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RESEARCH ARTICLE - CHEMICAL ENGINEERING

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Removal of Heavy Metals from Waste Water Using Black Teawaste

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Abstract Removal of heavy metals (Cobalt, Cadmium, and Zinc) from waste water was possible using black teawaste. Adsorption was observed for the three metals at 180 min. Under our experimental conditions, pH plays an important role in the adsorption process, particularly on the adsorption capacity of teawaste for the heavy metals under study. The pH level allowing for an optimum rate of adsorption was found to be 6 for Co, Cd, and Zn. We demonstrate that black teawaste has a relatively high adsorption capacity for these heavy metals; the quantities adsorbed per a half gram of black teawaste at equilibrium (q_e) are 15.39 mg/g for Co, 13.77 mg/g for Cd, and 12.24 mg/g for Zn. It was found that the percentage of removed metal ions is inversely proportional to initial metal ions concentration, but correlates with teawaste adsorbent dosage. The adsorption of heavy metals on black teawaste is described by an isotherm of type I and is fully verified by the Freundlich and Langmuir isotherms. The kinetics of the Cobalt, Cadmium, and Zinc adsorption on the teawaste were found to follow a pseudo first-order rate equation. This method has the advantage of being applicable in developing countries due to the low cost and availability of teawaste.

Keywords Teawaste · Heavy metal removal · Cobalt · Cadmium · Zinc · Isotherms · Kinetics

الخلاصه

وجد أنه من الممكن إزالة المعادن الثقيلة (الكوبالت والكادميوم والزنك) من مياه الصرف الصحي باستخدام نفايات الشاي الأسود. وقد وجد أن الامتزاز جرى للمعادن الثلاثة في 180 دقيقة. وفي ظل ظروفنا التجريبية فإن الرقم الهيدروجيني يلعب دورا هاما في عملية الامتزاز، وبخاصة على قدرة الامتزاز. والرقم الهيدروجيني للمحلول له تأثير كبير على قدرة الامتزاز من مخلفات الشاي للمعادن الثقيلة التي شملتها الدراسة. لقد وجد أن المعدل الأمثل للامتزازهو عند الرقم الهيدروجيني 6 للكوبلت والكادميوم والزنك. وتبين أن مخلفات الشاي الأسود لديها قدرة عالية نسبيا على امتزاز هذه المعادن الثقيلة؛ الكميات الممتزة في نصف غرام من مخلفات الشاي الاسود في حالة التوازن هي 15.39 مغ / غم للكوبلت، 13.77 مغ / غم للكادميوم و12.24 مغ / غم للزنك. لقد وجد أن نسبة الإزالة تقل بزيادة التركيز الابتدائي لأيونات المعدن، بينما تزداد هذه النسبة بزيادة وزن المادة الممتزة. لقد تم تمثيل الامتزازبشكل تام عن طريق أيزوثيرم من نوع فريندلخ ولانكماير. وقد وجد أن حركية الامتزاز للكوبالت والكادميوم والزنك على مخلفات الشاي تتبع معادلة من الدرجة الأولى الزائفة. ولهذا الامتزاز مزايا كونه من الممكن تطبيقه في البلدان النامية نظرا لانخفاض التكلفة وتوافر مخلفات الشاي.

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1 Introduction

The elimination of metal ions from aqueous solutions by biosorption plays an important role in water pollution control and has become a matter of concern over the last few decades. Toxic heavy metal contamination of industrial wastewater is an important environmental problem due to its non-biodegradability and persistence, leading to its accumulation in the environment, including the food chain, and may thus pose a significant danger to human health [1,2]. Many industries, such as the automotive, metal-finishing, electroplating, tannery, steel and textile industries as well as the manufacture of electrical equipment, paints, alloys, batteries, pesticides or preservatives, release various concentrations of heavy metals such as lead, cadmium, zinc, cobalt, nickel, copper, etc. The commonly used procedures for removing metal ions from effluents include chemical precipitation, lime coagulation, ion exchange, and solvent extraction [3]. These techniques, apart from being economically expensive, have disadvantages such as incomplete metal removal as well as high reagent and energy requirements. The widespread industrial use of low-cost adsorbents for wastewater treatment is thus highly desirable at present, due to their local availability, technical feasibility, engineering applicability and cost effectiveness [4]. Consequently, several serious efforts have been undertaken to find adequate efficient and low-cost materials. For instance, most agricultural waste or by-products are considered to be low-value products. Different types of biomass have been investigated for biosorption of Cr, Co, Ni, Zn, Pb and Cd. These include wool, rice, straw, coconut husks, peat moss, exhausted coffee [5], walnut skin, coconut fiber [6], cow bone charcoal [7], defatted rice bran, rice hulls, soybean hulls and cotton seed hulls [8,9], wheat bran, hardwood sawdust, pea pod, cotton and mustard seed cakes [4,10] and others.

Tea is one of the world's most popular beverages. Indeed, about 3.5 million tons of tea are consumed worldwide annually. A big volume of spent tealeaf or tealeaf residue is thus released into the environment through daily tea drinking, including instant tea ready-to-drink teas.

In recent years, there has been an interest in the use of used black tea leaves as a low cost adsorbent because of their high capacity for heavy metals removal. Some of the investigations have been mainly focused on the conformational aspects of their removal or sorption capacities. Others, however, have been interested in kinetics, an important physicochemical factor in evaluating the basic qualities of an adsorbent as well as the application of the adsorption process. Hossain et al. [11] carried out Kinetic investigations to evaluate the applicability of used black tea leaves to the removal of chromium(VI) from aqueous solutions. The effects of various kinetic parameters were investigated using a batch process. They found that adsorption of Cr(VI) on tea waste occurs rapidly in the first day, and is followed by a slow process that requires more than 10 days to reach its equilibrium. The rate of adsorption was found to be affected by the processing conditions such as the initial Cr(VI) concentration, solution pH, temperature and foreign ions.

Amarasinghe and Williams [12] conducted batch experiments to determine the factors affecting kinetics and adsorption of copper and lead ions onto tea waste from aqueous solutions. Fixed bed column experiments were performed to study practical applicability, leading to breakthrough curves being obtained. Tea waste is capable of binding significant amounts of Pb and Cu from aqueous solutions. The adsorption capacity was highest at solution pH range 5–6. The adsorbent-to-solution ratio and the metal ion concentration in the solution affect the degree of metal ion removal. Pb showed higher affinity and adsorption rates compared to Cu under all experimental conditions.

Yoshita et al. [13] prepared an adsorbent using spent tea leaves and used it to remove lead (Pb) from the solution. The Pb removal by the spent tea leaf adsorbent depend on its pretreatment, adsorption contact time and adsorbent dosage.

Antonio and Roberto [14] showed that removal efficiencies of up to 98–99 % can be achieved when using spent tea leaves as lead adsorbent. The results were only marginally affected by the type of tea waste used. At low-lead loading, the adsorption equilibrium was well described by the Langmuir equation, with a maximum adsorption capacity of 83–130 mg/g and an equilibrium constant ranging from 0.112–0.245 L/mg. A comparison with other adsorbents provided the following order for lead removal efficiency: Black tea, coffee grounds > green tea > Fuller's earth > activated carbon.

The aim of this research is to develop inexpensive and effective heavy metals adsorbents from abundant sources of natural waste, such as tea waste, to replace existing commercial materials. However, there have been few studies on the utilisation of black tea waste. The present study aims at using black tea waste as adsorbent to remove cobalt, cadmium and zinc from aqueous solutions. To our knowledge, no such study exists for cobalt adsorption on black teawaste. Moreover, there are few studies on the lack of adsorption kinetics of zinc on black teawaste. In our work, the impact of solution pH, initial metal ions concentration, shaking time and solid/liquid ratio on the removal of metal ions by teawaste biosorbent were studied.

