

Article

Evaluation of Groundwater and Grey Water Contamination with Heavy Metals and Their Adsorptive Remediation Using Renewable Carbon from a Mixed-Waste Source

Taghrid S. Alomar ¹, Mohamed A. Habila ^{2,*}, Zeid A. Allothman ² , Najla AlMasoud ^{1,*}  and Saad Saeed Alqahtany ²

¹ Department of Chemistry, College of Science, Princess Nourah bint Abdulrahman University, Riyadh 11671, Saudi Arabia; tsalomar@pnu.edu.sa

² Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia; zaiothman@ksu.edu.sa (Z.A.A.); ksasa911@hotmail.com (S.S.A.)

* Correspondence: mhabila@ksu.edu.sa (M.A.H.); nsalmasoud@pnu.edu.sa (N.A.); Tel.: +96-614-674-198 (M.A.H.); +966-11-8236046 (N.A.); Fax: +96-614-675-992 (M.A.H.)

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Abstract: The contamination of water sources with heavy metals is a serious challenge that humanity is facing worldwide. The aim of this work was to evaluate and remediate the metal pollution in groundwater and greywater resources from Riyadh, Saudi Arabia. In addition, we investigated the application of ultrasonic power before adsorption to assess the dispersion of renewable carbon from mixed-waste sources (RC-MWS) as an adsorbent and enhance the water purification process. The renewable carbon adsorbent showed high ability to adsorb Pb(II), Zn(II), Cu(II), and Fe(II) from samples of the actual water under study. The conditions for the remediation of water polluted with heavy metals by adsorptive-separation were investigated, including the pH of the adsorption solution, the concentration of the heavy metal(s) under study, and the competition at the adsorption sites. The enhanced adsorption process exhibited the best performance at a pH of 6 and room temperature, and with a contact time of 60 min. Kinetic studies showed that the pseudo-second-order kinetic model was fitted with the adsorption of Pb(II), Zn(II), Cu(II), and Fe(II) onto the RC-MWS. The adsorption data were well fitted by Langmuir isotherms. The Freundlich isotherm was slightly fitted in the cases of Cu(II), Zn(II), and Fe(II), but not in the cases of Pb(II). The developed adsorption process was successfully applied to actual water samples, including water samples from Deria and Mozahemia and samples from clothes and car washing centers in Riyadh city.

Keywords: heavy metals determination; groundwater; greywater; adsorption; separation; inductively coupled plasma mass spectroscopy

1. Introduction

Determining heavy metals contamination in water systems, including groundwater and greywater systems, is a prerequisite for employing or treating them. Greywater includes water used by clothes and car washing machines and basins in kitchens and bathrooms in houses and mosques. However, the term ‘black water’ refers to the water used by toilets. The water from groundwater or greywater resources is expected to be more suitable for economic wastewater treatment than black water [1–5]. Groundwater may be contaminated with heavy metals; for example, a risk of human exposure to heavy metals through groundwater used as a source of drinking water has been reported [6,7]. Water resource shortages have forced countries to use different water supply sources,

