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Research Article

Biosorption of Cd^{2+} Ni^{2+} and Zn^{2+} from Contaminated Well Water by Garlic Peel

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Abstract: The application of garlic peel was investigated as a low-cost biosorbent for Cd^{2+}, Ni^{2+}, Zn^{2+}, and Pb^{2+} from aqueous solutions in a continuous system. Experiments were carried out in a fixed bed column, and the influence of different flow rates (from 2.0 to 3.3 ml min^{-1}) on the breakthrough was studied. Column data obtained at different conditions were described using the Bohart-Adams, Thomas, and Yan models. The maximum amount of absorption was obtained for a lead ion with the amount of 490.68 mg g^{-1}. The column removed 472.78 and 135.17 mg g^{-1} of cadmium and nickel ions, respectively, and the minimum value was obtained for zinc ions (55.08 mg g^{-1}). The garlic peel was regenerated and reused two to four times in successive biosorption-desorption cycles. Differential pulse voltammetry (DPV) was used to measure kinetic models for the biosorption of lead and cadmium ions on garlic peels. Using DPV for lead and cadmium ions, the amount of adsorbed material was obtained at 2.58 and 2.23 mg g^{-1} using the pseudo 1st order equation and this value was obtained at 8.26 and 4.70 mg g^{-1} using the pseudo 2nd order equation for lead and cadmium ions, respectively. The results show that garlic peel absorbs lead and cadmium ions more than zinc and nickel ions. Because it is made up of several sulfur compounds, sulfur as a soft atom has a stronger interaction with lead and cadmium than other ions.

Keywords**:** biosorption, garlic peel, fixed-bed column, Bohart-Adams, Thomas and Yan models

1. Introduction

Toxic heavy metals such as Hg(II), Cd(II), and Pb(II) in the environment are considered because these metals seriously threaten the health of human populations and natural ecosystems.[1-4] Wastewater from many industries such as mining, textile, painting, electroplating, refining, and pesticides with various heavy metals pollute aquatic ecosystems. Some common techniques such as precipitation, ion exchange, reverse osmosis, nanofiltration[5] and adsorption are used to remove heavy metals.[6-7] Among the various techniques, adsorption is very popular because of its simplicity and low cost.[8-9] Active carbon is one of the most efficient adsorbents for the removal of heavy metals and can remove more than 99% of certain metal ions. However, it is expensive, prohibitively expensive to produce and cannot be regenerated and recycled.[10-11] The materials used in activated carbon adsorption are notably costly. Therefore, there is a constant need to search for an optimal technology taking into account its cost, materials used, regeneration, and efficiency. Biosorption has been proposed to meet these requirements.[12-13] The process of adsorption on the biomaterial has three mechanisms.

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(1) Physical biosorption: this mechanism is due to electromagnetic forces between the molecules of the adsorbent and the biosorbent (in this study: heavy metals), often van der Waals forces make binding between the adsorbent and the biosorbent. This binding causes the substances to be adsorbed and remain on the surface of the adsorbent.[14-15] (2) Chemical biosorption: This mechanism is based on a chemical bond between the biosorbent and the heavy metals, which is stronger than a physical bond, and in addition, the formation of this bond releases heat.[13,16] (3) Exchange biosorption: this mechanism is caused by an electrolytic attraction between ions of opposite charge.[17-18]

In this study, garlic peel is used as a biosorbent. Garlic peel contains organosulfur compounds such as diallyl disulfide (DADS), diallyl trisulfide (DATS), allicin (AL), dimethyl disulfide (DMDS), diallyl sulfide (DAS). These compounds inhibit chemically induced carcinogenesis in various organs of rodents, including the colon.[19-20] Many studies have provided strong evidence that allicin (diallyl disulfide) has caused the creation of most of the biological functions of garlic.[21] The study of the binding between Pb(II),[4] Cd(II),[22] and the organic sulfur compounds of garlic oil is particularly important in modeling the inhibitory effects of garlic on lead poisoning. In terms of Pearson's hard and soft acids and bases, Ni(II), Pb(II), Zn(II), and Cd(II) ions are classified as soft and should therefore form stable complexes with ligands containing sulfur as a soft atom.[23]

In general, zinc is an essential element for human, animal, and plant growth.[24] Zinc is an important component of enzymes in the human body. Each adult needs 15 mg of zinc per day for proper body function. Zinc deficiency can cause skin diseases, muscle weakness, and hair loss.[25-26] Zinc and nickel are also important in plant growth.[27] Although the presence of zinc and nickel ions are not considered dangerous metals, excessive accumulation of these ions in the body can cause poisoning in humans.[28] For example, the presence of too many zinc ions in the body causes the ion to bind to vital enzymes and macromolecules in the body and alter their function.[29] Also, the presence of nickel ions in high concentrations can cause respiratory problems.[30]

The characteristics of a biosorption process are usually studied in many papers.[31-32] They have been classified according to equilibrium isotherms and biosorption kinetics. The isotherms are also important because they can be used to interpret the biosorption mechanism. The biosorption process can be carried out in two modes: batch and continuous. A fixed-column biosorbent is usually used for the continuous process.

The Bohart-Adams, Thomas and Yan model has been widely used to predict the continuous mode curve of an adsorption process in a fixed column.[33-36] In the present study, the effectiveness of garlic peel as a biosorbent for the biosorption of Cd^{2+}, Ni^{2+}, Zn^{2+}, and Pb^{2+} was evaluated. The effect of different flow rates on the adsorption behavior was studied using a continuous column dynamic system. The dynamics of the adsorption process were modeled using the Bohart-Adams, Thomas, and Yan approaches. The adsorption capacity and kinetic constant for garlic peel were also determined.

