ORIGINAL PAPER

THE ISOTHERM AND KINETIC STUDIES OF THE BIOSORPTION OF HEAVY METALS BY NON-LIVING CELLS OF *CHLORELLA VULGARIS*

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ABSTRACT

In general, the biosorption of heavy metals by various types of non-living organisms appears to be a very effective, low-cost and innovative method for their removal from aquatic environments. The aim of this study was to determine the applicability of adsorption isotherms and kinetic models during the biosorbent activity of non-living *Chlorella* to the removal of Cd, Cu and Pb. Dead cells of *Chlorella vulgaris* were used to remove these heavy metals from aqueous solution in experimental conditions, i.e. under various condition of pH, biosorbent dosage and contact time. Afterwards, the Langmuir and Freundlich adsorption isotherm models and the sorption kinetics (pseudo-first and pseudo-second order models, and intraparticle diffusion) were applied to the experimental data to check the effectiveness of the removal process. The removal of heavy metals on *C. vulgaris* following the order of $Pb^{+2} > Cu^{+2} > Cd^{+2}$ was confirmed by the maximum biosorption capacities (q_{max}), the Langmuir constant (b), separation factor (R_L) and Freundlich intensity parameter ($1/n$) values. The equilibrium data were well fitted with the Langmuir and Freundlich isotherm models. The adsorption process followed the pseudo-second-order model and it suggested that such kinetics is the most effective. The present results confirmed highly efficient biosorbent activity of *C. vulgaris* in the removal of heavy metals, especially Cd, Cu and Pb, from aqueous solution. The environmentally friendly origin indicates that non-living cells of *C. vulgaris* could find many broad-scale, cost-effective and alternative applications.

Keywords: adsorption, green algae, Freundlich, Langmuir, kinetic, cadmium, lead, copper.

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INTRODUCTION

The non-degradability and toxicity of heavy metals (especially lead Pb, copper Cu and cadmium Cd) cause a serious problem in aquatic reservoirs, which consequently can become harmful to human health. Thus, they are a subject of special concern. The available technologies such as bioremediation or sorption/adsorption for removal of heavy metals should be considered (e.g. Li, Champagne 2009, Baskaran et al. 2010, Mann, Mandal 2014, Goher et al. 2016). Recently, alternative or innovative low-cost natural materials used as biosorbents have been searched for. The following have been tested: peat (Ho 2006), microbial and plant biomass (Ahluwalia, Goyal 2007, Duda-Chodak et al. 2012.) or even garden grass (Sulaymon et al. 2014).

Removal of toxic heavy metals from the environment is a big challenge and of great importance from the environmental viewpoint (Goher et al. 2015). Several methods for removing heavy metals from aqueous solutions have been developed. The use of microalgae in metal removal has been growing in recent years. As well as being environmentally friendly, this method offers potential advantages such as low operating costs, minimization of chemical or biological sludge, high efficiency of heavy metal removal from diluted solutions, regeneration of biosorbents, possibility of metal recovery (Ghoniem et al. 2014).

The adsorption process showing biosorbent usage can be well described in the form of models (adsorption isotherms) concerning the distribution of adsorbate species between the liquid and an adsorbent, based on a set of assumptions related mainly to the homogeneity/heterogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species. The models commonly used to describe adsorption isotherms are the Langmuir and Freundlich isotherm patterns (Benguella, Benaissa 2002, Mann, Mandal 2014). Furthermore, kinetic studies specifying the adsorption rate are helpful to determine the adsorbent's efficiency (Krishnan, Anirudhan 2003).

In this paper, the applicability of adsorption isotherms and kinetic models to assess the biosorbent activity of non-living *Chlorella vulgaris* Beyerinck [Beijerinck] cells in removal of Cd, Cu and Pb from aqueous solution are reported.

MATERIAL AND METHODS

The experiment with dead cells of *C. vulgaris* used to remove cadmium, copper and lead from aqueous solution under various condition of pH, biosorbent dosage (Table 1) and contact time (Table 2) was described in detail in Goher et al. (2016). The green alga *C. vulgaris* was isolated from Lake Man-