The adsorption equilibrium was described using Langmuir and Freundlich adsorption isotherms. The pseudo first-order (Langergren), pseudo second-order, and second-order rate models were investigated so as to determine the adsorption kinetics.

2 Materials and Methods

2.1 Biosorbent Materials

Used black tea leaves were obtained after extracting tea liquor from fresh leaves by boiling them in distilled water for 2 h. The tea liquor was then repeatedly leached with excess 0.01 M NaOH solution (30 g teawaste in 800 mL solution) at 50°C for 20 min with decanting and replacement of the NaOH until the yellow colour of the solution was no longer observed (2–3 solution changes). Afterward, the used black tea leaves were suspended in 0.01 M HNO_3 and poured through a filter funnel containing a Whatman 114 filter and then washed repeatedly with deionized water until a pH close to 7.0 was achieved. Finally, the tea leaves were dried at 100 °C for 24 h and then sieved out in a diameter of 0.25–0.50 mm. For preservation, they were kept in sealed polythene bags. In order to minimise contact with humidity all bottles were preserved in desiccators until the time of use.

Preliminary experiments employed black tea waste leached with deionized water only, and our subsequent work showed that this adsorbent continued to release soluble tea material on subsequent exposure to the aqueous solution. This complicates adsorption by competing for the metal cations. However, the alkali-leached material released very little coloured material.

2.2 Characterisation of Black Teawaste Sorbent

The specific surface area of the sorbent was determined using the methylene blue (MB) sorption method, as described elsewhere [15]. In brief, methylene blue aqueous solutions, in a concentration range of 10–50 mg/L, were allowed to agitate with 0.1 g of sorbent till the attainment of equilibrium. The concentration of MB solutions was determined at 664 nm. The adsorption isotherm data thus obtained (Fig. 1) was used to calculate specific surface area as per the equation below:

$$S_s = (M_f N/10^5) A_m 10^{-20}\ \mathrm{m^2/g} \tag{1}$$

where M_f is the amount of MB (in µmol) adsorbed per 100 g of the sorbent when the surface is completely covered with a monolayer of MB, N is the Avogadro number, and A_m is the cross-sectional area per molecule on the surface (130 A^2).

The value of M_f was obtained by extrapolating the isotherm to the q_e axis, and thus taken as a point of monolayer coverage. The calculated surface area is (192 m^2/g).

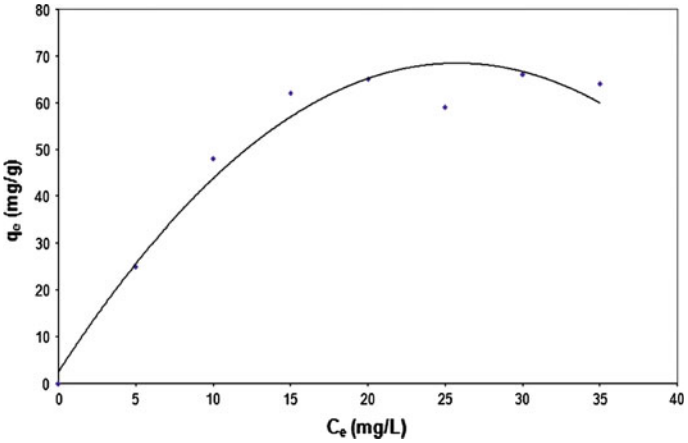

Fig. 1 Langmuir isotherm for methylene blue uptake on black teawaste

2.3 Reagents and Solutions

All chemicals were of analytical grade. Double-distilled water was used throughout. Standard Cd, Zn, and Co solutions with five different concentrations of 5, 15, 30, 50 and 100 mg/L were prepared synthetically using their metal salts. The pH of the solutions was adjusted using 0.1 N HCl or NaOH.

2.4 Biosorption Studies

A stock solution of metal ion was prepared by dissolving calculated amount of ultra pure metal salt in double-distilled water. All reagents were of analytical reagent grade. Biosorption experiments were performed in a rotary shaker at 120 rpm and at 25 °C using a 250 ml Erlenmeyer flask containing three different amounts of teawaste adsorbent: 0.5, 1.5 and 3 g in single solution, and 150 ml of 5, 15, 30, 50, and 100 mg/L solution. The experimental set was repeated for various time intervals of 15, 30, 60, 120, 180, 240 and 300 min. At the end of each contact time, the content of each flask was filtered using Whatman filter paper No. 1 to remove the suspended mass and was then analysed for residual pollutant.

Preliminary studies were performed to study the effect of pH on metal sorption using black tea, and to choose the optimum pH for a strong binding of the metals to the adsorbent. Six one and a half gram adsorbent were each suspended in a 150 mL of (5 mg/L) metal solution. Each solution corresponds to a pH value and blanks was also prepared at the various pHs. The suspension was agitated and the pH of the suspension was adjusted to the required value by adding dilute NaOH or HCl as required. pH buffers were avoided since they could compete as ligands for the metal cations. The final suspensions were further agitated for 3 h and then filtered and analysed. The pHs of the mixtures were varied as 2, 4, 6, 8, 10 and 12.

The kinetics study was carried out by agitating 250 mL flasks containing 1.5 g of adsorbent and 150 mL metal solutions with five different initial concentrations ranging from 5 to 100 mg/L of metal ion in a water bath shaker. The mixture was agitated at 120 rpm and 25 °C. The contact time ranged from 0 to 300 min. At predetermined times, the flasks were withdrawn from the shaker and the suspensions were filtered through Whatman filter paper No. 1. All the experiments were performed in duplicate and the presented results are based on averages. The filtrate samples were analysed for the target pollutant. Langmuir and Freundlich models were applied to the adsorption isotherm and different constants were generated. The Langmuir and Freundlich adsorption parameters and correlation coefficients were also calculated from the adsorption isotherm data.

The concentrations of Cd(II) and Zn(II) were determined by standard EDTA titration. 0.1 % xylenol orange was chosen as indicator and 30 % hexamethylene tetramine was used as buffer solution. The concentration of Co(II) was determined by a spectrophotometer. The wavelength used for monitoring Co(II) was 530.0 nm. A mix of 15 % sulfuric acid, 15 % phosphoric acid as oxidant, and 20 % sodium acetate was used as buffer solution [16].

A CECIL CE 3021 UV-Visible Spectrophotometer was used to measure absorbance levels of all analytical species. All spectral measurements were performed using the blank solution as a reference. Measurements of pH were carried out on a LaMotte pH meter using combined glass electrodes.

2.5 Data Evaluation

Based on the metal concentrations measured before and after the adsorption (C_o and C_e, mg/L, respectively) and the dry weight of the biosorbent (W, g), as well as the volume of aqueous solution (V, L), the uptake capacity of metal ion (q, mg/g) and the removal percentage (R, %) were calculated according to Eqs. (2) and (3):

$$q = \frac{(C_\mathrm{o} - C_\mathrm{e})\ V}{W}\quad R(\%) = \frac{C_\mathrm{o} - C_\mathrm{e}}{C_\mathrm{o}} \times 100 \tag{2}$$

Different sorption models were used to perform comparisons with experimental data [17].

2.5.1 Langmuir Model

The Langmuir model is based on three assumptions: that maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, that the energy of adsorption is constant and that no migration of adsorbate molecules occurs in the surface plane. The Langmuir isotherm is given by:

$$q_e = \frac{b\,q_m\,C_e}{1 + b\,C_e} \tag{3}$$

where q_e is the amount of metal adsorbed per unit mass of adsorbent at equilibrium, (mg/g), C_e is the equilibrium concentration in solution (mg/L), q_m is the maximum metal uptake capacity under the given conditions (mg/g), and b is the equilibrium constant related to the heat of adsorption.