2. Materials and methods

2.1 *Chemicals and instrument*

Nitric acid (HNO_3, 65%), hydrochloric acid (HCl, 37%), and sodium hydroxide (NaOH) were purchased from Merck. Stock solutions of Cd(II), Ni(II), Zn(II) and Pb(II) (0.01 mol L^{-1}) were prepared by dissolving an appropriate amount of $Cd(NO_3)_2 \cdot 4H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ and $Pb(NO_3)_2$ in doubly distilled water. Atomic absorption analyses were performed using a Varian AA-220 instrument.

2.2 *Sample preparation*

Garlic peel as a biosorbent was obtained from farms in Iran (Zanjan). White garlic was used. It has a milky white flesh with a firm texture and a naturally bright color with clean roots. It has no burnt or dirty skins and is free of mechanical damage. It has higher allicin and alliin content, as well as higher total phenolic, flavonoid, and antioxidant activity compared to other garlic ecotypes. The garlic peel was first pre-treated by the following steps: (1) immersing the sample in distilled water, (2) cutting into uniform approximate lengths of 1 cm, (3) washing with HNO_3 0.1 mol L^{-1}, (4) washing with distilled water, and (5) drying the sample in air.

2.3 *Continuous system*

The adsorption efficiency of garlic peel for removing Cd^{2+}, Ni^{2+}, Zn^{2+}, and Pb^{2+} was investigated using a fixed bed glass column. This column has an inner diameter of 3.0 cm and a length of 30.0 cm. Dry garlic peels were cut into 1 cm particles and packed into the column with plastic filters installed on both sides of the column. The column was packed with glass stone particles to obtain a uniform packing porosity. A solution with an initial concentration of 100 mg L^{-1} of Cd^{2+}, Ni^{2+}, Zn^{2+}, and Pb^{2+} was pumped from a container to the bottom of the column. The solution obtained at the outlet of the column was collected at regular intervals and analyzed by atomic absorption spectrometry (Varian AA-220). All experiments were carried out at an initial pH of 4.50 and 25 °C to prevent the formation of metal hydroxide.[22] The effect of liquid flow rates of 2.0, 2.5, and 3.3 ml min^{-1} was studied. In order to ensure the formation of $C/C_i \approx 1$, each experiment was run for approximately 3-10 h.

2.4 *Fixed bed column data analysis and modeling*

The analysis of experimental biosorption data and the dynamic behavior of the fixed bed column is important because it can help design the optimum conditions for an industrial adsorption process.[37-38] In fixed bed column adsorption, the effectiveness of the biosorbent under specific operating conditions can be evaluated from the effluent concentration versus time profile or volume (breakthrough curve).[39-40] Several models have been used to predict the breakthrough curve and calculate the maximum adsorption capacity of a column and the kinetic constants. These models, Bohart-Adams,[33,36] Thomas,[34,36] and Yan[35-36] are described by Eqs. (1), (2) and (3).

$$\ln\left(\frac{C_0}{C_{eff}}-1\right)=\frac{K_{TH}q_t m}{Q}-\frac{K_{TH}C_0 V}{Q} \tag{1}$$

$$\ln\left(\frac{C_{eff}}{C_0-C_{eff}}\right)=K_Y t-K_Y \tau \tag{2}$$

$$\ln\left(\frac{C_0}{C_{eff}}-1\right)=\frac{K_{BA}N_0 Z}{V}-K_{BA}C_0 t \tag{3}$$

Where C is the effluent solute concentration, C_i is the influent solute concentration, N_0 is the maximum volumetric adsorption capacity in mg L^{-1}, Z is the bed depth in the column in cm, K_{TH} is the Thomas rate constant, Q is the volumetric liquid flow rate, q_t is the maximum metal uptake to the solid adsorbent, m is the mass of adsorbent in the bed (g), V is the cumulative liquid flow volume, and K_{BA} is the Bohart-Adams rate constant. τ is the time required to retain 50% of the initial adsorbate in minutes, and K_Y is the Yan rate constant.

2.5 *Electrochemistry measurement*

A commercial micropotentiostat (PGSTAT 101, Eco-Chemie) was used for all electrochemical experiments (DPV). In all cases, a 2 mm diameter gold electrode (from PGSTAT 101, Eco-Chemie), an Ag/AgCl, KCl (3 mol L^{-1}), and platinum wire were used as working, reference, and counter electrodes, respectively. All electrochemical measurements were performed in a 12 mL cell. To clean the gold electrode, it was abraded with a fine-grade furrier's paper, polished to a mirror-like surface with 0.05 mm Al_2O_3 powder, immersed in NaOH (0.2 mol L^{-1}), and then ultrasonically rinsed with water and ethanol for 3 min.

