

Preparation of low-cost adsorbent from waste glass for the removal of heavy metals from polluted water.

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Abstract

Water pollution with heavy metals has become one of the most environmental problems nowadays. 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, followed by acidic activation of its surface by HCl. The prepared adsorbent was characterized by SEM, XRF, XRD, and BET surface measurement. Batch experiments were conducted to test the optimum conditions of the prepared adsorbent for the removal of Cd, Cu, Fe, Pb and Zn from their solutions. The experiments of the heavy metals adsorption by the developed adsorbent were performed at different metal ion concentrations, solution pH, adsorbent dosage and contact time. 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 and a constant contact time 2 h. The data obtained from adsorption isotherms of the metal ions at different times 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 its.

Keywords: Glass waste, adsorption, heavy metals, waste water, pollution

Accepted on November 12, 2018

Introduction

Pollution with toxic pollutants in the water body and wastewater has been increased nowadays as the result of different activities (industrial, agricultural and mining) [1]. Water pollution by heavy metals is of great concern due to the discharge of industrial wastewater to water surface, and to its difficulty of biodegradability [2]. Toxic heavy metals are hazardous for living organisms, in which they have accumulated and cannot be degraded, and so they represent a risk for human beings [3].

The removal of heavy metals from wastewater, surface water, and ground drinking water has attracted considerable attention. In recent years, different heavy metals removal methods (including flotation, chemical precipitation, reverse osmosis, biosorption, solvent extraction, ion exchange, membrane separation, and adsorption) have been developed for wastewater treatment [4-7].

Adsorption is one of the widely used techniques for heavy metals removal from wastewater. It has been an economic and efficient treatment for inorganic pollutants (includes heavy metals), and organic pollutants from polluted waters. Several adsorbents have been used for treatment of polluted water and wastewater [8-11].

Material recycling has been widely used today. Glass waste as one of these types of materials was 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 the total amount of glass bottles used was reused [12].

Research studies have been carried out to develop low-cost adsorbents. Used recycled porous glass bead was used to adsorb heavy metal ions from water. The porous glass beads show good ion exchangeability [13-14]. Modifiers contained in the porous glass, namely Na⁺, Ca²⁺, and Mg²⁺ could exchange with metal ions with higher electro-negativities or hydrogen ions as proven [13]. Some properties make ordering silica materials attractive for a wide range of applications such as selective adsorption [15].

Ibrahim et al. [16] used recycled waste glass for the adsorption of Cd (II), Cu (II) and Pb (II) from polluted solution. Ilkay et al. [17] used glass beads-immobilized calixarenes derivative as a new sorbent in sorption and removal of heavy metal ions from their solutions. Catalfamo et al. [18] studied the uses of glass residue as adsorbent for the removal of heavy metals from wastewater. Ryoji et al. [19] studied the ability of porous glass material (PGM) to adsorb phosphate. Liying et al. [20] studied the evaluation of doped mesoporous bioactive glass as adsorbent and its photocatalyst for removal of methylene blue from aqueous solution. Heavy metal bioremediation from polluted water using glass-ceramic materials was studied by Garcia et al. [21].

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

Materials and Methods

Sample collection

Waste glass samples: Waste glass bottles were collected from the house residues. The bottles were washed with tap water, followed by deionized water, crushed and ground to powder with a laboratory agate mortar and pestle to size -63 μm . The sample was oven dried at 105°C, and stored for subsequent use. The collected waste glass sample was made of silicate glass which is a type of glass with the main glass-forming constituent's silica. Typically, the resulting glass (WG) composition is about 59.7 wt. % SiO₂, 25.1 wt. % Na₂O, 9.8 wt. % MgO, and 4.9 wt. % CaO.

Well water samples: Well water samples were collected from two different areas from the west and east the River Nile sides at Qena governorate, Upper Egypt, Egypt. One liter of the well water was collected in a clean glass bottle, filtered and stored at -4°C until use. All reagents used in the experiments were of analytical grade.

Preparation of waste glass adsorbent (WGP) by hydrothermal treatment

Hydrothermal treatment of waste glass was processed according to Wange et al. [22], in which the mixture of the waste glass powder WG (63 μ) (20 g) and the distilled water (30 mL) was transferred into a Teflon container with 40% volume filling in the autoclave. The autoclave was put into an oven for heating and hydrothermal reaction was conducted at 180°C for 2 h. The waste glass adsorbent was separated by filtration and washed several times with deionized water [22].

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 [13]. For this modification, the obtained adsorbent (WGP) was treated with 500 mL of 0.5 M HCl acid. The mixture was shaken for 12 h at 160 rpm in a temperature controlled shaker at K. The modified WGP was separated from the solution through filtration and washed with deionized water until the washing water pH becomes neutral.

Characterization of the prepared adsorbent

The surface morphologies of the prepared activated waste glass adsorbent (WGP) were examined by SEM (SEM, JSM-6460LV, JEOL, Japan), scanning electron microscopy, 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) using Cu K α radiation ($\lambda = 0.15405$ 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.

Batch experiments

The following batch adsorption experiments were carried out to determine the optimum conditions for the adsorption process of the selected heavy metals (Cu²⁺, Cd²⁺, Fe²⁺, Pb²⁺ and Zn²⁺). Batch adsorption experiments included: pH, contact time, adsorbent dose and initial metal concentration.

Effect of pH on metal adsorption: The synthesized adsorbent (WGP) was stirred with 50ml of 50 mg/l single ion standard solution (Cu²⁺, Cd²⁺, Fe²⁺, Pb²⁺ and Zn²⁺) for 30 min by electrical motor (500 rpm). Solution pH was varied at 2, 5, 7 and 9 and adjusted using a pH meter and HNO₃ and NaOH solution. The solution was filtrated by Whatman filter paper 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 Equation 1:

$$R = \frac{C_{Asb} - C_{Asa}}{C_{Asb}} \times 100 \quad (1)$$

Effect of adsorbent dose: Different amounts (0.5, 1 and 1.5 g) of WGP adsorbent were stirred with 50 mL of 50 mg/L metal standard solution (Cu²⁺, Cd²⁺, Fe²⁺, Pb²⁺ and Zn²⁺) at pH 7 for 30 min by electrical motor (500 rpm). The mixture was filtered off and the metal ions were measured by atomic absorption spectrophotometer.