2.5.2 The Freundlich Model

The Freundlich isotherm model is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface. It assumes that different sites with several adsorption energies are involved. The Freundlich adsorption isotherm is the relationship between the amounts of metal adsorbed per unit mass of adsorbent, q_e, and the concentration of the metal at equilibrium, C_e.

$$q_e = K_f\,C_e^{1/n} \tag{4}$$

where K_f and n are the Freundlich constants characteristic of the system. K_f and n are the indicators of the adsorption capacity and adsorption intensity, respectively.

2.6 Kinetic Modelling

The kinetics of metal ions biosorption were modelled using the pseudo first-order (Langergren), pseudo second-order, and second-order rate equations, presented as Eqs. 6–8, respectively [18]:

$$\ln\left(1 - \frac{q_t}{q_e}\right) = -K_1 t \tag{5}$$

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{6}$$

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + K t \tag{7}$$

where q_e and q_t are the amounts of the metal ions adsorbed (mg/g) at equilibrium and at time t (min), respectively, K_1 is the pseudo first-order rate constant (1/min); and K_2 and K are the pseudo second-order and second-order rate constants of adsorption, (g/mg/min), respectively.

3 Results and Discussion

3.1 Effects of Adsorbent Dose

Table 1 shows the removal percentage from the initial concentration of Cobalt, Cadmium, and Zinc in the solution after a 3-h contact time, and for different amounts of adsorbent. Figure 2a–c presents the removal percentages from the initial concentration for various initial concentrations of the metals, with different amounts of adsorbent. As they make clear, teawaste is an excellent adsorbent for the removal of heavy metals from wastewater. The adsorption rate is dependent on the adsorbent quantity as well as the initial concentration of metal in the synthetic solutions. The percentage of heavy metals removal increased with the increase in the teawaste's adsorbent dosage. This is due to the increased adsorbent surface area and availability of more adsorption sites resulting from the increased dosage of the adsorbent. However, the removal percentage levels did show an almost linear regression relationship with the adsorbent dosage. Under the present experimental conditions, 80 % removal of cobalt from a 5 mg/L solution was possible by applying 0.5 g teawaste, although the same amount of adsorbent was not enough to treat a 100 mg/L cobalt solution to more than 51 % approximately. However, by increasing the amount of teawaste to 3 g, it was possible to increase the efficiency of adsorption to about 70 % for the same solution (100 mg/L C_o). As a result, a better treatment is achieved using higher amounts of teawaste. As this adsorbent is cheap and available, increasing consumption levels would be relatively unproblematic.

Table 1 Percentage removal of residual metal after adsorption by teawaste

Metal	W (g)	% R				
		5	15	30	50	100
Co	0.5	80.2	73	68.5	65.2	51.3
	1.5	94.3	91.2	83.4	74.4	62.7
	3	100	96.1	91.7	79.6	70.1
Cd	0.5	75.2	67.7	62.5	59.1	45.9
	1.5	90.7	85.1	81.3	69.7	56.1
	3	94.3	90.4	87.8	73.2	63.8
Zn	0.5	71.1	61.3	57.0	53.4	40.8
	1.5	87.1	80.6	74.2	61.6	51.25
	3	90.5	86.15	81.8	67.3	58.41

3.2 Effects of Initial Concentration

Metal adsorption is significantly influenced by the initial concentration of metal ions in aqueous solutions. In the present study, the initial metal concentration is varied from 5 to 100 mg/L for each of the adsorbent dosages. Figure 2a–c shows the effect of initial concentration on the removal percentage of metal ions. The percentage of Co removal, for instance, decreases from 80.2 % (for 5 mg/L) to 51.3 % (for 100 mg/L) at the same contact time and adsorbent dose. The percentage of metal ions removal is inversely proportional to an increase in the initial metal ions concentration, as seen in Fig. 3. This may be due to an increase in the number of metal ions for the fixed amount of adsorbent.

By comparing the results of the study, as presented in Table 1, we also conclude that the adsorption efficiency is dependent on the type of metal too. Indeed, for Zn, no more than 87.1 % removal has been obtained under the same conditions (1.5 g adsorbent in solutions of 5, 15, 30, 50 and 100 mg/L), whereas for Cd, and Co the efficiencies are reported to be 90.7, and 94.3 % respectively (Fig. 2a–c).

The ability of a waste material to bind heavy metal ions is the result of a variety of mechanisms, including chemisorption, complexation, adsorption complexation on surface and pores, ion exchange, micro precipitation, heavy metal hydroxide condensation and surface adsorption. In order to understand how metals are removed by the tea waste, it is essential to identify the functional groups responsible for metal binding. Although studies specifically concerned with this type of waste remain few, metal removal is believed to primarily involve charged and polar functional groups on the protein surface and phenolic compounds. These groups have the ability to bind heavy metals through the replacement of hydrogen ions by metal ions or the donation of an electron pair to form metal complexes [19].

3.3 Effects of pH

Table 2 and Fig. 4 show the pH dependence of metal ion adsorption at particular metal ions and teawaste adsorbent concentrations. The rate of adsorption was largely linked to pH levels over a wide pH range. In particular, it was significantly reduced at very low levels ($pH < 4$) and to a lesser extent at high pH ($pH > 10$). Good adsorption efficiency, however, is observed at intermediate pH values likely to be encountered in most waste waters. Figure 4 demonstrates that the optimum pH level for metal ions adsorption was 6 approximately, which is rather acidic. At low pH (below 4), there was excessive protonation of the active sites at the teawaste's surface and this often prevented the formation of links between metal ions and the active site. At moderate pH values (4–8), linked H^+ is released from the active sites and the adsorbed amount of metal ions is generally found to increase. At higher pH values (above 8), the precipitation is dominant or both ion exchange and aqueous metal hydroxide formation may become significant mechanisms in the metal removal process. This condition is often undesirable, as metal precipitation could lead to an incorrect evaluation of the adsorption capacity [17].

The increase in adsorption with increasing pH levels can be explained by the hydrolysis of heavy metals and the charge at an active site on the surface of the teawaste which allows metals to be complexed at the surface. In solutions of pH 2–5, investigated metals were in their double positively charged form. However, at increasing pH levels, they are hydrolysed to their hydroxide form. At low pH ($pH = 2$), on the other hand, the adsorption is very low. This effect is caused by a positive charge at the surface of the treated teawaste, which leads to repulsion between the surface charge and metal ion [20].