2.6 *Kinetic models*

Equations (4), (5), and (6) refer to pseudo 1st order, pseudo 2nd order, and *Elovich* models respectively.[41] Where q_1,

q_2, and q_t are the amounts of metal biosorbed at equilibrium and at a given time t respectively. k_1 and k_2 are the first and second-order rate constants respectively. a (in mg g^{-1} min^{-1}) is the amount of adsorbed material per minute and b (mg g^{-1}) is the amount of adsorbent per gram of adsorbent.

$$\ln\left(q_t - q_1\right) = -k_1 t + \ln q_1 \tag{4}$$

$$\frac{t}{q_t} = \frac{t}{q_2} + \frac{1}{k_2 \times q_2^2} \tag{5}$$

$$q_t = \frac{1}{b}\ln t + \frac{1}{b}\ln(a \times b) \tag{6}$$

3. Results and discussions

3.1 *Adsorption Cd^{2+}, Ni^{2+} and Zn^{2+} metal ions in fixed bed column*

To obtain the breakthrough curves for Cd^{2+}, Ni^{2+}, Zn^{2+}, and Pb^{2+}, experiments were carried out with a total operating time of 3-10 h. During this time, the column can be saturated with heavy metal ions under the experimental conditions. The breakthrough curves obtained for optimal conditions are shown in Figure 1. Using these curves, the significant parameters were obtained by the Bohart-Adams, Thomas, and Yan model. Parameters such as the maximum concentration of the solute in the solid phase (q_t), the maximum volumetric adsorption capacity (N_0), the time required to retain 50% of the initial biosorbate (τ), the Bohart-Adams kinetic constant (K_{BA}), the Thomas kinetic constant (K_{TH}) and the Yan kinetic constant (K_Y) were obtained. Figure 2 shows the fit of the experimental data by Bohart-Adams, Thomas, and Yan models and the data are presented in Table 1.

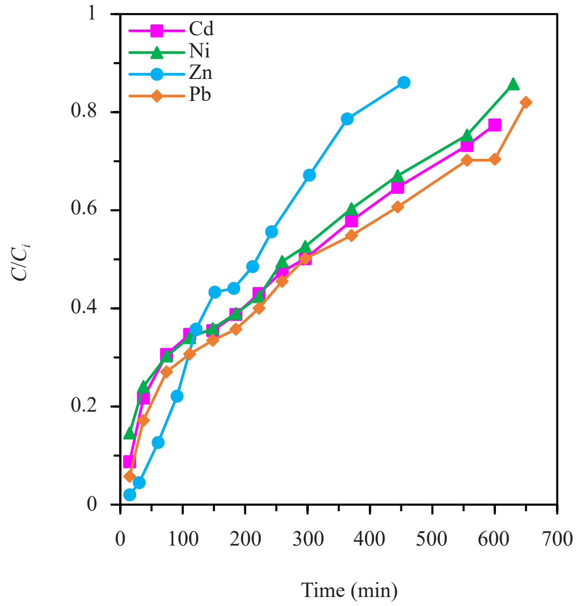
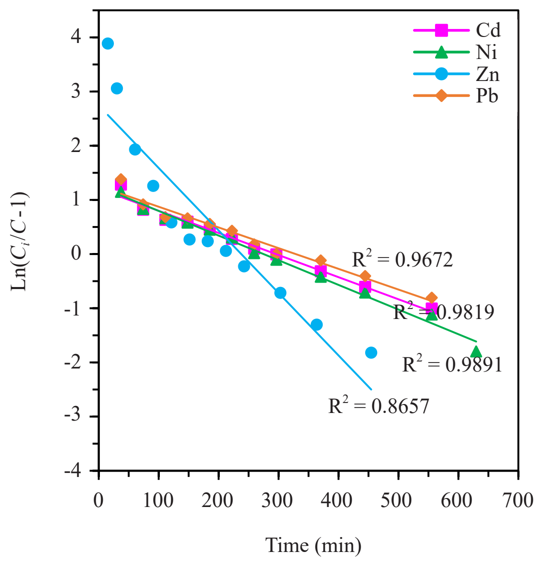
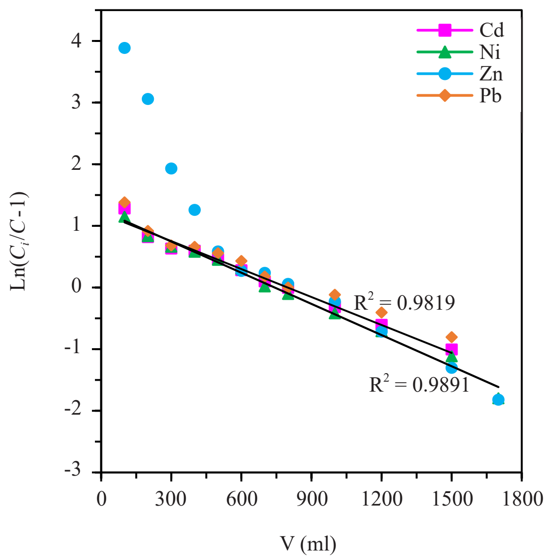


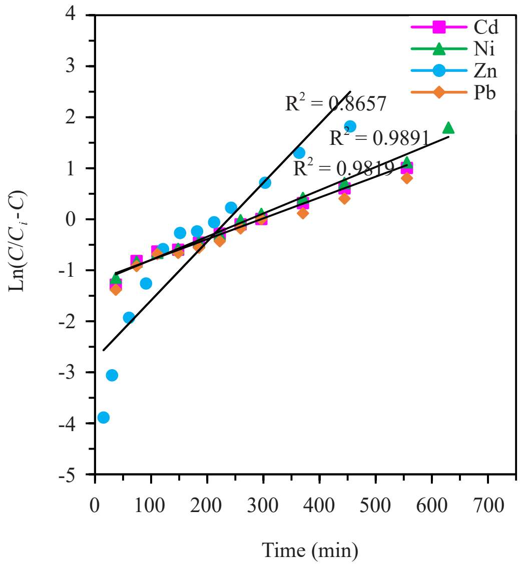
Figure 1. Experimental breakthrough curve for Cd^{2+}, Ni^{2+}, Zn^{2+} and Pb^{2+} removal by garlic peel



(a)



(b)



(c)