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 (Cu²⁺, Cd²⁺, Fe²⁺, Pb²⁺ and Zn²⁺) at pH 7 for different contact times (15, 30 and 45 min). The mixture was filtered off and the metal ions were measured by atomic absorption spectrophotometer.

Effect of initial metal concentration: Because the metal adsorption capacity was initial concentration independent, so results with different initial concentrations are comparable. The effect of initial metal ion concentration was conducted with 25, 50 and 100 mg/L metal standard solution (Cu²⁺, Cd²⁺, Fe²⁺, Pb²⁺ and Zn²⁺) at constant contact time 45 min, and pH 7.

Effect of solution temperature on metal adsorption: The effect of solution temperature on metal adsorption was investigated at constant contact time 45 min, and pH7. The solution was filtrated by Whattman filter paper No 42 and the metal ions in the filtrate were measured by atomic absorption spectroscopy.

Results and Discussion

Characterization of the prepared acid activated adsorbent (WGP)

XRD is an important method to determine the phase of the prepared adsorbent. Figure 1 shows XRD patterns of the waste glass powder (WG) and the prepared adsorbent (WGP). There is no sharp peak 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 amorphous property. After hydrothermal treatment, the adsorbent WGP still mainly consisted of amorphous materials Figure 1a and 1b.

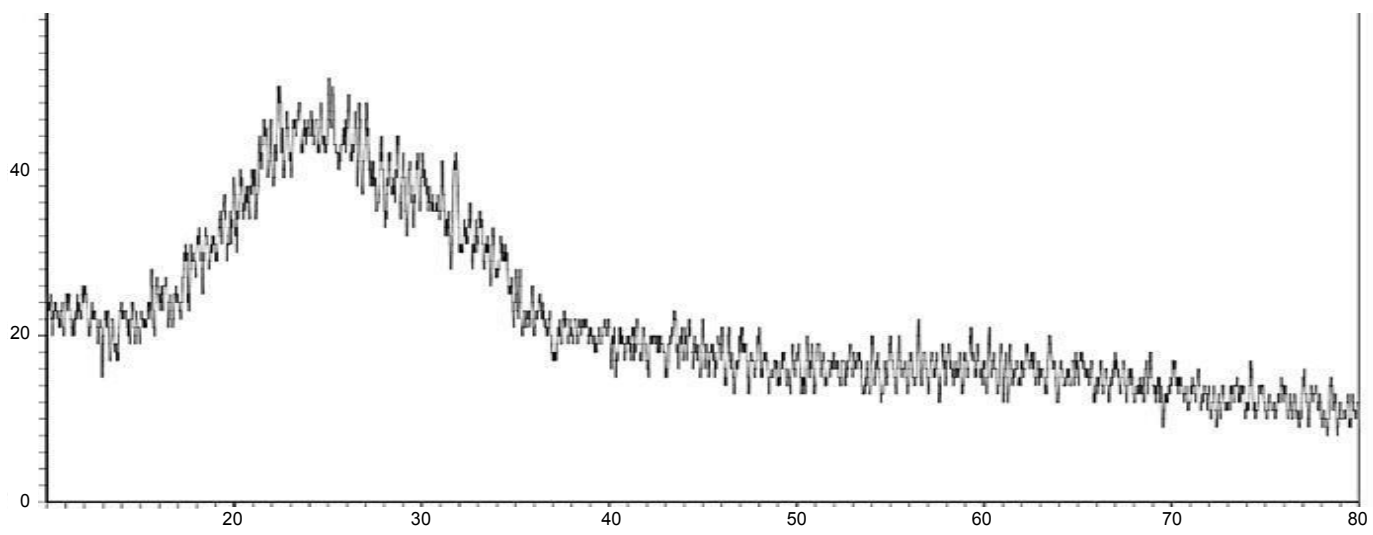


Figure 1A. X-ray diffraction (XRD) patterns of the waste glass WG before treatment.

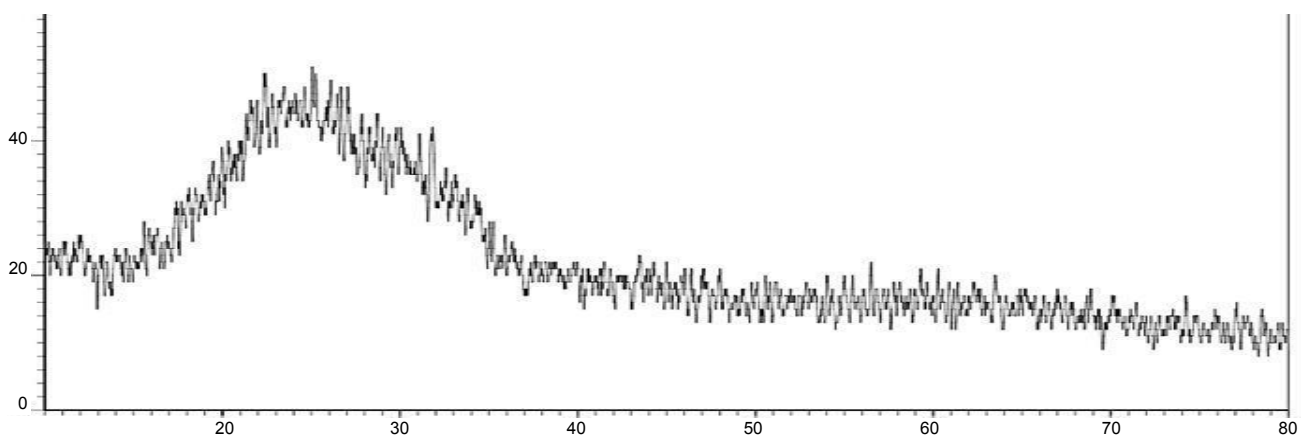


Figure 1B. X-ray diffraction (XRD) patterns of hydrothermally treated waste glass WGP after treatment at 180°C for 12 h.