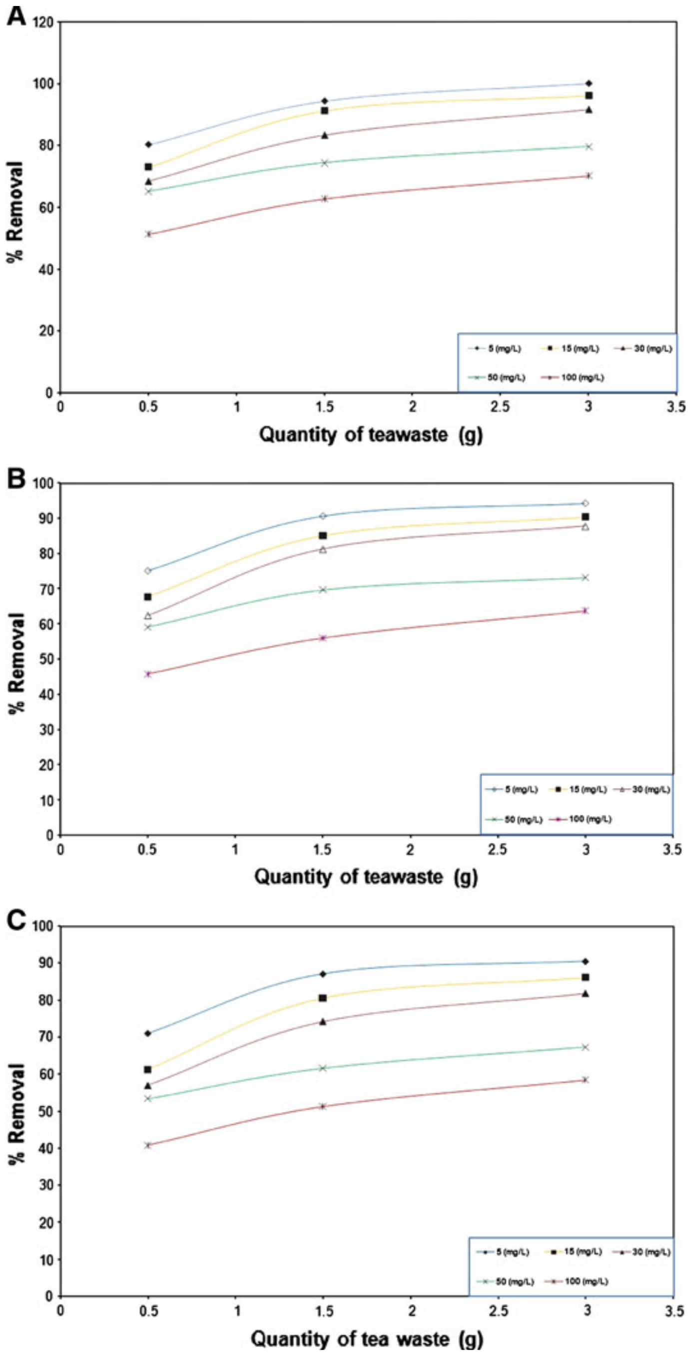

Fig. 2 **a** Effect of teawaste dosage on Cobalt percentage removal with different initial concentrations (pH = 6 and equilibrium time = 3 h). **b** Effect of teawaste dosage on Cadmium percentage removal with different initial concentrations (pH = 6 and equilibrium time = 3 h). **c** Effect of teawaste dosage on Zinc percentage removal with different initial concentrations (pH = 6 and equilibrium time = 3 h)

The effect of pH on the adsorption isotherm may be attributed to the interaction between ions in the solution and complexes formed at the adsorbent surface. Bodek et al. [21] reported the presence of different species of Zn (II) in the aqueous solution depending on the solution's pH levels. The speciation diagram illustrating this was provided by Carrott et al. [22] and can be obtained using the reaction and equilibrium constants given by Baes and Messmer [23]:

$$\mathrm{Zn}^{2+} + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{Zn(OH)}^{+} + \mathrm{H}^{+},\ \mathrm{pK}_1 = 8.96$$

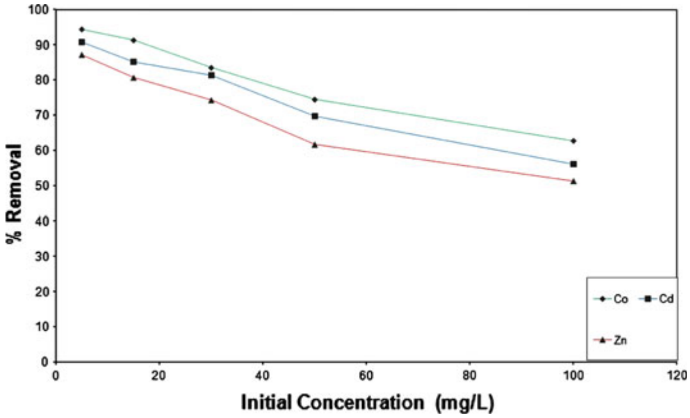

Fig. 3 Effect of initial concentration of metals on the removal (pH = 5, adsorbent dose = 1.5 g, and time = 3 h)

Table 2 Percentage removal as a function of pH

Metal	Co	Cd	Zn
pH	*% R*	*% R*	*% R*
2	20.3	18.7	14.5
4	79.8	75.5	71.2
6	94.3	90.7	87.1
8	85.2	82.4	80.6
10	71.7	65.3	68.9
12	65.9	52.1	48.1

$$\mathrm{Zn}^{2+} + 2\mathrm{H_2O} \rightarrow \mathrm{Zn(OH)_2} + 2\mathrm{H}^{+},\ \ \mathrm{pK_2} = 7.94$$
$$\mathrm{Zn}^{2+} + 3\mathrm{H_2O} \rightarrow \mathrm{Zn(OH)}_3^{-} + 3\mathrm{H}^{+},\ \ \mathrm{pK_3} = 11.50$$
$$\mathrm{Zn}^{2+} + 4\mathrm{H_2O} \rightarrow \mathrm{Zn(OH)}_3^{-2} + 4\mathrm{H}^{+},\ \ \mathrm{pK_4} = 12.80$$

Thus, the predominant ionic species is Zn^{2+} at pH < 7, whereas Zn (II) is present mainly as Zn^{2+}, $Zn(OH)_2$ and, in lesser quantity, as $Zn(OH)^{+}$, at pH between 8 and 9. Since all of the experiments were carried out at a maximum pH of 4.2, the predominant Zn (II) species found in solution and adsorbed on the TFW surface was Zn (II). At lower pH values, the H^{+} ions compete with metal cation for the exchange sites in the system thereby partially releasing the latter, which compete with the M^{2+} ions for the adsorption sites of waste tea. A decrease in adsorption at higher pH levels is due to the formation of soluble hydroxyl complexes. The heavy metal cations are completely released under circumstances of extreme acidic conditions [24].

As such, the effect of pH levels on metal ions biosorption can be explained by the acidic and basic sites of the adsorbents. Compared with raw teawaste, total acid sites of the biosorbent washed with alkali saponification decreased and total basic sites increased. Subsequently, when washing with acid after NaOH saponification, there were more acid sites than basic ones, which may be explained as follows: the surface of this adsorbent is acidic due to the presence of the acid sites, since the metal cations in aqueous solutions can be adsorbed on these sites. At lower pH levels, because H^{+} varies with metal ions, the sorbent surface takes up more H^{+}, reducing metal ions' bind on the sorbent surface. At higher pH, the formation of anionic hydroxide complexes decreases the concentration of free metal ions. As a result, the adsorption capacity of metal ions was reduced. This result indicates that an ion exchange mechanism is involved in the adsorption process [25].

3.4 Effect of Contact Time

The adsorption of different metal ions was measured at given contact times for five different initial metal concentrations of 5, 15, 30, 50 and 100 mg/L. The metal ion adsorption capacity of used teawaste increased with adsorption contact time, up to 3 h, and then remained almost constant, as seen in Fig. 5. This figure reveals that the rate of percent metal removal is higher at the beginning. This is probably due to a larger surface area

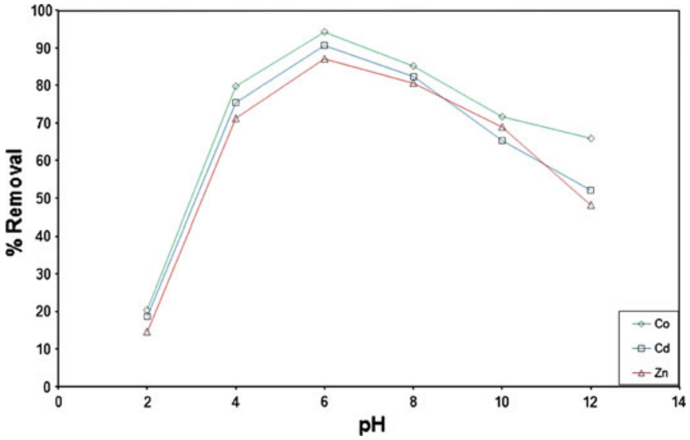

Fig. 4 Effect of solation pH on the percentage removal of metal ions by teawaste (initial metal concentration = 5 mg/L, adsorbent = 1.5 g and equilibrium time = 3 h