Figure 2. a) Bohart-Adams, b) Thomas and c) Yan model for metal adsorption in a garlic fixed bed for Cd^{2+}, Ni^{2+}, Zn^{2+} and Pb^{2+}

Table 1. Predicted parameters from Bohart-Adams, Thomas and Yan model for biosorption of Cd^{2+}, Ni^{2+}, Zn^{2+} and Pb^{2+} on garlic peel

	Flow rate (ml min^{-1})	q_t (mg g^{-1})	N_0 (mg L^{-1})	τ (min)	K_{TH} (L/mg·min)	K_{BA} (L/mg·min)	K_Y (min^{-1})
Cd^{2+}	2.5	472.78	285.24	315.0	2.34×10^{-4}	2.76×10^{-5}	0.004
Ni^{2+}	2.5	135.17	25.80	307.5	3.34×10^{-4}	5.92×10^{-5}	0.004
Zn^{2+}	2.5	55.08	55.17	225.4	1.60×10^{-4}	7.69×10^{-5}	0.013
Pb^{2+}	2.5	490.68	300.54	337.4	2.44×10^{-4}	2.88×10^{-5}	0.0038

3.2 *Effect of flow rate*

The breakthrough parameters for Cd^{2+}, Ni^{2+}, Zn^{2+}, and Pb^{2+} at different flow rates of 2.0, 2.5, and 3.3 ml min^{-1} are shown in Table 2. The results show that by increasing the flow rate from 2.0 to 3.3 ml min^{-1}, the breakthrough curves shift to a lower time scale, and the depletion time decreases. By increasing the flow rate, all the metal ions do not have enough time to penetrate from the solution to the garlic skin and bind with the functional groups of the biosorbent. On the other hand, when the flow rate was increased from 2.0 to 3.3 ml min^{-1}, the removal percentage of Cd^{2+}, Ni^{2+}, Zn^{2+}, and Pb^{2+} decreased to 7.6%, 9.5%, 15.0%, and 8.1% respectively (Table 2). This may be due to the fact that the metal ions would have left the column before the equilibrium between metal ions and biosorbent was reached.

Table 2. The Thomas, Bohart-Adams and Yan models constants for Cd^{2+}, Ni^{2+} and Zn^{2+} removal from metal solution at various flow rates

	Flow rate (ml min^{-1})	q_t (mg g^{-1})	N_0 (mg L^{-1})	τ (min)	K_{TH} (L/mg·min)	K_{BA} (L/mg·min)	K_Y (min^{-1})
Cd^{2+}	2.0	490.02	305.06	345.6	2.23×10^{-4}	2.56×10^{-5}	0.0044
	2.5	472.78	285.24	315.0	2.34×10^{-4}	2.76×10^{-5}	0.004
	3.3	455.52	257.8	275.5	2.54×10^{-4}	2.88×10^{-5}	0.0036
Ni^{2+}	2.0	142.87	23.09	337.5	3.14×10^{-4}	5.98×10^{-5}	0.0032
	2.5	135.17	25.80	307.5	3.34×10^{-4}	5.92×10^{-5}	0.004
	3.3	130.52	24.53	273.0	3.44×10^{-4}	6.12×10^{-5}	0.0047
Zn^{2+}	2.0	57.09	57.89	241.5	1.59×10^{-4}	7.539×10^{-4}	0.0125
	2.5	55.08	55.17	225.4	1.60×10^{-4}	7.69×10^{-4}	0.0134
	3.3	51.77	49.88	201.0	1.79×10^{-4}	7.89×10^{-4}	0.014
Pb^{2+}	2.0	520.03	315.26	364.6	2.45×10^{-4}	2.69×10^{-5}	0.0045
	2.5	490.68	300.54	337.4	2.44×10^{-4}	2.88×10^{-5}	0.0038
	3.3	478.22	269.7	295.7	2.67×10^{-4}	2.98×10^{-5}	0.0035

Tables 1 and 2 show that higher amounts of Pb^{2+} and Cd^{2+} are biosorbed by the adsorbent compared to Ni^{2+} and Zn^{2+} ions. Lead and cadmium ions are biosorbed 3.6 and 3.5 times more than nickel ions and 8.9 and 8.5 times more than Zn ions on garlic peel biomass. Organosulfur compounds comprise the bulk of garlic and its derivatives, such as oil, peel, stems, etc.[4,22] Therefore, it is able to easily absorb soft metal ions by considering the soft character of sulfur atoms.[42] Cd^{2+} is softer than Ni^{2+} and Zn^{2+} ions. So, sulfur compounds as soft Lewis bases can efficiently absorb Cd^{2+} ions.

In addition, the biosorption of metal cations on the garlic peel biosorbent may involve three steps: 1) migration of ions from the solution to the biosorbent surface, 2) biosorption of metal cations on the biosorbent surface, 3) migration of metal cations not adsorbed on the biosorbent surface into the solution and out of the biosorbent column.[43] The radii of lead, cadmium, nickel, and zinc ions are 119, 97, 83, and 75 Å, respectively. Therefore, according to the order of ion radius, lead, and cadmium ions appear to migrate more slowly and leave the biosorbent column. Consequently, they spend more time in contact with the biosorbent column and have more opportunities to be absorbed. Zinc and nickel have a higher charge density on their surface due to their smaller radius than cadmium ions. This causes more solvent molecules to bind to them. As a result, these ions are occupied and require more time and energy than cadmium ions to bind to the adsorbent surface.[44]