Figure 2 shows SEM micrographs of WG and WGP surfaces. It is observed that WG raw waste glass particles is irregular and smooth surface. After the hydrothermal treatment (WGP), the morphology of the WG surface was changed greatly and 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 were checked by BET measurement. The results showed that the specific surface areas for WG and WGP were 1.22 m²/g and 13.73 m²/g respectively.

Data from X-ray fluorescence (XRF) of WG and WGP showed that the elemental composition in WG were Si (55.93%), Mg (1.11%), Al (0.521%), Ca (36.254%) and Fe (0.62%), while in WGP it were Si (55.76%), Mg (1.31%), Al (0.478%), Ca (37.79%) and Fe (0.63%). This indicates that there was no change in the elemental composition after the hydrothermal treatment of WG Figure 2.

Parameters affecting the adsorption potential of WGP

Effect of pH on metal adsorption: The effect of pH on the metal uptake (Cd²⁺, Cu²⁺, Fe²⁺, Pb²⁺ and Zn²⁺) using WGP adsorbent is very important parameter. The concentration of

the metal ion uptake from the single metal ion solution was examined for different pH values (2, 5, 7 and 9) and represented in Figure 3.

The results show that the removal percentage of Cd²⁺, Cu²⁺, Fe²⁺, Pb²⁺ and Zn²⁺ ions by WGP adsorbent increased with the increase of pH from 2 to 9. At pH 2, low uptake of metal ions was noted; this is probably due to the competition effect with H₃O⁺ ion. The small adsorption appears at low pH and it is often attributed to a competition between and metal ion on the same sites [23]. Hence the low removal yield of metal ions is due to the electrostatic repulsion forces between positively charged H₃O⁺ (Sorbent surface) and metal ions. At pH 5 metal ion adsorption sharply increased and reached to plateau value at a pH range of 5 to 7. The increase of pH, cause an increase in the negative charge density on the surface which is due to the deprotonisation of positively charged groups on the surface (sorbent surface). Thus, the most suitable pH values for the maximum adsorption of all metal ions were found at pH (5-7), while after that, pH values increased slowly at pH 9 as the result of precipitation.

Oshima et al. [24] investigated the adsorption behavior of the metal ions using mesoporous silicate, MCM-41, and found

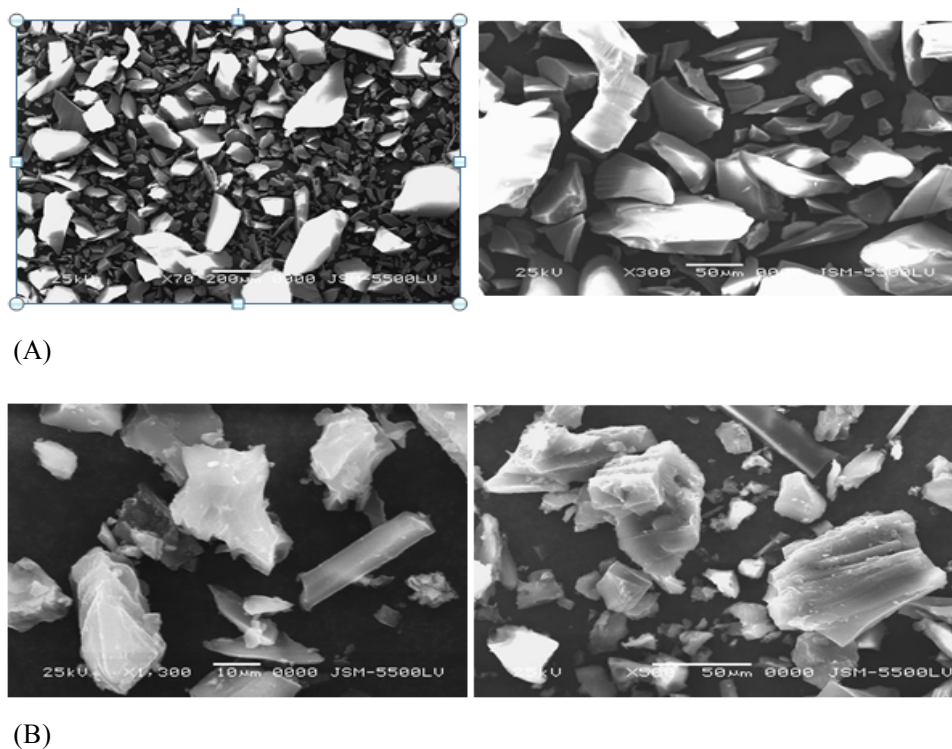


Figure 2. Micrographs of waste glass (WG) before treatment (A), and after hydrothermal treatment (WGP) (B).

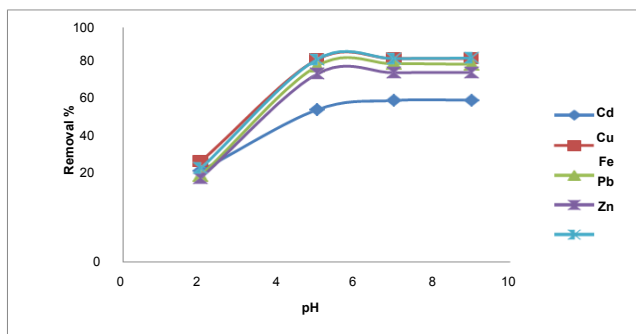


Figure 3. Removal percentage of Cd^{2+} , Cu^{2+} , Fe^{2+} , Pb^{2+} and Zn^{2+} by WGP at different pH 2, 5, 7 and 9.

that the optimum pH for the adsorption was at 6.2. Givianrad [25] studied the use of activated carbon and silica aerogel for removal of cadmium ions from aqueous solutions and found that Cd^{2+} adsorption by adsorbents was performed at pH 6.0. The adsorption of heavy metals $Cd(II)$, $Cu(II)$ and $Pb(II)$ by recycling waste glass powder was investigated and found that the maximum metal adsorption was at pH 5.6 [16]. Removal of heavy metals $Cd(II)$ and $Fe(II)$ ions from aqueous solutions by snail shell powder as adsorbent reveals that the optimum adsorption value was at pH 7 [26].