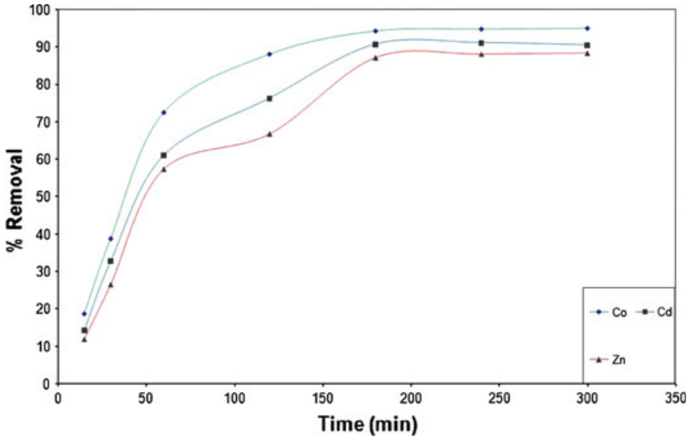

Fig. 5 Effect of time on percentage removal of heavy metals on tea waste (metal concentration = 5 mg/L, adsorbent dose = 1.5 g/150 ml, pH = 6 and equilibrium time = 3 h

of the teawaste being available at the beginning for the adsorption of metal ions. As the surface adsorption sites become exhausted, the uptake rate is determined by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. According to Fig. 5, metals uptake was relatively fast for all concentrations studied and the uptake reached a 50–76 % equilibrium capacity of biosorption in 60 min. This rapid kinetic has significant practical importance as it will facilitate smaller reactor volumes, thus ensuring efficiency and economy.

3.5 Adsorption Isotherms

Adsorption isotherms, which represent the amount of solute adsorbed per unit of adsorbent as a function of equilibrium concentration in bulk solution at constant temperature, were studied. In order to optimise the design of a sorption system to remove metal ions from aqueous solutions, it is important to establish the most appropriate correlation for the equilibrium curve. Two isotherm equations have been tested in the present study, namely: Langmuir and Freundlich.

The adsorption of metal ions on teawaste in this study was analysed using Langmuir and Freundlich isotherm models. According to the Langmuir model, adsorption occurs uniformly on the active sites of the adsorbent and, once an adsorbate occupies a site, no further adsorption can take place at the same site. The Langmuir model is given by Eq. (8),

$$C_e/q_e = 1/(q_m b) + C_e/q_m \tag{8}$$

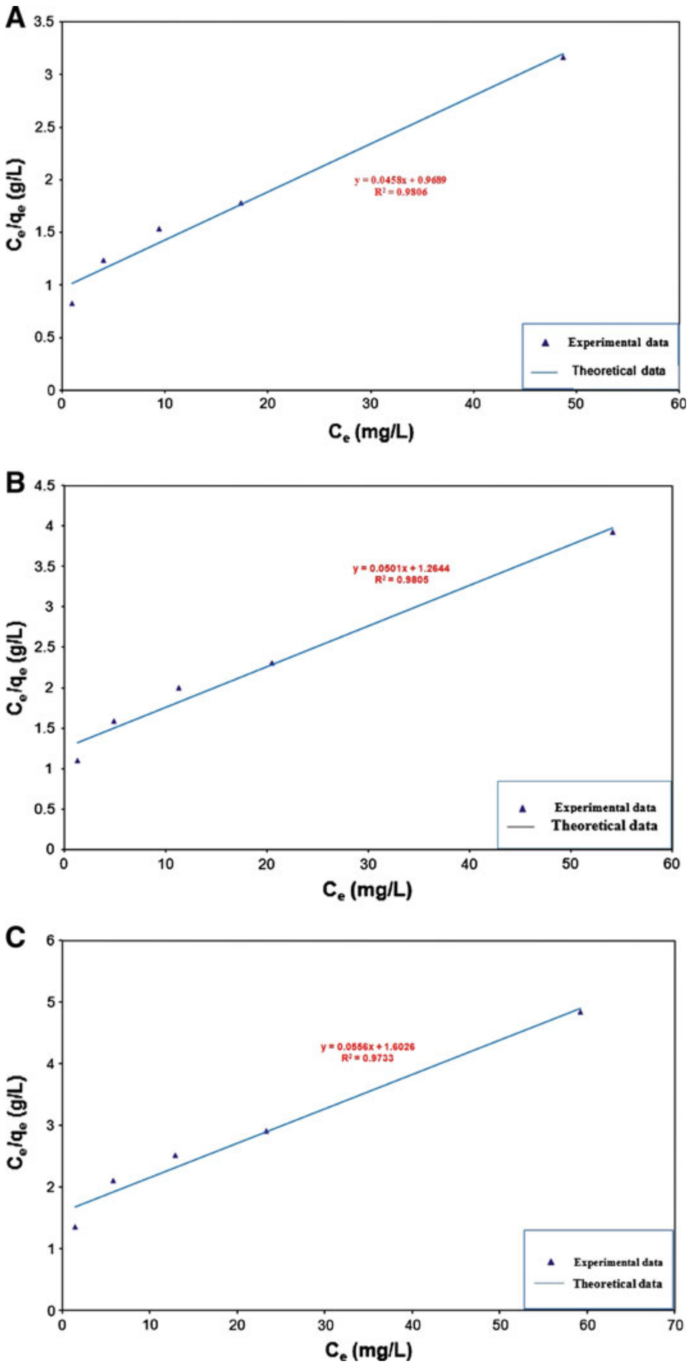

Fig. 6 **a** Langmuir adsorption isotherm for Co biosorption on teawaste. **b** Langmuir adsorption isotherm for Cd biosorption on teawaste. **c** Langmuir adsorption isotherm for Zn biosorption on teawaste

where C_e is the equilibrium concentration (in mg/L), q_e is the amount of metal ion adsorbed at equilibrium (mg/g) whereas q_m and b are, respectively, Langmuir constants related to adsorption capacity and energy of adsorption. The linear plots of $C_\mathrm{e}/q_\mathrm{e}$ versus C_e show that the adsorption obeys the Langmuir isotherm model, as seen in Fig. 6a–c. q_m and b were determined from the slope and intercept of the plot presented in Table 3. The Langmuir parameters can be used to predict the affinity between the adsorbate and adsorbent using the dimensionless separation factor, RL, defined by Hall et al. [25] as Eq. (9)

$$R_\mathrm{L} = 1/1 + bC_\mathrm{o} \tag{9}$$

Table 3 Langmuir adsorption parameters and regression coefficient for the five metal ions on teawaste

Metal	q_m (mg/g)	b (L/mg)	R^2	Initial concentration (mg/L)	R_L
Co	21.8341	0.04727	0.9806	5	0.8088
				15	0.5851
				30	0.4135
				50	0.2973
				100	0.1746
Cd	19.9601	0.03962	0.9805	5	0.8346
				15	0.6272
				30	0.4569
				50	0.3355
				100	0.2015
Zn	17.9856	0.03469	0.9733	5	0.8522
				15	0.6577
				30	0.49
				50	0.3657
				100	0.2238

where C_o is the initial metal concentration (mg/L) and b is the Langmuir constant (L/mg). The magnitude of the R_L value gives an idea of the nature of adsorption equilibrium: the process is non-spontaneous when R_L is greater than one; favourable when R_L lies between 0 and 1; and irreversible when R_L is zero. In all the systems under study, R_L values obtained for all metals adsorption are greater than zero and less than unity thus showing favourable adsorption of these metals onto teawaste, as illustrated in Table 3.