3.3 *Real sample*

The real samples of heavy metal ions have complex matrixes. Groundwater, environmental samples, and well water have also some amounts of alkaline/earth metal ions.[45-46] Therefore, a suitable adsorbent should be able to remove heavy metal ions in the presence of an excess of other coexisting species, such as cationic and anionic species. In this study, garlic peel was used as a biosorbent to remove heavy metal ions from well water in the presence of Fe^{3+}, SO_4^{2-}, Mg^{2+}, and other ions. Before using the well water, the amount of heavy metals in the well water was measured, and then an appropriate amount of heavy metal was spiked into the well water (see Table 3). The biosorption capacity of Ni^{2+} and Zn^{2+} from well water was reduced by about 10-20%. However, for Pb^{2+} and Cd^{2+}, it was reduced by about 65% and 68% (Figure 3). The presence of other ions in well water and the higher affinity of alkaline/earth metal ions for the amine and sulfur sites of the adsorbent cause saturation of the garlic skin surface.[47] Therefore, there is the limited position available for binding Pb^{2+} and Cd^{2+} with garlic peel in competing alkaline/earth metal ions. The data in Table 4 indicate that the garlic peel biosorbent can sufficiently remove the heavy metal ions from the well water in the presence of other coexisting ions.

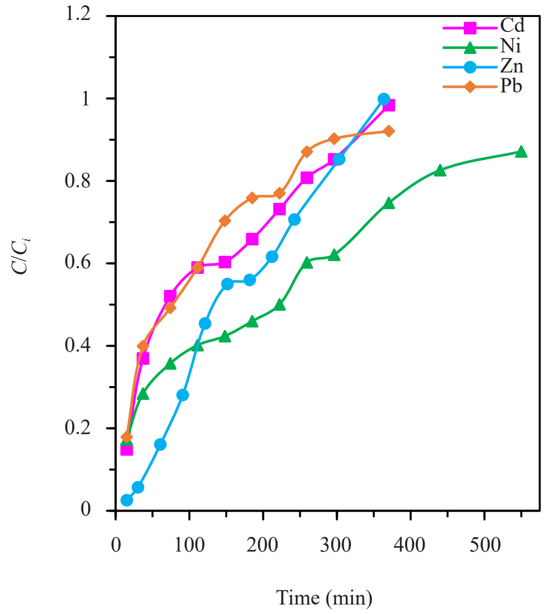


Figure 3. Removal of Cd^{2+}, Ni^{2+}, Zn^{2+} and Pb^{2+} from well water with adsorption on the garlic peel

Table 3. The amount of Cd^{2+}, Ni^{2+}, Zn^{2+} and Pb^{2+} before and after spike in well water

Amount metals (mg L^{-1})	Cd^{2+}	Ni^{2+}	Zn^{2+}	Pb^{2+}
before spike	0.08	0.35	0.23	0.002
After spike	34.8	72.50	82.0	70.40

Table 4. Predicted parameters from Thomas, Bohart-Adams and Yan model for biosorption of Cd^{2+}, Ni^{2+}, Zn^{2+} and Pb^{2+} on garlic peel in well water

	Cd^{2+}	Ni^{2+}	Zn^{2+}	Pb^{2+}
q_t (mg g^{-1})	147.06	100.24	41.41	168.97
N_0 (mg L^{-1})	89.90	27.80	48.87	95.96
τ (min)	94.0	245.0	170.0	108.21
K_{TH} (L/mg·min)	3.98×10^{-4}	4.01×10^{-4}	2.39×10^{-4}	4.08×10^{-4}
K_{BA} (L/mg·min)	4.69×10^{-5}	6.92×10^{-5}	9.89×10^{-4}	4.98×10^{-5}
K_Y (min^{-1})	0.0070	0.0046	0.0148	0.080
Flow rate (ml min^{-1})	2.5	2.5	2.5	2.5
Bed high (cm)	2.0	2.0	2.0	2.0

3.4 *Desorption*

The desorption capacity of garlic peel was evaluated by HCl and HNO_3 acid treatment. The 0.5 mol L^{-1} HNO_3 was found to be more effective than other concentrations and better than HCl. The adsorbent was reused in four consecutive biosorption-desorption cycles for Cd^{2+}, Ni^{2+}, Zn^{2+}, and Pb^{2+} and three and two reuse cycles, respectively. It can be concluded that garlic peel is suitable for practical applications for the removal of Cd^{2+}, Ni^{2+}, Zn^{2+}, and Pb^{2+} from wastewater and any other polluted water. Table 5 shows the results of the desorption of the garlic peel column. The results of Table 5 show that the maximum amount of adsorbed ions on the garlic peel for lead and cadmium ions decreased more than nickel and zinc ions. This is because lead and cadmium ions are considered to be soft ions that easily bind to the sulfur of the garlic peel, which is also a soft element, and this bond is difficult to break. However, nickel and zinc ions are soft and hard intermediate ions, and their bond with sulfur is not as strong, so this bond is easier to break.