such as groundwater, seawater, rainwater, riverwater, and wastewater [8–10]. The availability and purity of water have a direct impact on public health. The desalination and reuse of wastewater have attracted interest in fields of applied science in some countries, including Saudi Arabia [8,11–15]. The most common permanent pollutants of water systems are heavy metals from natural or industrial sources [16,17]. Heavy metals are characterized by having an atomic weight in the range of 63.5–200.6. The major industries that discharge heavy metals are the mining and metal plating industries. The discharge from these industries has led to a large amount of heavy metals in the water system [18,19]. The most damaging impact of heavy metals pollution is their accumulation inside living beings, particularly fishes, in the marine environment. In addition, they accumulate in plants and animals to reach higher levels in the food chain and become very dangerous to humans. Moreover, it is very difficult to biodegrade heavy metals in the environment [20]. Many dangerous and chronic diseases result from contamination with heavy metal cations, such as chromium, copper, zinc, lead, iron, manganese, cadmium, and mercury cations. Municipal wastewater represents another prominent source of metal pollution, which may include cadmium, arsenic, selenium, zinc, and nickel [16,19,20]. The World Health Organization (WHO) reported that the serious toxicity of heavy metals may have damaging health impacts on many human organs, such as the nervous system and gastrointestinal (GI) systems. In addition to that, it may have harmful effects on the lungs, the renal system, and the liver, and in some cases may lead to more complicated diseases, including cancer [20]. The treatment of wastewater helps to protect the environment and solve water shortage problems [21–25]. This trend has attracted increasing interest, especially for greywater, which is produced by hand-washing basins and washing machines and is not allowed to come into contact with toilet water at all [1–3]. There are many technologies for treating wastewater containing heavy metals, such as membrane separation, chemical oxidation, and chemical reduction, carbon adsorption, liquid extraction, electrolytic treatment, ion exchange, electro precipitation, coagulation, evaporation, flotation, hydroxide and sulfide precipitation, ultrafiltration, crystallization, and electro-dialysis [26–28]. The flotation process has successfully been applied for the separation of ions with the assistance of surfactants or dispersant gases [29–34]. However, adsorption exhibits superior efficiency in the removal of heavy metals from wastewater [35,36]. The main goal of the adsorption process is to decrease the level of heavy metals pollution in wastewater; however, different adsorbents have different efficiencies and the cost is highly variable [26,36–40]. Improvements in the adsorptive treatment are usually based on the development of a highly porous or functionalized adsorbent [18,41]. Activated carbon is known to be a highly effective adsorbent for the removal of heavy metals from wastewater, and it readily dissolves in an extreme pH medium, which facilitates its application and makes the process more suitable for a large number of pollutants of organic and inorganic species [35,42–44]. The main advantage of the application of activated carbon for controlling pollution by adsorption is its low price compared with other materials as well as being easy to produce from various waste sources [45–47]. In addition, activated carbon from waste sources is considered to be a safe adsorbent for wastewater treatment [48–51]. Ultrasonic waves have recently been proposed and used to enhance ion transfer, penetration, and separation. In addition, ultrasonic waves are applied in liquid extraction to improve interactions and enhance the mass transfer [52,53]. This study aimed to develop an improved separation process for removing metal pollutants from groundwater and grey water, investigate the characteristics of adsorption with the help of ultrasonic waves, and evaluate the competition in the adsorption process in the case of a mixed heavy metal solution system. We also optimized the pH, contact time, and metal ion concentrations, in order to adjust the adsorption process. The developed adsorptive separation process was employed to remove Pb(II), Zn(II), Cu(II), and Fe(II) from groundwater and greywater to improve the overall water quality.

2. Experimental

2.1. Water Samples from Different Regions of Riyadh City and Surrounding Cities

Water samples were collected from Riyadh city as well as from cities surrounding it, including Deria and Mozahemia. The water samples included drinking water samples, groundwater samples, and samples from a clothes washing center and a car washing center. The samples were acidified with nitric acid after being put in polypropylene bottles, and then analyzed for the heavy metals Pb(II), Zn(II), Cu(II), and Fe(II). In addition, the collected samples were applied in an adsorption process for the evaluation of the heavy metal separation efficiency.

2.2. Determining Heavy Metals and Optimizing the Adsorptive Remediation Process

Nitric acid, hydrochloric acid, sodium hydroxide, lead nitrate, zinc nitrate, copper nitrate, and ferrous nitrate were purchased from Sigma-Aldrich, St. Louis, MO, USA. All reagents were of analytical grade. The renewable carbon from a mixed-waste source (RC-MWS) used in this study is prepared in our laboratory and it was previously characterized [44]. The adsorptive remediation process for adsorbing Pb(II), Zn(II), Cu(II), and Fe(II) from an aqueous solution onto renewable carbon from a mixed-waste source (RC-MWS) was assessed by a group technique in which the primary model metal solutions for Pb(II), Zn(II), Cu(II), and Fe(II) (500 parts per million, ppm) were made in the laboratory by employing nitrate salts, and metal solutions (400, 300, 200, 100, and 50 ppm) were prepared daily by dilution. A 50-mL metal cation solution was added to 0.03 g of RC-MWS. Blank experiments were carried out without the addition of an adsorbent. The mixtures were exposed to ultrasonic waves for 2 min, and then shaken for a certain period of time. Then, after filtration, the decrease in the amount of the heavy metal in the solution was measured throughout the treatment by inductively coupled plasma mass spectrometry (ICPMS) using Equation (1):

$$q_e = \frac{(C_0 - C_e) * V}{M} \quad (1)$$

where C_0 represents the initial concentration of metal ions in the solution, C_e is the equilibrium concentration of metal ions in the solution, V is volume of the solution (L), and M is the mass of the adsorbent (g).