The maximum adsorption of Cu^{2+} ion by glass containing the ligand at pH 5.5 was studied by Zaitoun et al. [27]. Harry et al. [28] 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. [16] studied the recycled waste glass powder as adsorbent for the removal of $Cd(II)$, $Cu(II)$ and $Pb(II)$ ions. The maximum sorption capacity was at pH 6. These results from the previous literatures were agreed with our result of pH measurement.

Effect of contact time on metal adsorption: Contact time is an important parameter for the efficiency 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 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 Figure 4 and 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 it gives 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 be due to the nature of the sorbent and its available sorption sites that affect the time needed to reach equilibrium [29].

Ibrahim et al., [16] 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 [30]. The removal of Cu^{2+} increases rapidly until it reached an equilibrium state after 45 min by using bentonite treated with ammonium chloride [31]. Karthikeyan and Sivaillango [32] 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.

The adsorption data for the removal of Cd^{2+} , Cu^{2+} , Fe^{2+} , Pb^{2+} and Zn^{2+} by WGP adsorbent at different doses (0.5, 1.0 and 1.5 g) under the same experimental condition parameters (initial concentration; 50 mg/L; at pH 7) were studied and represented in Figure 5. It was observed that WGP doses of 1.5 g reveals

higher removal percentage of Cd^{2+} , Cu^{2+} , Fe^{2+} , Pb^{2+} and Zn^{2+} (68%, 88%, 88.7%, 87.6%, 86%, respectively) than with the other WGP doses. The order of the amount adsorbent dose for the removal of Cd^{2+} , Cu^{2+} , Fe^{2+} , Pb^{2+} and Zn^{2+} follows in order as WGP 1.5 g > WGP 1 gm > WGP 0.5 g. Thus WGP 1.5 g was selected for all the adsorption experiments in which it has a higher removal of Cd^{2+} , Cu^{2+} , Fe^{2+} , Pb^{2+} and Zn^{2+} than with the other adsorbent doses. Metal ion removal was noted to increase with the increase of the amount of adsorbent, because of the greater availability of the adsorbing surface area. The increasing in the amount of adsorbent enhances the removal of metal ions until it reaches the optimum dose Figure 5.

Givianrad et al., [25] used silica aerogel / activated carbon for the 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 0.10 g. Ajay et al., [33] reported that the removal percentage of Cd, Pb, Hg, Mn, Ni and Zn ions increases rapidly with the increase in the amount of chemically (Na_2S) treated granular activated carbon. Moyo et al., [34] studied 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.

Effect of initial concentration on metal adsorption: Figure 6 represented 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 decreases with the increase of heavy metal concentration. At 25 ppm of heavy metals concentration, 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 percentage. On the other hand, the highest heavy metal concentration (100 ppm) led to the lowest removal 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

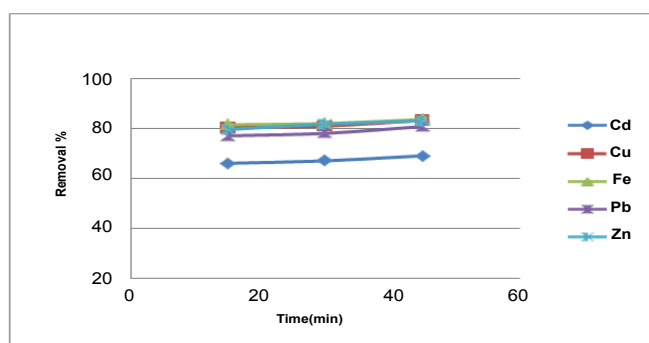


Figure 4. Removal percentage of Cd^{2+} , Cu^{2+} , Fe^{2+} , Pb^{2+} and Zn^{2+} by WGP adsorbent at different contact time 15, 30 and 45 min.

of all the tested metals was the highest at 25 ppm and decreased with the increase in metal concentration. El-Ashtoukhy et al., [35] 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 Yukihiro [36] reported that the maximum adsorption of Pb^{2+} by silica ceramic adsorbent was at 50 mg/L.

Effect of temperature on metal adsorption: The effect of solution temperature on the adsorption efficiency of the studied heavy metals is presented in Figure 7. The results show that with the increase of solution temperature from 25°C, the adsorption removal percentage of Cd^{2+} , Cu^{2+} , Fe^{2+} , Pb^{2+} and Zn^{2+} ions increased until reaching high adsorption at 45°C (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 [37]. Effect of temperature on removal of Pb ion using silica ceramic was studied by Salim and Yukihiro [36] their results revealed that Pb uptake increases when temperature of the solution increases from 20 to 30°C, and the adsorption is the highest at 40°C.

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 are usually the ratio between the quantity adsorbed and that remaining in the solution at fixed temperature on the equilibrium. The most commonly used adsorption models are Langmuir, Freundlich, Temkin and Dubinin- Radushkevich isotherms.

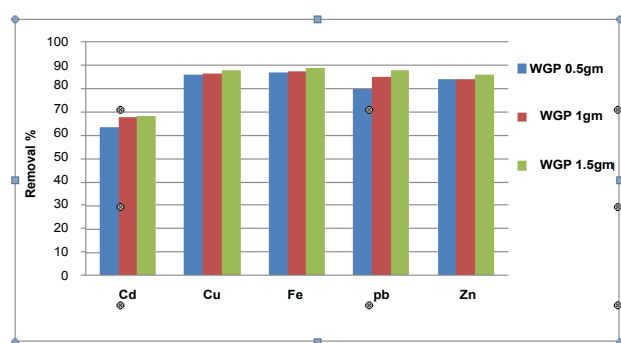


Figure 5. Effect of WGP adsorbent dose on the removal of the studied metals.

Table 1. The adsorption data for the removal of Cd^{2+} , Cu^{2+} , Fe^{2+} , Pb^{2+} and Zn^{2+} on WGP adsorbent at different contact time 15, and 3, 45 min.