Table 1

Effect of *Chlorella vulgaris* dose on removal of Cd, Cu and Pb

Metal　　　　Dose (g dm^{-3})	Cd		Cu		Pb	
	adsorption capacity (q)	removal percentage $R(\%)$	adsorption capacity (q)	removal percentage $R(\%)$	adsorption capacity (q)	removal percentage $R(\%)$
0.25	95.176	23.794	129.720	32.430	133.752	33.438
0.5	86.448	43.224	95.520	47.760	118.680	59.340
1	71.736	71.736	87.680	87.680	96.410	96.410
1.5	52.632	78.947	64.227	96.340	65.992	98.988
2	47.771	95.542	48.845	97.690	49.711	99.422
3	31.847	95.542	32.563	97.690	33.141	99.422
4	23.886	95.542	24.423	97.690	24.856	99.422

Table 2

Effect of contact time on removal of Cd, Cu and Pb by *Chlorella vulgaris*

Time (min)　　Metal	2	4	6	8	10	20	30	60	90	120
Cd	55.560	57.840	60.040	61.880	67.994	70.854	77.242	83.902	87.486	95.542
Cu	89.200	93.572	93.768	93.932	96.090	97.690	97.690	97.690	97.690	97.690
Pb	95.267	95.849	96.640	97.400	98.476	99.422	99.422	99.422	99.422	99.422

zala (Egypt) and it was grown in enriched seawater medium. After that, it was transferred, adapted to a fresh culture medium and cultivated outdoors using growth media with pH of nearly 7.5. After cultivation, the cells were harvested by coagulation and then they were prepared to set up an experiment including such factors as different pH, adsorbent dose and contact time. The effects of this experimental research were continued to identify the equilibrium relationships. For the isotherm study, equilibrium concentrations of heavy metals at various sorbent doses (0.25, 0.5, 1, 1.5 and 2 g dm^{-3}) at the ambient temperature were used. Meanwhile, the effect of contact time (2, 4, 6, 8, 10 and 20 min) and (2, 4, 6, 8, 10, 20, 30, 60, 90 and 120 min) was used for the kinetic models for Cu and Pb and For Cd, respectively.

Adsorption study
Langmuir adsorption isotherm

The Langmuir adsorption isotherm model describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and no further adsorption takes place after that. Thereby, the Langmuir

isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases (HALL et al. 1966). The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate in the plane of the surface. Based upon these assumptions, the Langmuir isotherm is represented by the following equation:

$$q_e = x \ / \ m = q_{max}bC_e \ / \ (1+bC_e).$$

While, the linear form of isotherm equation is:

$$1 \, / \, q_e = 1 \, / \, q_{max} + (1 \, / \, b \ q_{max}) \ (1 \, / \, C_e),$$

where: C_e – the equilibrium concentration of adsorbate (g dm^{-3});
q_e – the amount of metal adsorbed per 1 g of the adsorbent at equilibrium (mg g^{-1});
q_{max} – the maximum sorbate uptake (mg g^{-1}); and b – the Langmuir isotherm constant (dm^3 mg^{-1}).

Freundlich isotherm

The Freundlich isotherm gives the relationship between equilibrium liquid and solid phase capacities based on the multilayer adsorption (heterogeneous surface) properties. This isotherm is derived from the assumption that adsorption sites are distributed exponentially with respect to the heat of adsorption. The model is described by the following equation:

$$q_e = K_f C_e^{1=n}.$$

The logarithmic form of the Freundlich model yields a linear relation by plotting of $log \ q_e$ versus $log \ C_e$:

$$\log q_e = \log K_f + 1 \, / \, n \ \log C_e.$$

The constant K_f (the Freundlich capacity factor) is an approximate indicator of adsorption capacity, while $1 \, / \, n$ is the Freundlich intensity parameter.

Sorption kinetics

The general formula for pseudo-first-order equation model (the Lagergren equation, LAGERGREN 1898 cited in HO 2004) was given as follows:

$$\frac{dC_t}{dt} = K_1(q_e - q_t).$$

The integrated form (the linear form) of the pseudo-first-order model was given in the following equation (McKAY et al. 1982).

$$\ln (q_e - q_t) = \ln q_e - k_1\, t,$$

where: q_t – the metal ion adsorbed (mg g^{-1}) at time t (min), q_e – the metal ion adsorbed (mg g^{-1}) at equilibrium time and K_1 – the pseudo-first order adsorption rate constant (L min^{-1}).

The pseudo-second order chemisorption kinetic rate equation is expressed in the following formula (Ho, McKay 1998).

$$\frac{1}{q_t} = \frac{1}{K_2} + \frac{t}{q_e}$$

where: K_2 – the pseudo-second order adsorption rate constant (g mg^{-1} min^{-1}).