A Freundlich isotherm model was also used to explain the observed phenomenon (Freundlich 1906). The Freundlich isotherm is represented by Eq. (10)

$$\log q_e = \log K_f + (1/n) \log C_e \tag{10}$$

where C_e is the equilibrium concentration (mg/L), K_f and n are constants incorporating all factors affecting the adsorption process, such as adsorption capacity and intensity, respectively. Linear plots of log q_e versus log C_e show that the adsorption follows Freundlich isotherm model as well, Fig. 7a–c. K_f and n are calculated from the intercept and slope of the plots presented in Table 4. According to the literature, values of n between 1 and 10 are considered to indicate a good adsorbent, thus confirming teawaste's effective adsorption. The Freundlich model described the isotherms of heavy metals biosorption using a correlation coefficient ($R^2 > 0.99$) that was better than the Langmuir model's ($R^2 > 0.91$).

3.6 Adsorption Kinetics

Kinetic parameters of rate equations for biosorption of Co, Cd, and Zn by teawaste are shown in Table 5.

Figure 8a–c shows kinetic modelling of heavy metal ions biosorption using linear plots of the pseudo first-order, pseudo second-order, and second-order rate equation (Eqs. 6–8). A Lagergren pseudo first-order rate equation has been applied to the adsorption of the liquid/solid system based on adsorption capacity. According to this model, one adsorbate species reacts with one active site on surface. Lagergren's pseudo first-order rate, Eq. (5), cited by Ho and McKay [27] was applied to the kinetic behaviour of heavy metals adsorption on the teawaste. Lagergren's equation is suitable for a homogeneous surface, which suggests that the surfaces of teawaste are homogeneous, Fig. 8a–c.

Ritchie's pseudo second-order rate equation was also applied to the adsorption kinetics of the present system. The linear plots of t/q_t against t, as shown in Fig. 9a–c, represent a good fit over the whole range of the initial concentration of Cd, and Zn, and an acceptable fit for Co and contact time. Ritchie's pseudo second-order rate equation was derived by assuming that two surface sites could be occupied by one divalent adsorbate ion. Thus, Eq. (6) would be expected to be applicable for the adsorption of Cd and Zn only.

From Table 5, the correlation coefficient R^2 is the highest one given by the model of the pseudo first order for Zn, Cd, and Co, respectively. We can deduce that the adsorption kinetics of these three metals by the teawaste is described by the model of pseudo first order.

The correlation coefficients for the second-order rate equation, Eq. (7) and Fig. 10a–c, are close to that of the pseudo second order but still lower than the first-order rate equation. Also, the calculated q_e values obtained using the kinetic first-order model were found to be in good agreement with experimental values.

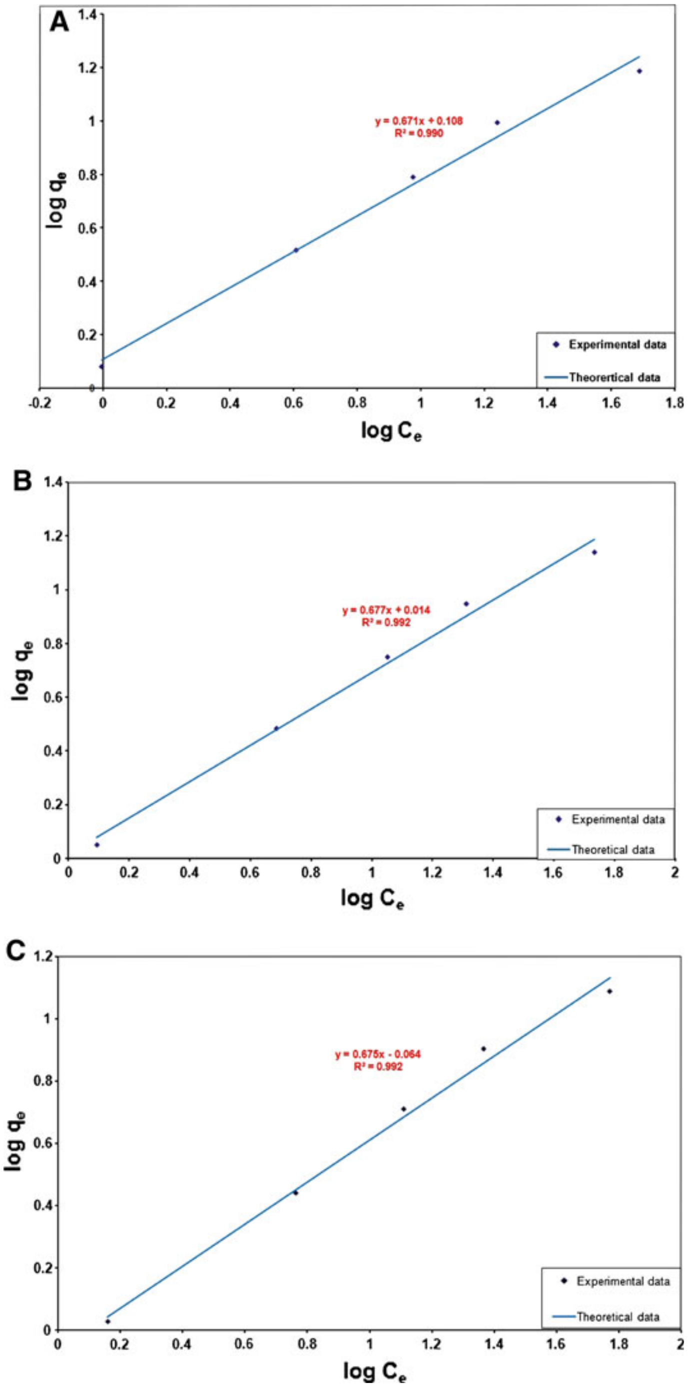

Fig. 7 **a** Freundlich adsorption isotherm for Co biosorption on teawaste. **b** Freundlich adsorption isotherm for Cd biosorption on teawaste. **c** Freundlich adsorption isotherm for Zn biosorption on teawaste

Table 4 Freundlich adsorption parameters and regression coefficients for the metal ions on teawaste

Metal	K_f	n	R^2
Co	1.284	1.489	0.9905
Cd	1.033	1.476	0.992
Zn	0.8614	1.481	0.9928

Table 5 Kinetic parameters of rate equations for biosorption of Co, Cd, and Zn by teawaste

Metal	Pseudo first-order model		Pseudo second-order model		Second-order model	
	K_1 (1/min)	R^2	$K_2 \times 10^3$ (g/mg/min)	R^2	K(g/mg/min)	R^2
Co	0.0118	0.9722	1.4187	0.8449	0.0416	0.8772
Cd	0.0181	0.9881	10.327	0.9921	0.1441	0.8433
Zn	0.0122	0.9967	3.703	0.9414	0.0442	0.9403