Tim (min)	Removal %									
	Cd		Cu		Fe		Pb		Zn	
	Ce ppm	%	Ce ppm	%	Ce ppm	%	Ce ppm	%	Ce ppm	%
15	17.11	66%	9.826	80.30%	9.275	81.40%	11.6	77%	10.25	79.50%
30	16.63	67%	9.537	80.90%	9.021	81.90%	11.01	78%	9.172	81.60%
45	15.54	69%	8.429	83.10%	8.247	83.50%	9.63	80%	8.507	83%

Langmuir isotherm: The Langmuir isotherm is represented by the following equation.

$$C_e/q_e = C_e/Q_0 + 1/Q_0b \quad (2)$$

Where C_e is the equilibrium concentration (mgL⁻¹), q_e is the

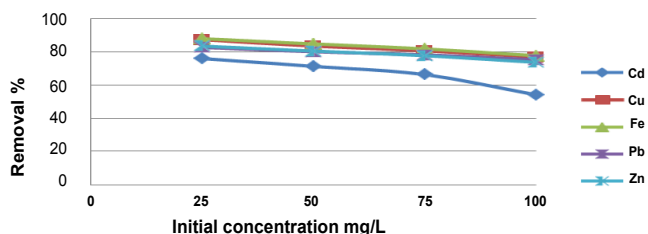


Figure 6. Removal percentage of Cd²⁺, Cu²⁺, Fe²⁺, Pb²⁺ and Zn²⁺ by WGP adsorbent at different initial metal concentration 25, 50, 75 and 100 mg/L.

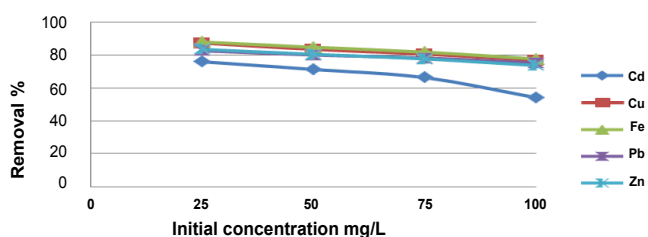


Figure 7. Removal percentage of Cd²⁺, Cu²⁺, Fe²⁺, Pb²⁺ and Zn²⁺ by WGP adsorbent at different temperatures 25, 35 and 45°C.

amount of adsorbate 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 the slope and intercepts of the plots.

The resulting data are represented in the Figure 8 and listed in Table 2. The maximum adsorption for Cd²⁺, Cu²⁺, Fe²⁺, Pb²⁺ and Zn²⁺ on WGP were 10.204 mg/g, 11.904 mg/g, 10.309 mg/g, 10.101 mg/g, and 12.195 mg/g, respectively. These values indicated that the order of metal ions according to their affinity to adsorption on WGP were Zn²⁺ > Cu²⁺ > Fe²⁺ > Cd²⁺ > Pb²⁺. The correlation coefficient for the adsorption of Cd²⁺, Cu²⁺, Fe²⁺, Pb²⁺ and Zn²⁺ onto WGP were 0.953, 0.991, 0.989, 0.98 and 0.978 respectively. The fit to the linear form models was examined by calculation of the linearity coefficient (R²). Regression values (R²) were presented in the Table 2 and indicates that the adsorption data for Cd²⁺, Cu²⁺, Fe²⁺, Pb²⁺ and Zn²⁺ fitted better the Langmuir model than the freundlich model for all adsorbents.

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

$$q_e = Kf + C_e^{1/n} \quad (3)$$

Equation 3 can also be expressed in the linearized logarithmic form

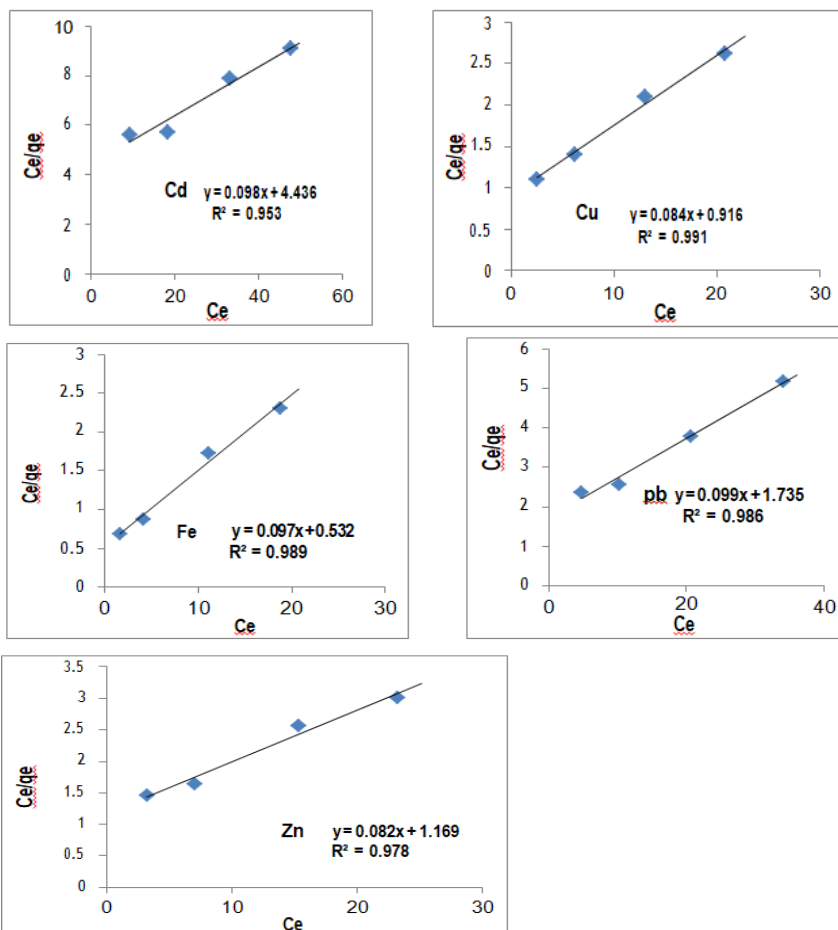


Figure 8. Langmuir isotherm plot for the adsorption of heavy metals by WGP adsorbent.

$$\log q_e = \log K_f + 1/n \log C_e \quad (4)$$

Where q_e is the amount of metal ions adsorbed per unit weight (mg/g adsorbent), C_e is the equilibrium concentration (mg/L) 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, whereas the slope, $1/n$ is an indicator of adsorption intensity. The Freundlich parameters for the adsorption of metal ions given Figure 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 Figure 9.