Table 5. Predicted parameters from desorption of biosorption for Cd^{2+}, Ni^{2+}, Zn^{2+} and Pb^{2+}

	Number cycles of reuse	q_t (mg g^{-1})	% Loss of adsorption capacity compared to the first cycle
Cd^{2+}	3	285.5, 260.90, 290.80	38.6%
Ni^{2+}	4	142.50, 123.40, 125.67, 122.67	8.6%
Zn^{2+}	4	49.80, 51.02, 47.09, 48.80	5.7%
Pb^{2+}	3	315.2, 290.40, 335.90	35.7%

3.5 *Differential pulse voltammetry study of Pb^{2+} and Cd^{2+} biosorption on garlic peel*

An atomic absorption spectrometer is used to measure the amount of heavy metals. This device converts heavy metals into vapor for measurement.[48-49] Steam control is a difficult task and can cause many diseases and cancers.[49] Therefore, it is better to look for a suitable method and device to measure these metals with less risk. Using a solution instead of steam to measure heavy metals reduces the risk of many diseases. One of the methods used to measure metals in solution is the voltammetric method. These methods have a low detection limit and can measure heavy metals with high accuracy.[50] Because lead and cadmium ions are unnecessary and toxic metals for the body, breathing the vapors produced by atomic absorption of these metals is harmful to humans. Therefore, voltammetric methods such as DPV can be used to measure lead and cadmium ions. To study the biosorption of lead and cadmium ions on garlic skin, DPV, and kinetic models were used to show that the process of biosorption of these toxic ions on the adsorbent can be studied with less risk.

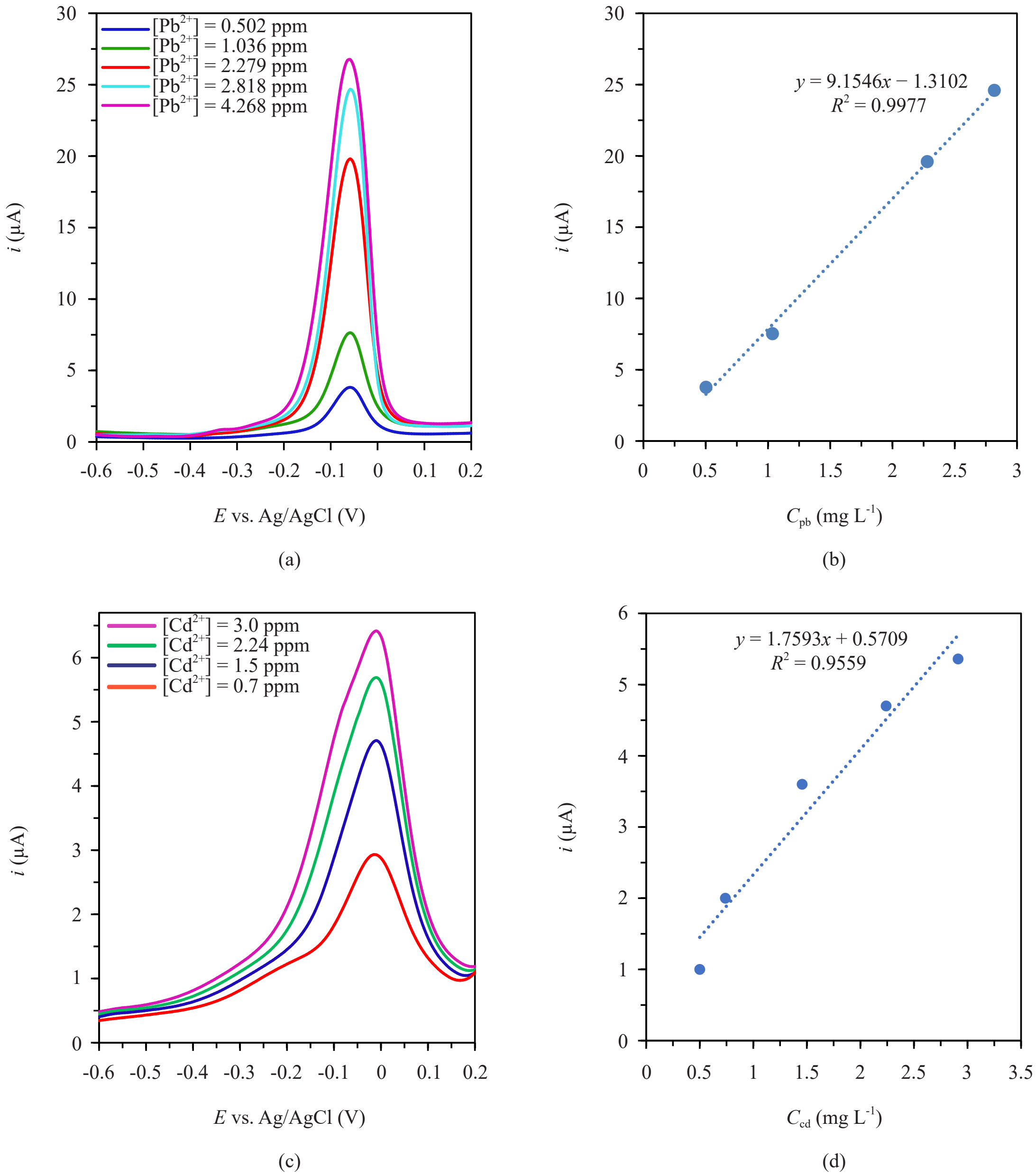


Figure 4. The voltammogram for (a) Pb^{2+} and (c) Cd^{2+} in the different concentrations, and the calibration curve for the (b) Pb^{2+} and (d) Cd^{2+}

To measure lead and cadmium ions with DPV, it is first necessary to determine the concentration ranges in which the relationship between concentration and current is linear. This range is shown in Figure 4 for both ions. The curve for both is linear in the concentration range 0.3 to 3 mg L^{-1}. Above 3 mg L^{-1}, the peaks of both ions become forked, which is not acceptable. Now 100 ml of 100 mg L^{-1} lead or cadmium ion is placed in a container. To this is added 1.5 g of garlic peel biosorbent. The solution is rotated on a magnetic stirrer at 300 rpm for various times in contact with the biosorbent. The solution is then filtered, and a voltammogram is prepared to check the amount of ions remaining in the solution. These voltammograms are shown in Figure 5.