The adsorption procedure was optimized for heavy metals by determining the impact of pH in the range from 2 to 7, contact time from 5–120 min, and metal cation concentration in the range 25–500 ppm on the treatment procedure.

Finally, the collected water samples, including drinking water and groundwater samples and samples from clothes and car washing centers, were used to evaluate the treatment's efficiency, which was calculated using Equation (2):

$$\text{The removal efficiency \%} = \left(\frac{C_0 - C_e}{C_0} \right) * 100 \quad (2)$$

where C_0 represents the initial concentration of metal ions in the solution, and C_e is the equilibrium concentration of metal ions in the solution.

3. Results and Discussion

3.1. Evaluation of the Adsorptive Remediation Process for Separation of Pb(II), Zn(II), Cu(II), and Fe(II) from an Aqueous Medium Using the Model Solutions

3.1.1. Effect of pH on the Metal Ion Solution Medium

Because the pH of an aqueous solution that contains metal ions is a crucial parameter that controls an adsorption process, the role of the hydrogen ion concentration was determined by employing solutions with pH values ranging from 2 to 7. As shown in Figure 1, the adsorption capacity, q_e (mg/g),

of RC-MWS for Pb(II), Zn(II), Cu(II), and Fe(II) became larger by increasing the pH value from 2 to 6. Indeed, the maximum adsorption capacity of Pb(II), Zn(II), Cu(II), and Fe(II) was achieved at a pH value of 6. Similar results were reported in studies adsorbing heavy metals in a less acidic medium onto different biomass systems [39]. These results could be attributed to the chelation's lower stability in a highly acidic medium.

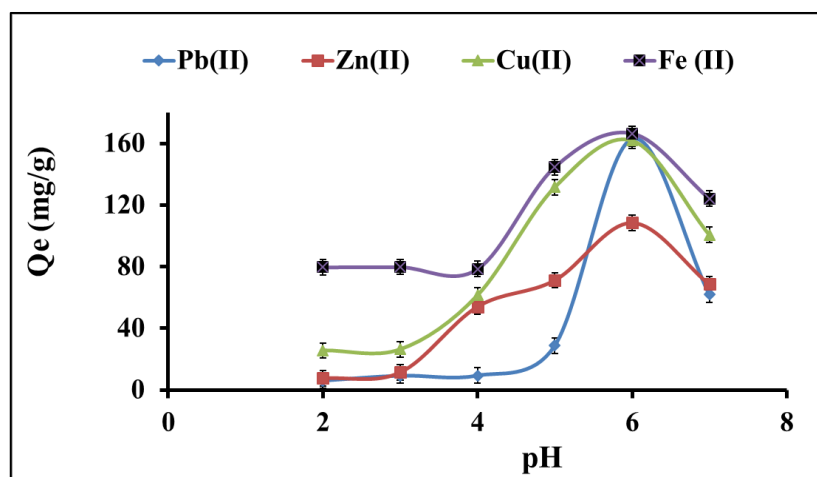


Figure 1. Effect of pH on the adsorption of Pb(II), Zn(II), Cu(II), and Fe(II) onto 0.03 g of renewable carbon from a mixed-waste source (RC-MWS) at room temperature and with a contact time of 60 min.

3.1.2. Competition for the Adsorption of Pb(II), Zn(II), Cu(II), and Fe(II) Onto RC-MWS

The application of RC-MWS for the adsorption of Pb(II), Zn(II), Cu(II), and Fe(II) was done and the adsorption capacities are shown in Figure 2. The highest adsorption capacity was reached with Fe(II), followed by Pb(II), Cu(II), and then Zn(II).

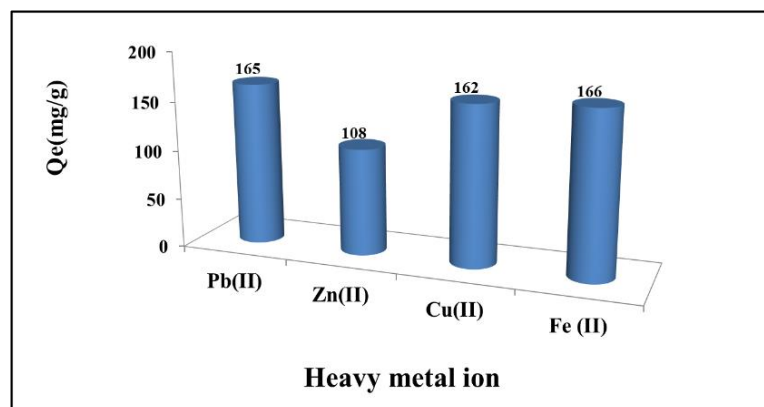


Figure 2. The competition for the adsorption of Pb(II), Zn(II), Cu(II), and Fe(II) onto RC-MWS.