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 Equation 5.

$$\ln q_u = \ln q_m - B\varepsilon^2 \quad (5)$$

Where B a constant related to the adsorption energy (mol²/kJ²), q_m is a constant that indicates the sorption degree characterizing the sorbent (mg/g), ε is the polanyi potential, which can be obtained by the following equation:

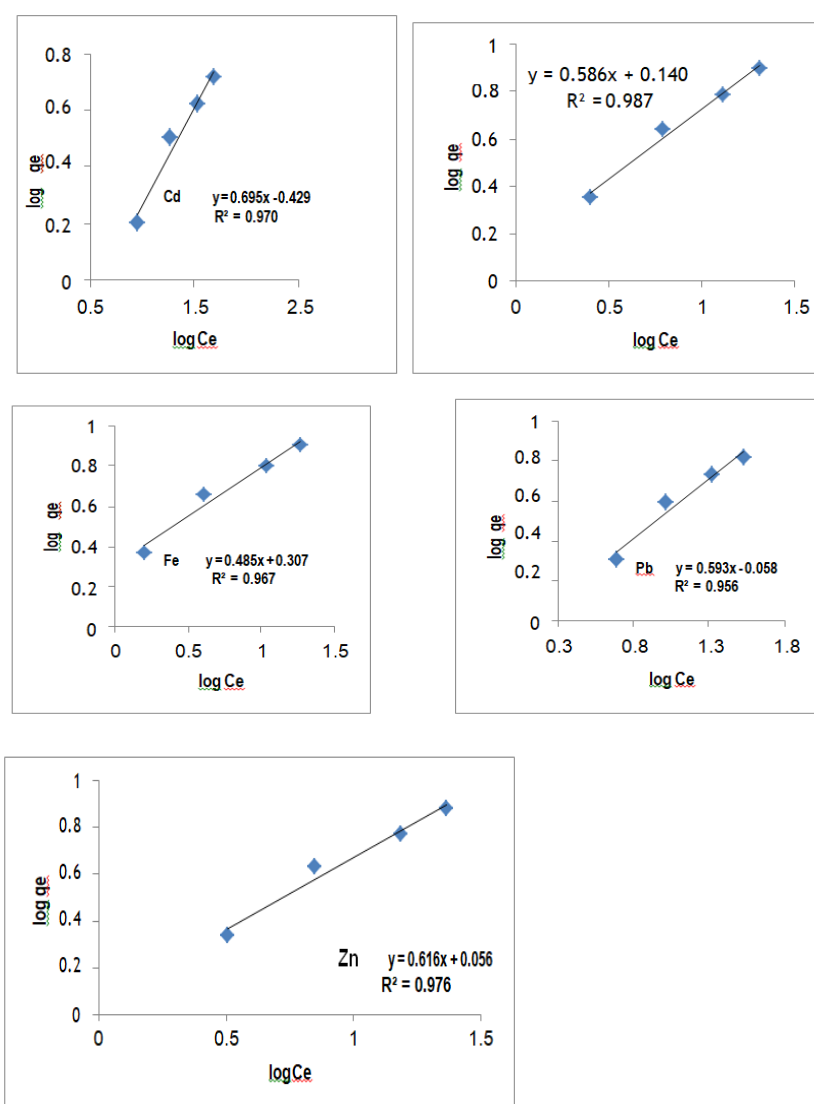


Figure 9. Freundlich Isotherm plot for the adsorption of metals by WGP adsorbent.

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

Solute	Langmuir Constant			Freundlich Constant		
	Q_0	b	R_2	$1/n$	K_f	R_2
Cd^{2+}	10.204	0.022	0.953	0.69	2.686	0.97
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	0.07	0.978	0.61	1.137	0.976

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (6)$$

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

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

If the value of E lies between 8 and 16 kJ/mol the sorption process is a chemisorption one, while values less than 8 kJ/mol indicate a physical adsorption process [38].

The Dubinin-Radushkevich (D-R) parameters for the adsorption of metal ions is given in Figure 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 are less than 8 kJ/mol indicate a physical adsorption process between WGP adsorbents and the adsorbate.

The Temkin isotherm: Temkin isotherm model contains a factor that describes adsorbing species- adsorbate interactions [39].

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 more linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm has commonly been applied in the following form (Equation 8).

$$q_e = RT / b \ln(Kt C_e) \quad (8)$$

$$B = RT / bt$$

Equation 2 can be linearized as

$$q_e = B \ln Kt + B \ln C_e \quad (9)$$

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 Kt (L/mg) is the equilibrium binding constant corresponding to the maximum binding energy. Both Bt and Kt can be calculated from the slope and the intercept of the linear plot based on