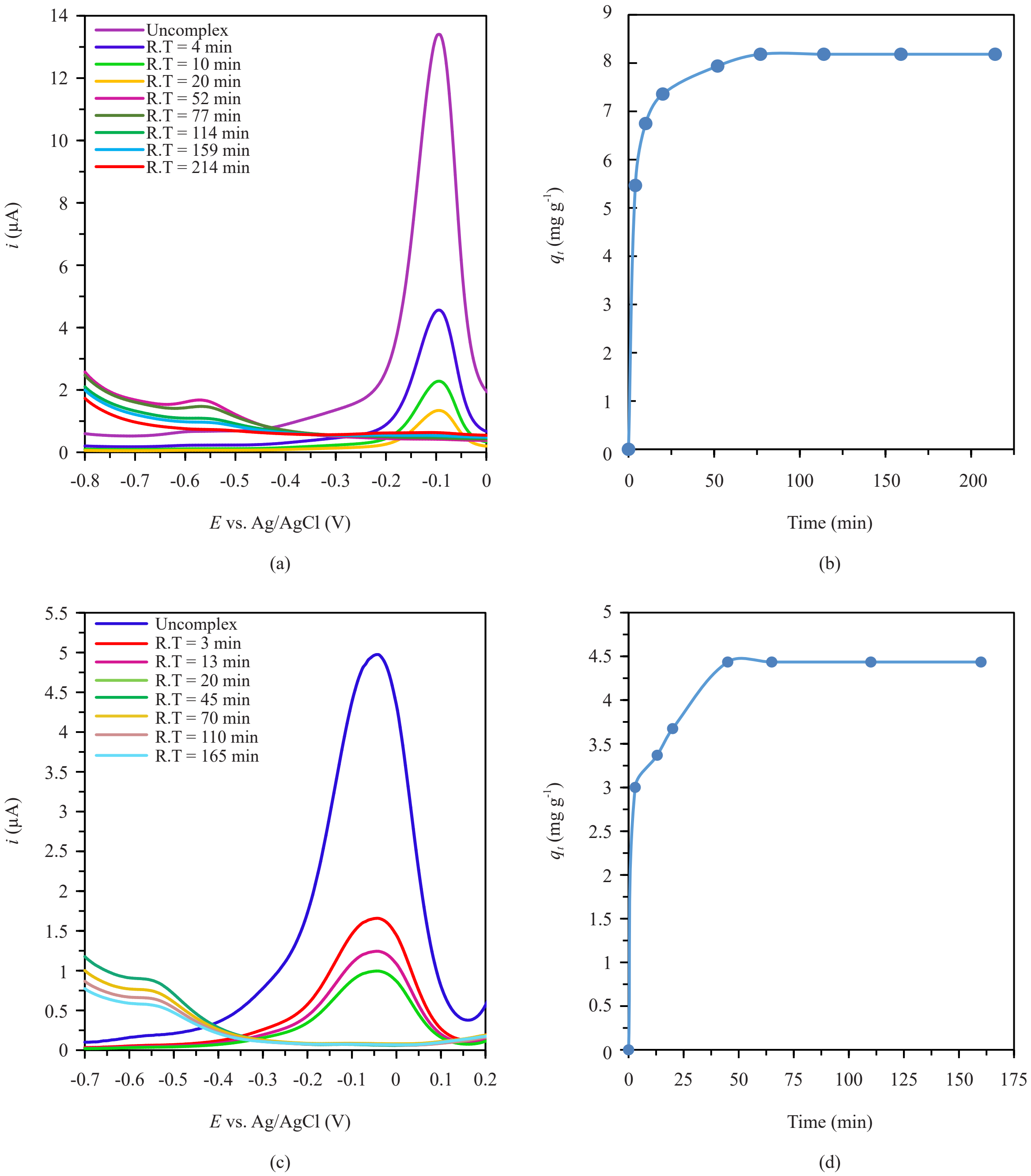


Figure 5. The DPV for solution rotates at different times in contact with the biosorbent on a magnetic stirrer at 300 rpm and 100 ml 100 mg L^{-1} from (a) Pb^{2+} and (c) Cd^{2+}, and the time evolution of sorption capacity for the (b) Pb^{2+} and (d) Cd^{2+}

The results concerning the biosorption kinetics of lead and cadmium ions using DPV are presented in Table 6. The results of this table show that the biosorption of lead ions on garlic peel is more than cadmium ions. The amount of biosorbed material was 2.58 and 2.23 mg g^{-1} using the pseudo 1st order equation for lead and cadmium ions, respectively and 8.26 and 4.70 mg g^{-1} using the pseudo 2nd order equation for lead and cadmium ions respectively. *a* and *b* from the *Elovich* equation were 85.44 mg g^{-1} min^{-1} and 1.04 mg g^{-1} for lead ion and 2.8 mg g^{-1} min^{-1} and 0.27 mg g^{-1} for cadmium. This is because the radius of lead ion was larger than that of cadmium and it moved slower than that of cadmium ion, giving it a greater chance of biosorbing on garlic peel than other ions. The same result was obtained in atomic absorption spectroscopy (AAS). In addition, in this work, kinetic data is presented using an atomic absorption device. The difference between the values obtained by DPV and AAS may be partly related to the sulfur compounds released into the solution by the garlic peel. A large proportion of garlic peel consists of sulfur compounds. Sulfur compounds in solution can also form complexes with cadmium and lead ions, reducing the flow of free lead and cadmium ions in solution. This is the case when the atomic absorption method is used, it breaks down the complex of lead and cadmium ions for the measurement of them. Figure 6 shows the peak of the presence of sulfur compounds in solution at a potential of -0.57 volts. From these results, it can be seen that even if some lead and cadmium ions cannot be adsorbed on the biosorbent surface, with the presence of sulfur compounds in the solution they are not free and form a complex and the severity of the risk in the solution is reduced. According to the results obtained from DPV, it can be concluded that this method is suitable for the measurement of heavy metal ions and even one of the advantages of DPV method over AAS is that it can evaluate the presence of some biosorbent compounds in the solution. Therefore, the toxicity of the solution removed from the adsorbent can be investigated.