3.1.3. Kinetic Studies on the Adsorption of Pb(II), Zn(II), Cu(II), and Fe(II) Onto RC-MWS

The rate of adsorption of Pb(II), Zn(II), Cu(II), and Fe(II) onto RC-MWS with the assistance of ultrasonic waves was determined by measuring the concentration of the remaining Pb(II), Zn(II), Cu(II), and Fe(II) in the aqueous solution at different times. By testing the effect of different contact times (from 5 to 120 min), it was discovered that the maximum adsorption capacity was achieved with a contact time of 60 min (Figure 3). The adsorption capacity did not significantly change with further increases in the contact time.

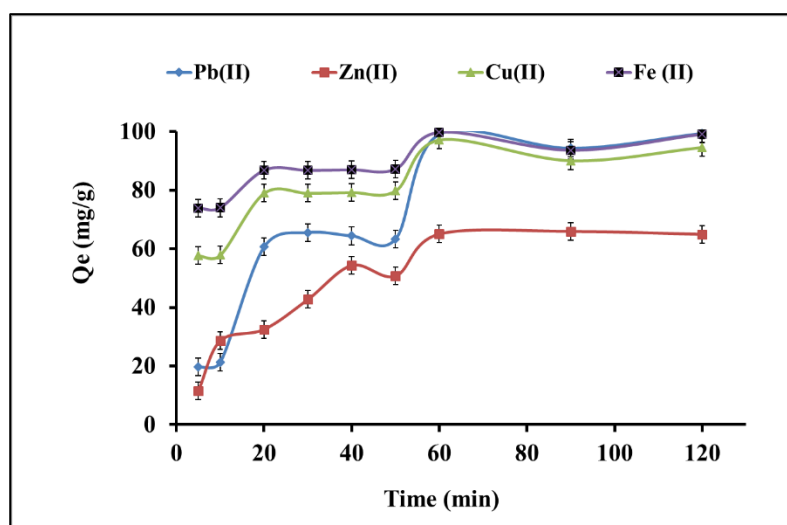


Figure 3. The effect of contact time on the adsorption of Pb(II), Zn(II), Cu(II), and Fe(II) onto 0.05 g of RC-MWS.

The pseudo-first-order equation, in its integrated form [54], is expressed as in Equation (3):

$$\log(q_e - q_t) = -\frac{k_1}{2.303}t + \log(q_e) \quad (3)$$

where q_e and q_t are the amounts of adsorbate uptake per mass of adsorbent at equilibrium and at any time t (min), respectively, and k_1 (min^{-1}) is the rate constant of the pseudo-first-order kinetic model.

The pseudo-first-order rate constant, k_1 , was obtained by plotting $\log(q_e - q_t)$ versus time t , (Figure 4). It can be seen that the correlation coefficient value, R_1^2 , is weak. In addition, the calculated adsorption capacity (Table 1) was different and far from the experimental q_e , therefore, the adsorption data for Pb(II), Zn(II), Cu(II), and Fe(II) onto RC-MWS is not fitted well with the pseudo-first-order kinetic model. McKay et al. suggested that in some adsorption cases the pseudo-first-order kinetic model is not suitable, due to the boundary layer which may control the adsorption at the beginning [55].