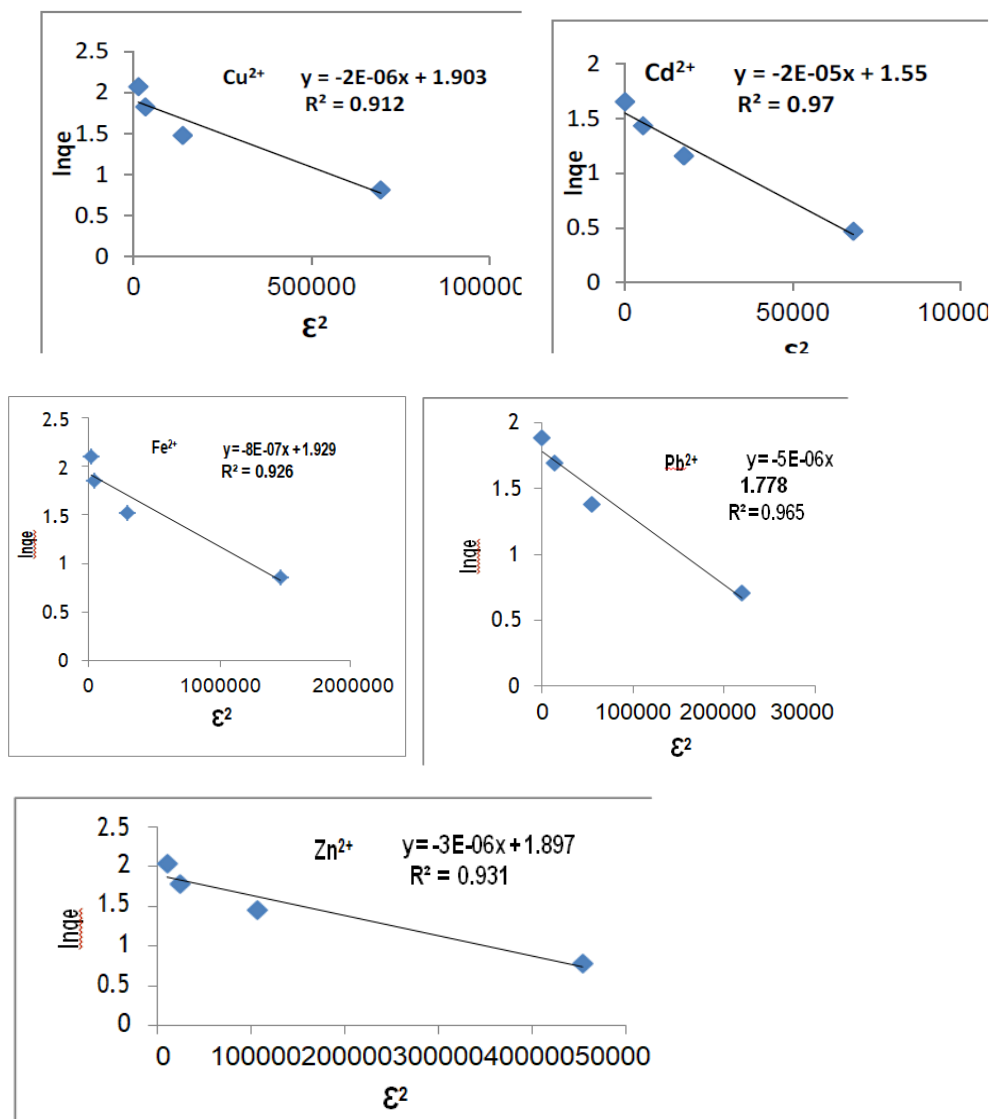


Figure 10. Dubinin-Radushkevich Isothermal plot for the adsorption of Cd^{2+} , Cu^{2+} , Fe^{2+} , Pb^{2+} and Zn^{2+} by WGP adsorbent. *J Ind Environ Chem* 2018 Volume 2 Issue 2

q_e versus $\ln C_e$, respectively. The Temkin parameters for the adsorption of metal ions given Figure 11 and listed in Table 3. From Temkin constant, the value of K_t for the adsorption on WGP was 0.238, 0.901, 1.792, 0.518 and 0.694 for Cd^{2+} , Cu^{2+} , Fe^{2+} , Pb^{2+} and Zn^{2+} respectively and 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 B_t and K_t 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 bt (variation of the adsorption energy (J/mol)) is positive, which indicates that the reaction of the adsorption is exothermic.

Kinetic models

Kinetic models are helpful to understand the mechanisms of metal adsorption, and so it evaluates performance of the adsorbents for metal removal. The kinetics 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 onto WGP adsorbent.

The pseudo-first-order model: The Lagergren's rate equation [40] 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:

$$\log(q_e - qt) = \log q_e - (kf / 2.303).t \quad (10)$$

Where, q_e (mg/gm) and qt (mg/gm) are the amount adsorbed on the sorbents at equilibrium and at time t , respectively; k_f (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 $\log(q_e - qt)$ versus t were used to determine the pseudo first-order constant k_f and equilibrium adsorption density q_e .

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 expressed by the following equation:

$$t / qt = 1 / (ks.qe^2) + t / qe \quad (11)$$

Where, the pseudo-second-order kinetic constant represented as ks ($\text{gm mg}^{-1} \text{min}^{-1}$), q_e (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 $t \rightarrow 0$ is defined as:

$$h = Ksqe^2$$

The plot t/qt versus t should give a straight line if pseudo-second-order kinetics is applicable and q_e , 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 are presented in Table 4 along with the corresponding correlation coefficients.

From pseudo-first-order rate constant, the obtained values of q_e for adsorption on WGP adsorbent were 0.2495, 0.151, 0.1455, 0.5035 and 0.4187 mg g^{-1} for Cd^{2+} , Cu^{2+} , Fe^{2+} , Pb^{2+} and Zn^{2+} respectively.

The previous values of q_e are decreasing with increasing in initial metal concentrations, which indicated that the values of q_e from the pseudo first-order kinetic model did not give reasonable values, and also did not agree very well with the experimental data. This suggests that the adsorption of Cd^{2+} , Cu^{2+} , Fe^{2+} , Pb^{2+} and Zn^{2+} ions by WGP are 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^{-1} , respectively. The previous values of q_e are increased with the increase in initial metal ions concentrations, and this is due to the adsorption of a large number of these metal ions at the available adsorption sites. This is indicated that the values of q_e from the pseudo-second-order kinetic model give reasonable values

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	Dubinin-Radushkevich Constant				Temkin Constant		
	B(mol ² /kJ ²)	Ln qm(mg/g)	E(KJ/mol)	R ₂	kt (L/mg)	bt (J/mol)	R ₂
Cd ²⁺	2x10 ⁻⁵	4.711	0.158	0.97	0.238	1171.982	0.993
Cu ²⁺	2x10 ⁻⁶	6.706	0.5	0.912	0.901	945.638	0.991
Fe ²⁺	8x10 ⁻⁷	6.882	0.79	0.926	1.7923	1099.188	0.99
Pb ²⁺	5x10 ⁻⁶	5.918	0.316	0.965	0.518	1073.471	0.997
Zn ²⁺	3x10 ⁻⁶	6.665	0.408	0.931	0.694	925.849	0.998

Table 4. Parameters of the kinetic models (pseudo first-order and pseudo second order for the adsorption of Cd^{2+} , Cu^{2+} , Fe^{2+} , Pb^{2+} and Zn^{2+} onto WGP adsorbent.