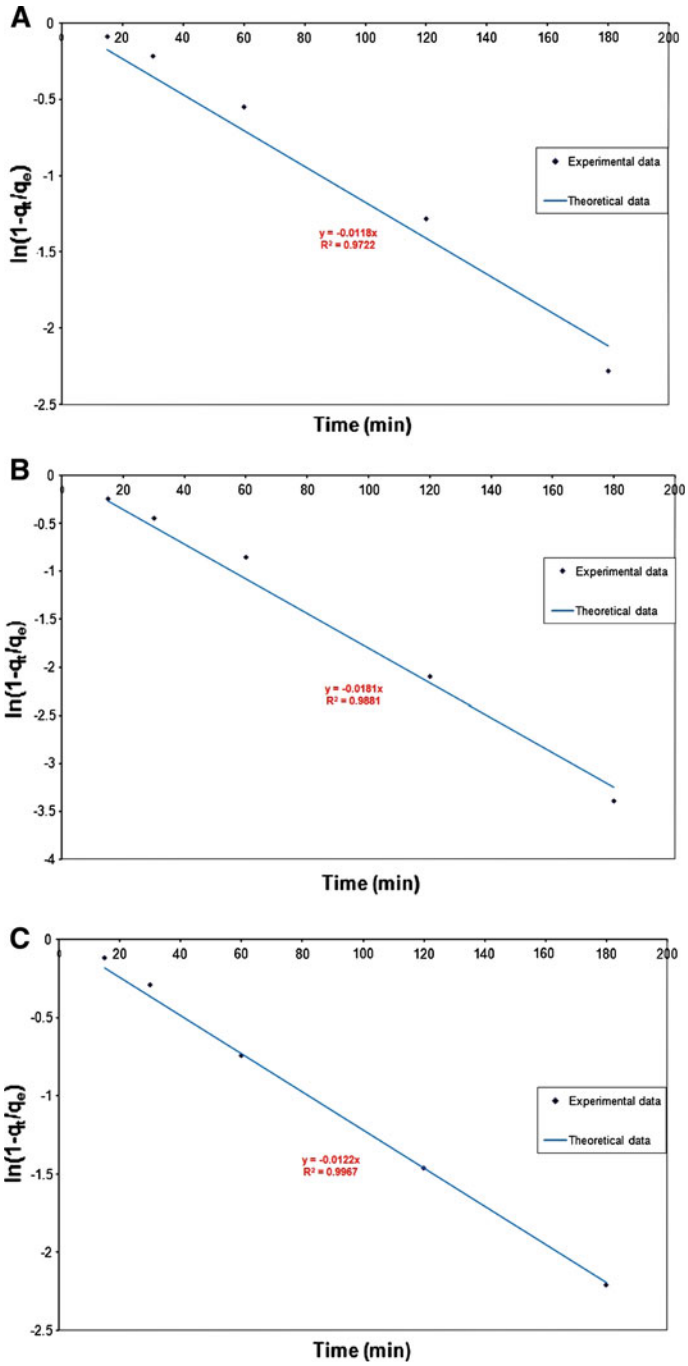

Fig. 8 **a** Pseudo first-order kinetics for the adsorption of Co onto teawaste. **b** Pseudo first-order kinetics for the adsorption of Cd onto teawaste. **c** Pseudo first-order kinetics for the adsorption of Zn onto teawaste

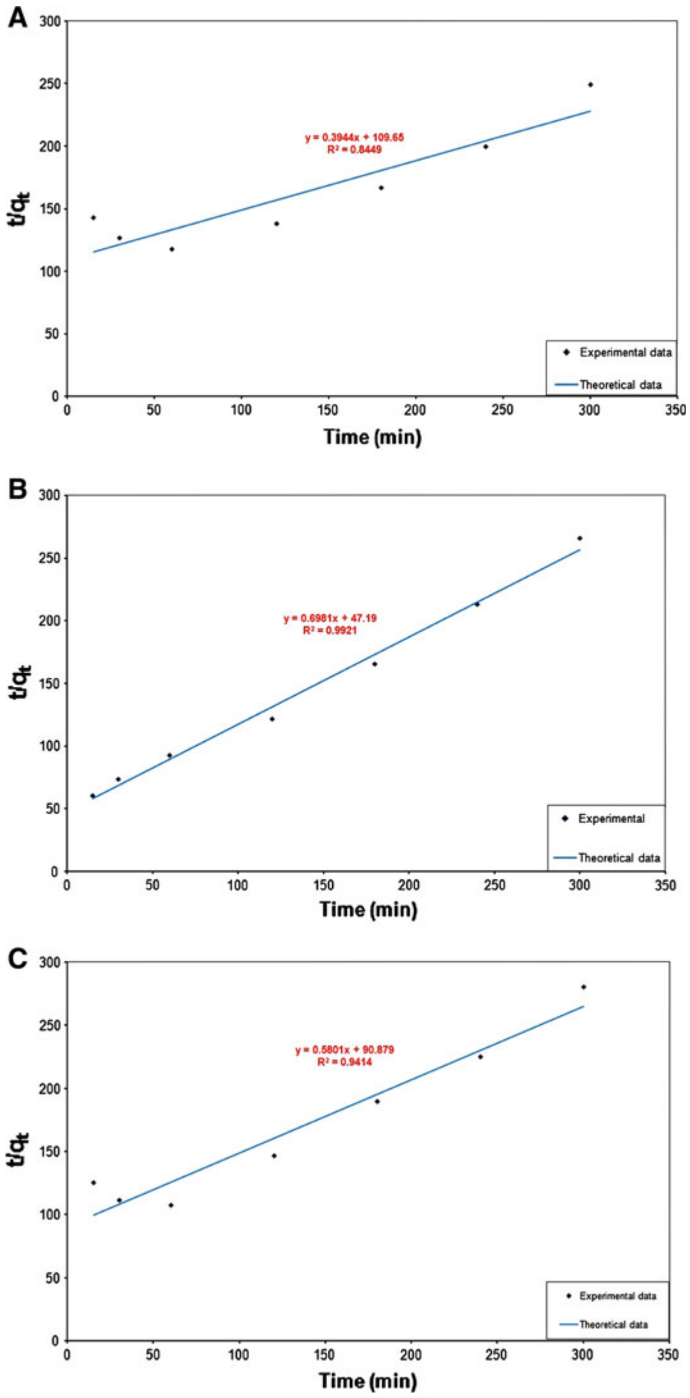

Fig. 9 **a** Pseudo second-order kinetics for the adsorption of Co onto teawaste. **a** Pseudo second-order kinetics for the adsorption of Cd onto teawaste. **c** Pseudo second-order kinetics for the adsorption of Zn onto teawaste

4 Conclusion

Analyses of results of this study have indicated that teawaste, like most other natural absorbents, can be used in the treatment process of heavy metals, with a treatment efficiency as high as 100 %, by carefully and precisely determining the adsorbent amount. Batch experiments showed that initial metal concentration, solution pH levels and contact time all have a profound effect on the adsorption rate. Experimental and calculated kinetic