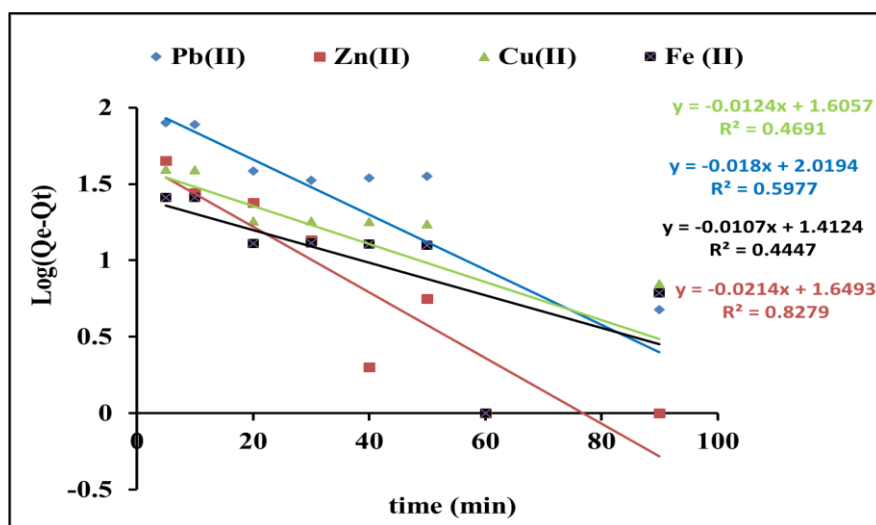


Figure 4. The pseudo-first-order model of the adsorption of Pb(II), Zn(II), Cu(II), and Fe(II) onto RC-MWS, (A) considering time from 0 to 40 min and (B) considering time from 0 to 90 min.

Table 1. Parameters for the kinetics of the adsorption of Pb(II), Zn(II), Cu(II), and Fe(II) onto RC-MWS.

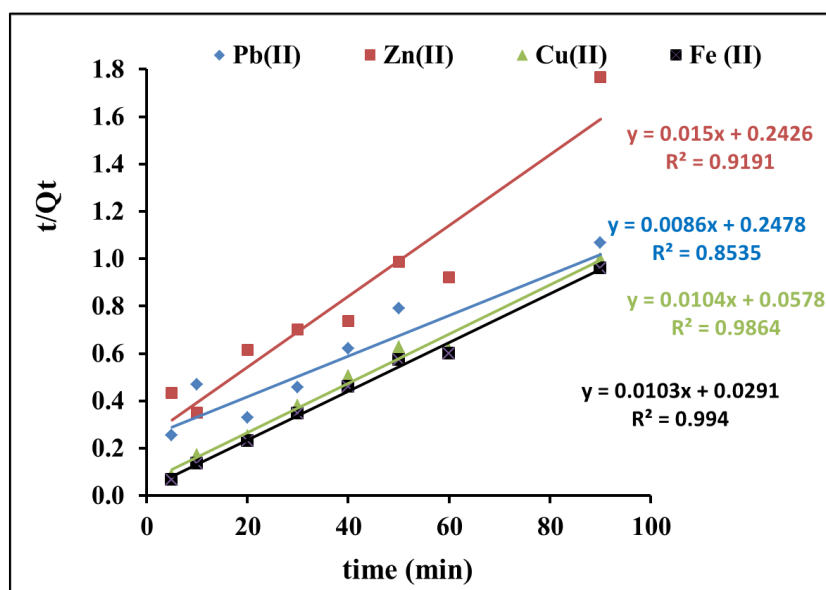
	q_e , exp (mg/g)	Pseudo First Order		R^2	Pseudo Second Order		R^2
		k_1 (min ⁻¹)	q_e , cal (mg/g)		k_2 (g/mg·min)	q_e , cal (mg/g)	
Pb(II)	99	0.041	104.5	0.59	9.2×10^{-4}	66.6	0.92
Zn(II)	65	0.049	44.5	0.82	3.6×10^{-3}	97	0.99
Cu(II)	97	0.028	40.3	0.46	2.9×10^{-4}	116.2	0.85
Fe(II)	100	0.024	25.8	0.44	1.8×10^{-3}	96.1	0.98

The pseudo-second-order kinetic equation, in its integrated form, is expressed as in Equation (4) [56]:

$$\frac{t}{q_e} = \left(\frac{1}{q_e} \right) \cdot t + \frac{1}{K_2 q_e^2} \quad (4)$$

where q_e and q_t are the amounts of adsorbate uptake per mass of adsorbent at equilibrium and at any time t (min), respectively, and k_2 (g/mg·min) is the pseudo-second-order rate constant.

q_e and k_2 are calculated by plotting t/q_t versus t from the slope and intercept (Figure 5). From the data shown in Table 1, it can be seen that the data of the adsorption of Pb(II), Zn(II), Cu(II), and Fe(II) onto the RC-MWS is fitted with the pseudo-second-order kinetic model, which suggest that the reaction rate is primarily controlled by the movement of the metal ions from the solution to the surface of the adsorbent [27].

