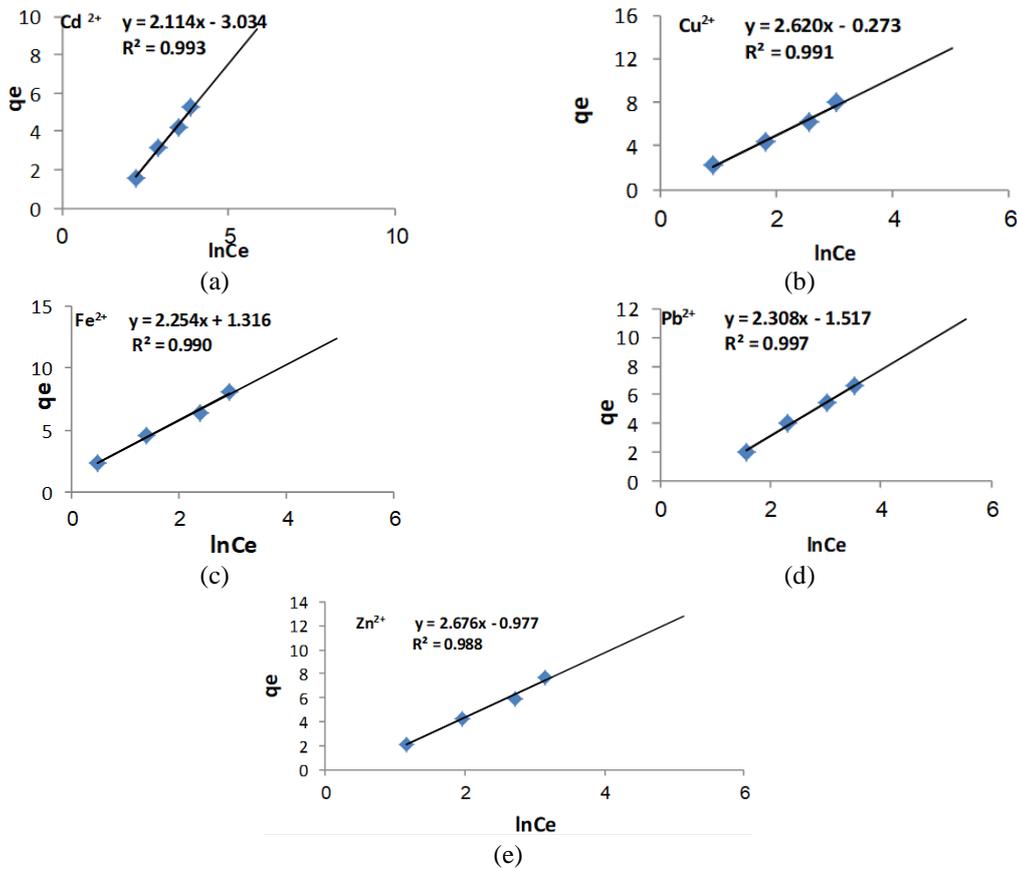

Fig. 11 Temkin isotherm plots for the adsorption of $Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+}$ and Zn^{2+} by WGP adsorbent

evaluates performance of the adsorbents for metal removal. The kinetics of $Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+}$ and Zn^{2+} ions adsorption onto WGP adsorbent is required for selecting optimum operating conditions that are helpful for the prediction of adsorption rate. Lagergren pseudo-first-order and pseudo-second-order kinetic models were used for the adsorption of $Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+}$ and Zn^{2+} ions adsorption onto WGP adsorbent.

3.4.1 The pseudo-first-order model

The Lagergren's rate equation (Kumara *et al.* 2011) is one of the most widely used rate equation to describe the adsorption of an adsorbate from the liquid phase. The linear form of pseudo-first-order equation is given as

$$\log (qe - qt) = \log qe – (kf / 2.303) .t \tag{10}$$

where qe (mg/gm) and qt (mg/gm) are the amount adsorbed on adsorbent at equilibrium and at time t, respectively; kf (min^{-1}) is the rate constant of pseudo-first-order kinetic model and t (min) is the agitation time. The slopes and intercepts of plots of log(qe-qt) versus t were used to determine the pseudo first-order constant k_f and equilibrium adsorption density qe.

3.4.2 The pseudo-second-order rate equation

The pseudo-second order kinetic model is based on the assumption that chemisorption is the rate determining step and is given as (Kumara *et al.* 2011). Pseudo-second order is expressed by the following equation

$$t /qt = 1 / (ks . q_e^2) + t / qe \tag{11}$$

where the pseudo-second-order kinetic constant represented as ks $(gm\ mg^{-1}\ min^{-1})$, qe (mg/gm) and qt (mg/gm) are the amount adsorbed on the sorbents at equilibrium and at time t, respectively adsorption rate, h (mg/g.min) at t→0 is defined as h= $K_s\ q_e^2$.

The plot t/qt versus t should give a straight line if pseudo-second-order kinetics is applicable and qe, k and h can be determined from the slope and intercept of the plot, respectively. The pseudo-first-order and pseudo-second-order rate constants determined is presented in Table 4 along with the corresponding correlation coefficients.