Table 6. The results related to the biosorption pseudo 1st order, pseudo 2nd order and *Elovich* equation of lead and cadmium ions using DPV

	Pseudo 1st order			Pseudo 2nd order			*Elovich*		
	q_1	K_1	R^2	q_2	K_2	R^2	*a*	*b*	R^2
Pb (DPV)	2.58	0.038	0.94	8.26	0.054	0.99	85.44	1.04	0.96
Pb (AAS)	3.13	0.010	0.94	7.90	0.015	0.99	13.64	1.00	0.95
Cd (DPV)	2.23	0.046	0.98	4.7	0.12	0.99	2.8	0.27	0.99
Cd (AAS)	3.01	0.008	0.92	4.2	0.09	0.99	2.1	0.25	0.99

Using voltammetry, we can also absorb zinc and nickel ions with garlic peels. However, since the two ions of cadmium and lead are more toxic than the other ions and unnecessary for the body, we have shown the results for this ion to show that the absorption of heavy metals by garlic peel can be done using voltammetry instead of atomic absorption.

Table 7 shows a comparison between the heavy metal adsorption capacity of garlic peel and other adsorbents. From this comparison, it can be concluded that garlic peel has a high affinity for binding and absorbing heavy metals due to the presence of sulfur compounds in its structure.

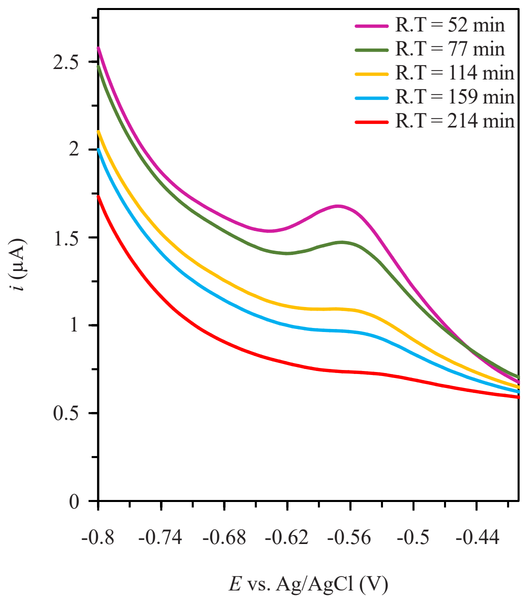


Figure 6. DPVs for solution rotate at different times in contact with the biosorbent and release sulfur compound in solution

Table 7. The comparison between the adsorption capacity of garlic peel to remove heavy metals with other adsorbents

Metal ion	Absorbent	q_t (mg/g)	N_0 (mg/L)	τ (min)	Flow rate (ml/min)	Ref.
Cd^{2+}	Wheat straw	19.8	311	230	1.0	51
Pb^{2+}	Melanin impregnated activated carbon	11.61	2.63 mg/g	-	0.5	52
Pb^{2+}	Melanin-coated PVDF membranes	2.49	-	249.55	0.5	53
Ni^{2+} Zn^{2+}	Clay minerals	-	-	$C/C_0 = 0.1$ 170 160	0.8 0.8	54
Pb^{2+} Cd^{2+} Ni^{2+} Zn^{2+}	Activated charcoal derived from Neem Leaf Powder (Ac-NLP)	205.6 154.5 120.6 133.3	9,557.5 9,025.2 8,956.1 8,356.9	-	-	55
Pb^{2+} Cd^{2+} Zn^{2+}	Multi-Metal Binding Biosorbent (MMBB)	108.12 38.25 35.23	-	-	10	56
Pb^{2+} Zn^{2+}	Hydrolyzed olive cake	13.22 4.58	-	585 595	-	57
Pb^{2+} Cd^{2+} Ni^{2+} Zn^{2+}	Garlic peel	490.68 472.78 135.17 55.08	300.54 285.24 25.80 55.17	337.4 315.0 307.5 225.4	2.5 2.5 2.5 2.5	This work

4. Conclusion

Garlic peel has the potential to be an effective biosorbent for the removal of Cd^{2+}, Ni^{2+}, Zn^{2+}, and Pb^{2+} from polluted water. The Thomas, Adams, and Yan models can be fitted to the progress curves obtained under different column conditions. The results obtained by analyzing the progress curves at different column flow rates showed that the adsorption capacity could be increased by reducing the flow rate from 3.3 to 2 mL min^{-1}. This bioabsorbent is renewable and can be used several times. For each column condition, the biosorption capacity of the metal ions studied was in the order of $Pb^{2+} > Cd^{2+} > Ni^{2+} > Zn^{2+}$, indicating that garlic peel has a higher affinity for binding Pb^{2+} than other ions. In addition, the adsorption of lead and cadmium ions was studied using DPV. Information from this method was used to test the pseudo 1st order, pseudo 2nd order, and *Elovich* kinetic models.

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Conflict of interest

The authors declare no competing financial interest.

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