**Figure 5.** The pseudo-second-order model of the adsorption of Pb(II), Zn(II), Cu(II), and Fe(II) onto RC-MWS.

3.1.4. Isotherm Studies

The data for adsorption of Pb(II), Zn(II), Cu(II), and Fe(II) onto RC-MWS at equilibrium were analyzed by using the Langmuir model [57] as expressed in Equation (5):

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_{max}^0} \right) C_e + \frac{1}{Q_{max}^0 K_L} \quad (5)$$

where Q_{max}^0 (mg/g) is the maximum saturated monolayer adsorption capacity of the RC-MWS, C_e (mg/L) is the adsorbate concentration at equilibrium, q_e (mg/g) is the amount of adsorbate uptake at equilibrium, and K_L (L/mg) is a constant related to the affinity between an adsorbent and adsorbate. The correlation

coefficient, R^2 , for the adsorption of Pb(II), Zn(II), Cu(II), and Fe(II) onto RC-MWS showed that the adsorption data was well fitted by the Langmuir isotherm (Figure 6) suggesting monolayer adsorption.

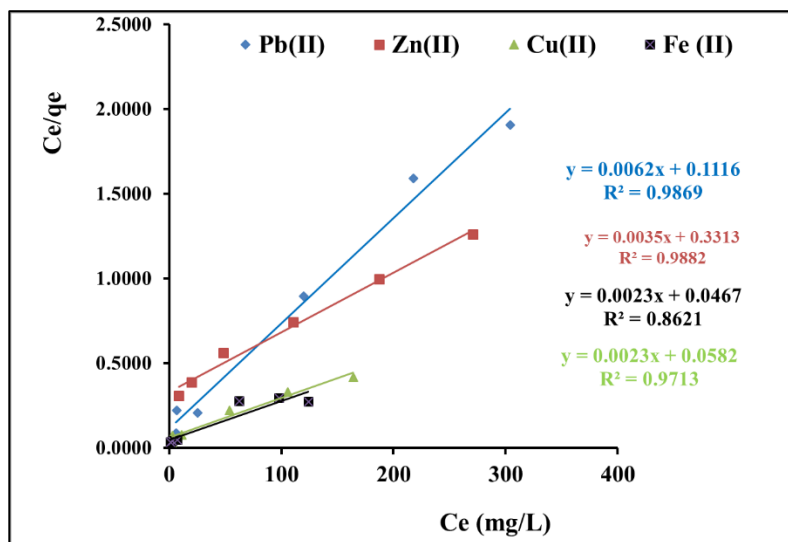


Figure 6. Langmuir adsorption isotherms for the adsorption of Pb(II), Zn(II), Cu(II), and Fe(II) onto RC-MWS.

The Freundlich isotherm [58] is expressed as in Equation (6):

$$\log q_e = n \log C_e + \log K_f \quad (6)$$

where q_e (mg/g) is the amount of adsorbate uptake at equilibrium, C_e (mg/L) is the adsorbate concentration at equilibrium, K_f (mg/g)/(mg/L) ^{n} is the Freundlich constant, and n (dimensionless) is the Freundlich intensity parameter, which indicates the magnitude of the adsorption driving force or the surface heterogeneity.

The Freundlich isotherm model is commonly used to describe the adsorption data characteristic for heterogeneous surfaces at equilibrium [59–62]. The plots of $\log q_e$ and $\log C_e$ (Figure 7) gave a linear line, from which n and K_f were calculated (Table 2). The values of the Freundlich intensity parameter (n) lower than 1 indicate favorable adsorption; however, the value of correlation coefficient, R^2 (Table 2), indicate that the adsorption of Pb(II), Zn(II), Cu(II), and Fe(II) onto RC-MWS tends to be more comfortable with the Langmuir model rather than the Freundlich model.