From pseudo-first-order rate constant, the values of q_e for adsorption on WGP adsorbent were 0.2495, 0.151, 0.1455, 0.5035 and 0.4187 mg/g for $Cd^{2+}, Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+}$ and Zn^{2+}, respectively.

The previous values of q_e were decreasing with increasing initial $Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+}$ and Zn^{2+} concentrations. This indicated that the values of qe from the pseudo first-order kinetic model did not give reasonable values and they did not agree very well with the experimental data. This suggested that the adsorption of $Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+}$ and Zn^{2+} ions by WGP were not a pseudo first-order-reaction. As shown in Table 4, first-order linear correlation coefficients are best between 0.901 and 0.999. In contrast, second-order linear correlation coefficients are best because they are equal to 1 for most heavy metals and are increased by increasing concentrations of Cd^{2+}, $Cu^{2+}, Fe^{2+}, Pb^{2+}$ and Zn^{2+} ions.

From pseudo-second-order rate constant, the values of q_e for adsorption of $Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+}$ and Zn^{2+} on WGP adsorbent were 2.985, 4.386, 0.292, 3.968, 4.31, and 5.917 mg/g , respectively. The previous values of q_e are increased with increase in initial Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} concentrations due to large number of these metal ions are adsorbed at the available adsorption sites. This indicated that the values of qe from the pseudo-second-order kinetic model

Table 4 Parameters of the kinetic models (pseudo first-order and pseudo second-order for the adsorption of Cd, Cu, Fe, Pb and Zn onto WGP adsorbent

Solute	Peudo first-order			Pseudo second-order			
	R^2	q_e(mg/g)	K_f	R^2	h (mg g^{-1}min^{-1})	q_e(mg/g)	K_s g mg^{-1}min^{-1}
Cd	0.999	0.2495	0.0023	1	16.129	2.985	1.811
Cu	0.902	0.151	0.007	1	9.901	4.386	0.514
Fe	0.979	0.1455	0.023	0.992	1.251	0.292	14.69
Pb	0.993	0.5035	0.0299	1	3.134	3.968	0.199
Zn	0.980	0.4187	0.0414	1	4.975	4.31	0.267

Table 5 Removal percent of metal ions (Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+}) before after treatment of real well drinking water sample (Al-Ka'aimat well west of Abu Tesht)

	Removal percent %									
	Cd^{2+}		Cu^{2+}		Fe^{2+}		Pb^{2+}		Zn^{2+}	
	C	%	C	%	C	%	C	%	C	%
Before treatment	5.120		5.072		5.228		5.172		5.103	
After reatment	1.351	73.6	0.541	89.3	0.638	87.8	0.827	84	0.551	89.2

Table 6 m Removal percent of metal ions (Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} after treatment of real well drinking water sample (Al-Maharza well east of Abu Tesht) with WGP adsorbent

	Removal percent %									
	Cd^2		Cu^{2+}		Fe^{2+}		Pb^{2+}		Zn^{2+}	
	C	%	C	%	C	%	C	%	C	%
Before treatment	3.005		3.102		3.358		3.150		3.107	
After treatment	0.814	72.9	0.405	86.9	0.457	86.4	0.524	83.3	0.382	87.7

gave reasonable values and they agree very well with the experimental data. As shown in Table 4, the correlation coefficients for the second order rate equation, for all the metals, are greater than 0.992 or equal to 1(R^2 values close or equal to 1). These values are substantially higher than that for the first-order rate equation. These observations indicate that the adsorption system studied belongs to the second order kinetic model.

3.5 Application of metal ion adsorption from real well drinking water samples

The real well drinking water samples were obtained from two different locations, from Abu Tesht (Al-Ka'aimat well west of Abu Tesht and the well of Marharza east of Abu Tesht). Adsorbent sample WGP (1.5 gm) was used for adsorption of Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} ions at optimum pH7, contact time 45 min and temperature of 25 °C. The obtained result is summarized in Tables 5 and 6. The data given in Tables show that the removal percent of metal ions Cd^{2+},

Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} with WGP adsorbent were removed well with WGP adsorbent. So, the prepared WGP adsorbent was effective for higher removal efficiency of heavy metals from well drinking water.

4. Conclusions

Eco-freindlly adsorbent was successfully prepared from waste glass by hydrothermal treatment followed by acidic activation of its surface by HCl. The prepared adsorbent was characterized by SEM, XRF, XRD, and BET surface measurement. The developed adsorbent was successfully applied for the removal of heavy metals (Cd, Cu, Fe, Pb and Zn) from well water at the optimum adsorption conditions of pH7, contact time 45 min, adsorbent dose 1.5 g and temperature 25℃. Adsorption isotherms (Langmuir and Freundlich) as well as kinetic adsorption models (pseudo first-order and pseudo second-order) explained the adsorption phenomena well. The adsorption of the studied heavy metals onto the prepared adsorbents fitted well with Langmuir and pseudo second-order models.

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