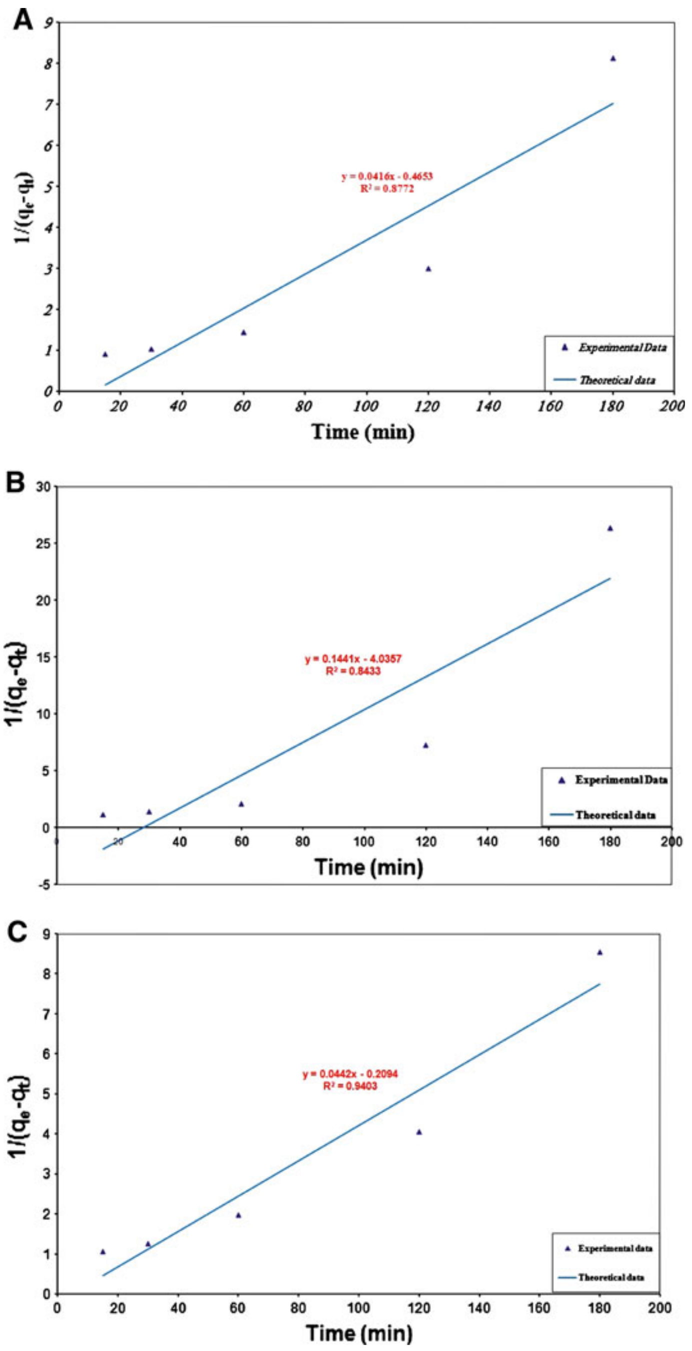

Fig. 10 **a** Second-order kinetics for the adsorption of Co onto teawaste. **b** Second-order kinetics for the adsorption of Cd onto teawaste. **c** Second-order kinetics for the adsorption of Zn onto teawaste

data for equilibrium are well expressed by Freundlich and Langmuir isotherms. The adsorption kinetics is described successfully using Lagergren pseudo first order rate equation. Teawaste is a cheap resource and its use in industrial wastewater treatment plants would thus be highly convenient. Finally, we recommend that the effect of pretreatment processes for this type of treatment should be evaluated. The probable changes of adsorption efficiency under different conditions involving various metals in actual wastewaters should also be investigated. Teawaste is produced in nearly all regions of the world and, although of little commercial value in itself, its disposal is costly and not devoid of adverse environmental impacts. The exploitation of spent tea leaves as an adsorbent of lead or of other metal ions may therefore represent an attractive strategy for the effective reduction and reuse of this type of waste.

References

1. Bakkaloglu, I.; Butter, T.J.; Evison, L.M.; Holland, F.S.; Hancock, I.C.: Screening of various types biomass for removal and recovery of heavy metals (Zn, Cu, Ni) by biosorption, sedimentation and desorption. Water Sci. Technol. **38**, 269–277 (1998)
2. Yetis, U.; Ozcengiz, G.; Filiz, B.; Ergen, N.; Erbay, A.; Dolek, A.: Heavy metal biosorption by white-rot fungi. Water Sci. Technol. **38**, 323–330 (1998)
3. Juang, R.S.; Shiau, R.C.: Metal removal from aqueous solutions using chitosan-enhanced membrane filtration. J. Membr. Sci. **165**(2), 159–167 (2000)
4. Iqbal, M.; Saeed, A.; Akhtar, N.: Petiolar feltsheath of palm: a new biosorbent for the removal of heavy metals from contaminated water. Bioresour. Technol. **81**, 151–153 (2002)
5. Dakiky, M.; Khamis, M.; Manassra, A.; Mereb, M.: Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents. Adv. Environ. Res. **6**(4), 533–540 (2002)
6. Espinola, A.; Adamian, R.; Gomes, L.M.B.: An innovative technology: natural coconut fiber as adsorptive medium in industrial wastewater cleanup. In: Proceedings of TMS Fall Extraction and Processing Conference **3**, 2057–2066 (1999)
7. Juan, C.M.; Rigoberto, G.; Liliana, G.: Removal of Mn, Fe, Ni and Cu ions from wastewater using cow bone charcoal. Materials **3**, 452–466 (2010)
8. Marshall, W.E.; Champagne, E.T.: Agricultural byproducts as adsorbents for metal ions in laboratory prepared solutions and in manufacturing wastewater. J. Environ. Sci. Health—Part A Environ. Sci. Eng. **30**(2), 241–261 (1995)
9. Tarley, T.; Cesar, R.; Zezzi, A.; Marco, A.: Biosorption of heavy metals using rice milling by-products. Characterization and application for removal of metals from aqueous solutions. Chemosphere **54**(7), 905–915 (2004)
10. Saeed, A.; Iqbal, M.; Akhtar, M.W.: Application of biowaste materials for the sorption of heavy metals in contaminated aqueous medium. Pak. J. Sci. Ind. Res. **45**(3), 206–211 (2002)
11. Hossain, M.A.; Mikio, K.; Yoshimasa, M.; Shigeru, M.: Kinetics of Cr(VI) adsorption on used black tea leaves. J. Chem. Eng. Jpn. **38**(6), 402–408 (2005)
12. Amarasinghe, B.M.; Williams, R.A.: Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. Chem. Eng. J. **132**(1), 299–309 (2007)
13. Yoshita, A.; Lu, J.L.; Ye, J.H.; Liang, Y.R.: Sorption of lead from aqueous solutions by spent tea leaf. Afr. J. Biotechnol. **8**(10), 2212–2217 (2009)
14. Antonio, Z.; Roberto, L.: Adsorption of Pb(II) on spent leaves of green and black tea. Am. J. Appl. Sci. **7**(2), 153–159 (2010)
15. Sunil, K.B.; Arti, J.: Removal of copper(II) from aqueous solution using spent tea leaves (STL) as a potential sorbent. Water SA **36**(3), 221–228 (2010)
16. Abdollahi, H.; Panahi, S.M.; Khoshayand, M.R.: Simultaneous spectrophotometric determination of iron, cobalt and copper by partial least-squares calibration method in micellar medium. Iran. J. Pharm. Res. 207–212 (2003)
17. Senthil, P.K.; Gayathri, R.: Adsorption of Pb^{2+} ions from aqueous solutions onto Bael tree leaf: Isotherms, kinetics, and thermodynamics study. J. Eng. Sci. Technol. **4**(4), 381–399 (2009)
18. Mamisahebei, S.; Jahed, K.; Torabian, A.; Nasseri, S.; Naddafi K.: Removal of arsenic from an aqueous solution by pretreated waste tea fungal biomass. Iran. J. Environ. Health. Sci. Eng. **4**(2), 85–92 (2007)
19. Demirbas, A.: Heavy metal adsorption onto agro-based waste materials: a review. J. Hazard. Mater. **157**, 220–229 (2008)
20. Suwan, C.; Pachernchai, C.; Chutima, S.: Removal of cadmium and nickel from aqueous solution by adsorption onto treated fly ash from Thailand. Thammasat Int. J. Sci. Tech. **1 l**(2), 13–20 (2006)
21. Bodek, I.; Lyman, W.J.; Reehl, W.F.; Rosenblatt, D.H.: Environmental inorganic chemistry properties, processes and estimation methods. SETAC Special Publications Series. Pergamon Press, USA (1995)
22. Carrott, P.J.; Ribeiro, C.M.; Nabais, J.M.; Prates, R.J.: Influence of surface ionization on the adsorption of aqueous zinc species by activated carbons. Carbon **35**(3), 403–411 (1997)
23. Baes, C.F.; Messmer, R.E.: The hydrolysis of cations. Florida (1976)
24. Kailas, L.W.: Adsorption of metals onto tea factory waste: a review. IJRRAS **3**(3), 303–322 (2010)
25. Shukla, S.S.; Yu, L.J.; Dorris, K.L.; Shukla, A.: Removal of nickel from aqueous solutions by sawdust. J. Hazard. Mater. B **121**, 243–246 (2005)
26. Hall, K.R.; Eagleton, L.C.; Acrivos, A.; Vermeulen, T.: Pore and solid diffusion Kinetics in fixed bed adsorption under constant pattern conditions. Ind. Eng. Chem. Fundam. **5**, 212–223 (1966)
27. Ho, Y.S.; McKay, G.: The sorption of lead(10) ions on peat. Water Res. **33**, 578–584 (1999)