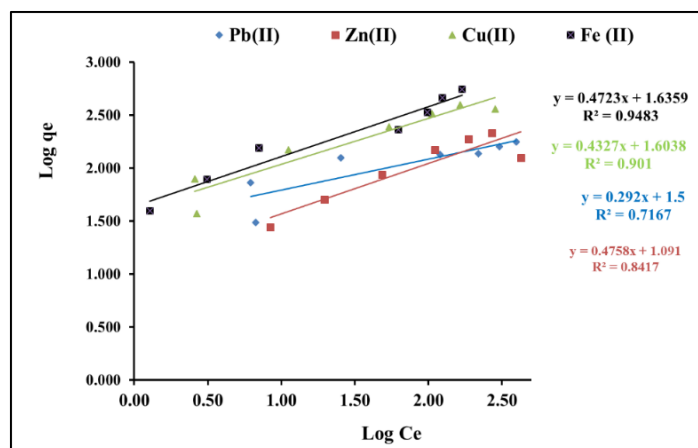


Figure 7. Freundlich adsorption isotherms for the adsorption of Pb(II), Zn(II), Cu(II), and Fe(II) onto RC-MWS.

Table 2. Langmuir and Freundlich constants for the adsorption of Pb(II), Zn(II), Cu(II), and Fe(II) onto RC-MWS.

	Langmuir Constants		Correlation Coefficients R^2	Freundlich Constants		Correlation Coefficients R^2
	K_L (L/mg)	Q_{max}^0 (mg/g)		K_f (mg/g)/(mg/L) ⁿ	n	
Pb(II)	0.05	161.2	0.98	31.6	0.29	0.71
Zn(II)	0.01	285.7	0.98	12.3	0.47	0.84
Cu(II)	0.039	434.7	0.97	40.1	0.43	0.90
Fe(II)	0.049	434.7	0.86	43.2	0.47	0.94

The following Equation (7) is applied for the Freundlich isotherm:

$$q_e = K_f C_e^{\frac{1}{n}} \quad (7)$$

where K_f and $1/n$ are Freundlich constants, related to the adsorption capacity and adsorption intensity (heterogeneity factor), respectively. In this case, the n with a value in the range of 0 to 10 indicates the favorable adsorption; however, this index has some applicable limitation practically due to the fact that the n value should not exceed 10 [63].

The Application of the Adsorption Process to Actual Water Samples

The adsorption process was applied to remove Pb(II), Zn(II), Cu(II), and Fe(II) from actual water samples. Water samples were collected from Deria, Mozahemia, and clothes and car washing centers in different regions. The initial Pb(II), Zn(II), Cu(II), and Fe(II) concentrations in the samples were determined by ICP-MS [64,65]. Then, the treatment by adsorption onto RC-MWS was applied under the optimal conditions (a pH of 6, room temperature, and a contact time of 60 min). After the treatment, the Pb(II), Zn(II), Cu(II), and Fe(II) concentrations were once again measured by ICP-MS. Then, we used Equation (2) to calculate the removal efficiency percentage (%). The results are presented in Tables 3 and 4. All of the tested water samples were found to contain a very small amount of Pb(II), Cu(II), and Fe(II), at values below the permitted concentrations, which demonstrates the high level of safety of the tested water samples. However, the detected concentrations were further reduced after the adsorption of Pb(II), Cu(II), and Fe(II) onto RC-MWS.

Table 3. Efficiency of the removal of Pb(II), Zn(II), Cu(II), and Fe(II) from different water samples from Deria and Muzahemia.

Water Sample	Pb(II) Investigations			Zn(II) Investigations			Cu(II) Investigations			Fe(II) Investigations		
	Initial Concentration of Pb(II) (ppm)	Final Concentration of Pb(II) (ppm)	Efficiency %	Initial Concentration of Zn(II) (ppm)	Final Concentration of Zn(II) (ppm)	Efficiency %	Initial Concentration of Cu(II) (ppm)	Final Concentration of Cu(II) (ppm)	Efficiency %	Initial Concentration of Fe(II) (ppm)	Final Concentration of Fe(II) (ppm)	Efficiency %
Deria-1	0.2151	0	100	1.3	0	100	1.26	0.00	100	3.54	1.17	97
Deria-2	0.1357	0	100	1.2	0.091	92	0.33	0.00	100	0.70	3.31	53
Deria-3	0.2313	0	100	2.1	0.064	97	0.11	0.00	100	2.42	8.71	64
Deria-4	0.0436	0	100	1.4	0.075	95	0.25	0.00	100	0.28	0.18	94
Deria-5	0.1305	0	100	1.6	0	100	0.16	0.00	100	0.22	0.66	70
Deria-6	0	0	-	1.8	0.019	99	0.46	0.00	100	0.36	0.05	99
Deria-7	0	0	-	1.4	0.063	96	0.00	0.00	-	1.23	1.90	85
Deria-8	0	0	-	1.4	0	100	1.10	0.00	100	5.42	2.89	95
Deria-9	0	0	-	1.2	0	100	0.22	0.00	100	4.47	2.23	95
Deria-10	0	0	-	1.1	0.08	93	0.24	0.29	88	1.94	2.31	88
Deria-11	0.0405	0	100	0.8	0.01	99	0.25	0.00	100	14.60	1.48	99
Mozahemia-1	0.0833	0	100	2.1	0.056	97	0.25	0.00	100	0.31	0.14	96
Mozahemia-2	0	0	-	1.2	0.038	97	0.00	0.00	-	0.17	0.00	100
Mozahemia-3	0	0	-	1.0	0.033	97	0.06	0.00	100	11.19	2.22	98