Solute	Pseudo first-order			Pseudo second-order			
	R ₂	qe(mg/g)	Kf	R ₂	h (mg g ⁻¹ min ⁻¹)	qs (mg/g)	Ks g mg ⁻¹ min ⁻¹
Cd ²⁺	0.999	0.2495	0.0023	1	16.129	2.985	1.811
Cu ²⁺	0.902	0.151	0.007	1	9.901	4.386	0.514
Fe ²⁺	0.979	0.1455	0.023	0.992	1.251	0.292	14.69
Pb ²⁺	0.993	0.5035	0.0299	1	3.134	3.968	0.199
Zn ²⁺	0.98	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 and after treatment of real well drinking water sample (Al-Ka'aimat well west of Abu Tesht).

	Removal %									
	Cd^{2+}		Cu^{2+}		Fe^{2+}		Pb^{2+}		Zn^{2+}	
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%
Before treatment	5.12		5.072		5.228		5.172		5.103	
After treatment	1.351	73.6	0.541	89.3	0.638	0.638	0.827	84	0.551	89.2

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

	Removal %									
	Cd^{2+}		Cu^{2+}		Fe^{2+}		Pb^{2+}		Zn^{2+}	
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%
Before treatment	3.005	-	3.102	-	3.358	-	3.15	-	3.107	-
After treatment	0.814	72.9	0.405	86.9	0.457	86.4	0.524	83.3	0.382	87.7

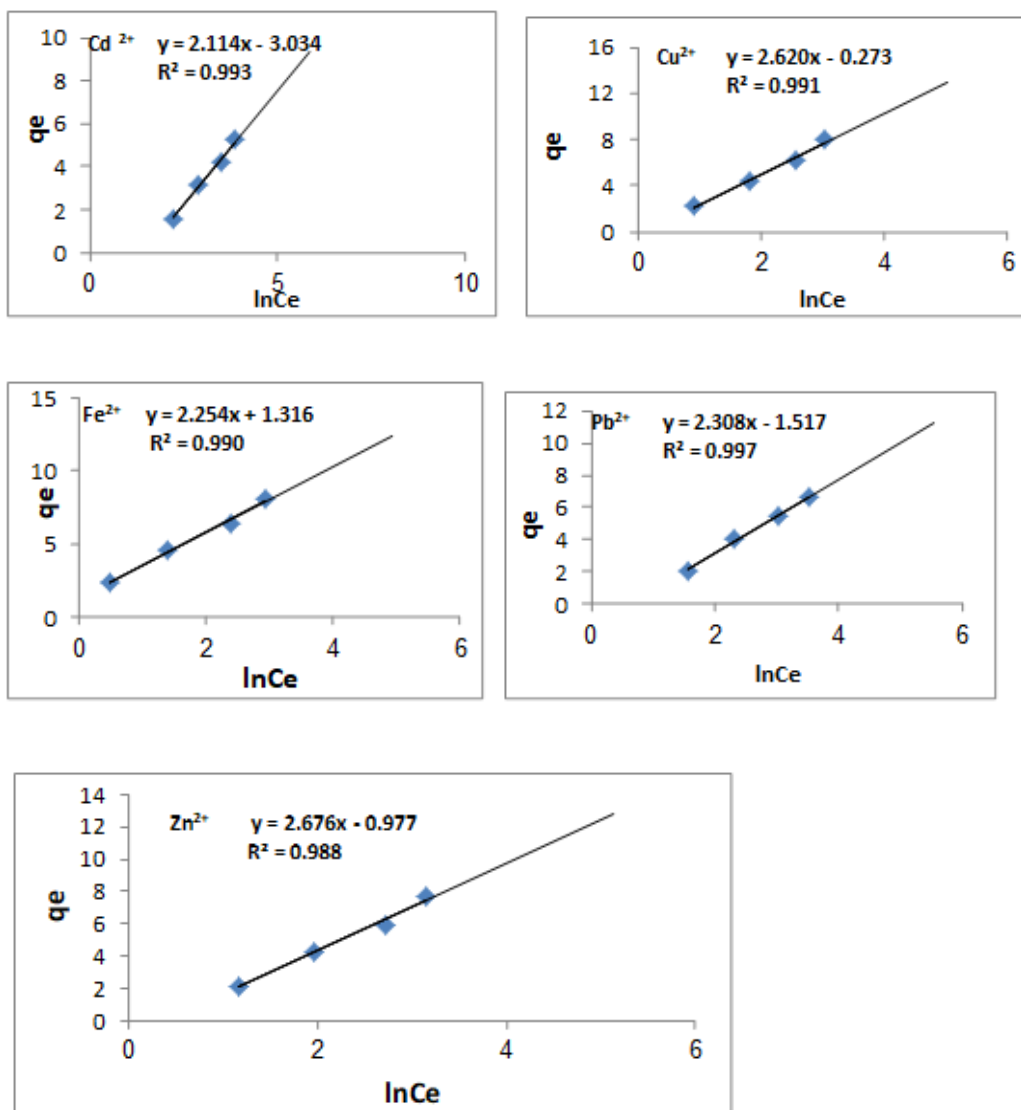


Figure 11. Temkin isotherm plots for the adsorption of Cd^{2+} , Cu^{2+} , Fe^{2+} , Pb^{2+} and Zn^{2+} by WGP adsorbent.

also 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) and substantially higher than that for the first-order rate equation. These indicate that the

adsorption system studied belongs to the second order kinetic model.

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 g) was used for adsorption of Cd^{2+} , Cu^{2+} , Fe^{2+} , Pb^{2+} and Zn^{2+} ions at optimum pH 7, contact time 45 min and a temperature of 25°C from real well drinking water samples. The obtained result is tabulated 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 highly adsorbed with WGP adsorbent. So, the prepared WGP adsorbent was effective for higher removal efficiency of heavy metals from well drinking water.

Conclusion

Eco-friendly 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 pH 7, contact time 45 min, adsorbent dose 1.5 g and temperature 25°C. Adsorption isotherms (Langmuir and Freundlich) as well as kinetic adsorption models (pseudo first-order and pseudo second-order) were applied and ended to that the adsorption of the studied heavy metals onto the prepared adsorbents fitted well Langmuir and pseudo second-order models.

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