Table 4. Efficiency of the removal of Pb(II), Zn(II), Cu(II), and Fe(II) from water samples from different clothes and car washing centers in Riyadh city.

Water Samples	Pb(II) Investigations			Zn(II) Investigations			Cu(II) Investigations			Fe(II) Investigations		
	Initial Concentration of Pb(II) (ppm)	Final Concentration of Pb(II) (ppm)	Efficiency %	Initial Concentration of Zn(II) (ppm)	Final Concentration of Zn(II) (ppm)	Efficiency %	Initial Concentration of Cu(II) (ppm)	Final Concentration of Cu(II) (ppm)	Efficiency %	Initial Concentration of Fe(II) (ppm)	Final Concentration of Fe(II) (ppm)	Efficiency %
clothes-1	0	0	-	905.21	12.59	99	11.18	1.92	98	5.31	3.87	93
clothes-2	0	0	-	997.08	1.69	100	0.16	0.00	100	2.20	1.09	95
clothes-3	6.1151	0.215386	96.5	862.14	0.85	100	1.84	0.87	95	1.32	3.17	76
clothes-4	0.4854	0.003688	99.2	4600.01	1.09	100	1.86	1.16	94	4.21	9.25	78
clothes-5	5.039	0.025297	99.5	1019.94	0.87	100	0.39	0.00	100	2.15	3.42	84
clothes-6	0	0	-	638.83	0.35	100	0.53	0.00	100	4.48	3.09	93
clothes-7	0.0024	0	100	977.57	0.00	100	0.24	0.00	100	9.42	3.08	97
clothes-8	0.2102	0	100	904.20	1.56	100	0.71	0.62	91	4.56	5.68	88
cars-1	0	0	-	923.95	3.78	100	15.09	28.41	81	47.54	0.59	100
cars-2	0	0	-	1217.16	7.21	99	21.11	7.31	97	1.95	0.18	99
cars-3	1.787	0	100	842.75	14.36	98	39.94	73.41	82	15.87	6.13	96
cars-4	0	0	-	865.13	8.00	99	92.67	270.09	71	373.65	3.71	100
cars-5	0	0	-	1056.29	12.91	99	50.99	79.33	84	7.86	1.00	99
cars-6	0	0	-	1228.33	0.00	100	0.30	0.00	100	41.20	19.86	95
cars-7	0	0	-	956.51	0.25	100	0.11	0.00	100	9.18	0.36	100
cars-8	0	0	-	1174.11	10.11	99	30.34	27.44	91	81.47	2.91	100

4. Conclusions and Recommendations

The most important parameters for optimizing the adsorption of Pb(II), Zn(II), Cu(II), and Fe(II) onto RC-MWS were investigated to enhance water purification. The optimized conditions were at a pH of 6, a contact time of 60 min, an adsorbent dose of 0.03 g RC-MWS, and at room temperature. Water samples, including groundwater and greywater samples, were collected from the Riyadh, Deria, and Mozahemia regions, and analyzed for contamination with heavy metals and subjected to treatment by adsorption of Pb(II), Zn(II), Cu(II), and Fe(II) onto RC-MWS. The trace amounts of Pb(II), Zn(II), Cu(II), and Fe(II) that were detected by ICP-MS in water samples indicated the existence of low concentrations of these heavy metals in some cases. However, by applying the adsorption procedure, the heavy metals were successfully removed from all tested samples. The process for adsorbing Pb(II), Zn(II), Cu(II), and Fe(II) onto RC-MWS is recommended for the optimization of water quality.

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