Mechanism of sorption

The Weber and Morris model (1963) is the most widely applied intraparticle diffusion equation for a biosorption system in the form:

$$q_t = k_{id} t^{1/2} + C$$

where: C – the intercept, q_t – the metal ion adsorbed (mg g^{-1}) at time t (min), and k_{id} – the intraparticle diffusion rate constant (mg g^{-1} $t^{-1/2}$).

RESULTS AND DISCUSSION

The Langmuir and Freundlich models are commonly applied to describe isotherms in adsorption studies (Dada et al. 2012). The Langmuir and Freundlich constants and coefficients of determination are illustrated in Table 3

Table 3

Langmuir and Freundlich isotherm constants for Cu, Pb and Cd adsorption
by *Chlorella vulgaris*

Metals	Langmuir isotherm				Freundlich isotherm			
Symbol	b	q_{max}	R^2	R_L	n	$1/n$	K_f	R^2
Cd	0.491	45.045	0.929	0.039	4.141	0.241	19.355	0.996
Cu	0.658	57.143	0.960	0.030	4.261	0.235	26.002	0.901
Pb	2.254	62.5	0.994	0.009	5.491	0.182	36.216	0.910

and Figures 1 and 2. The results showed that the Langmuir and Freundlich isotherm models were well fitted for the studied metal ions for the sorbent material with a high correlation expressed as determination coefficient (R^2) values. It was observed that the Langmuir adsorption isotherm provides a better fit to the experimental data (Table 1) of copper and lead in terms of R^2 value (Table 3). Also, the separation factor (R_L), which is a dimensionless
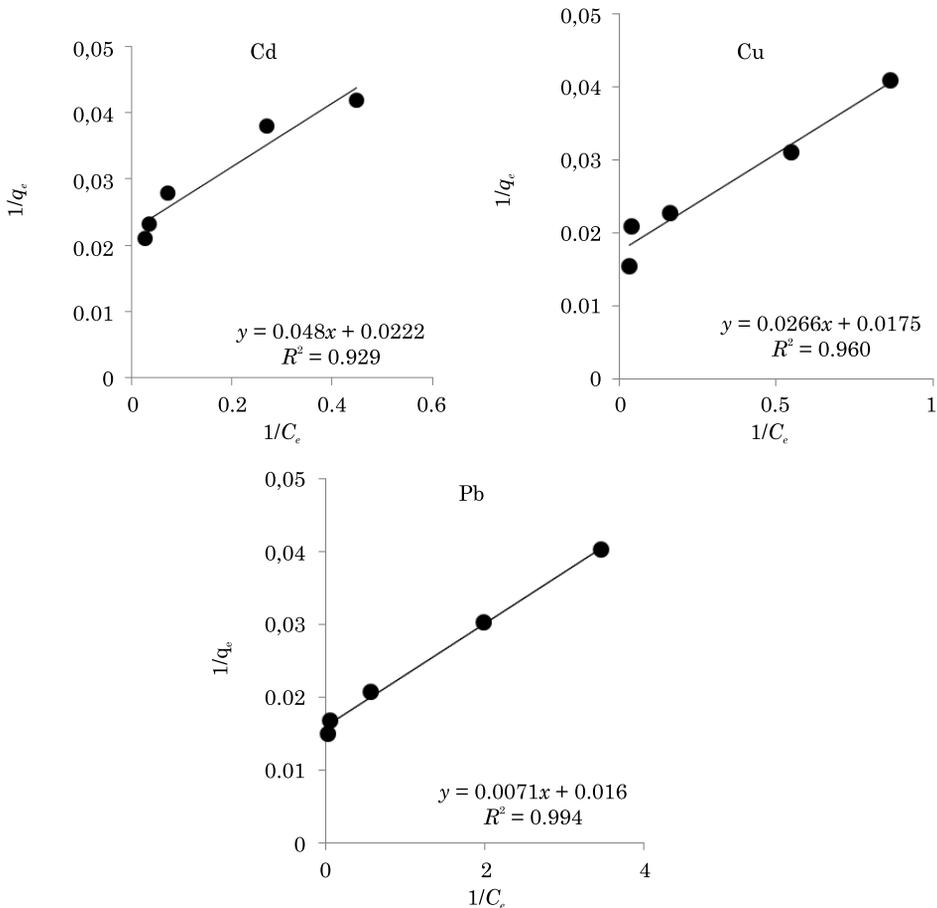
Fig. 1. Langmuir isotherm plot for biosorption of cadmium, copper and lead ions
by *Chlorella vulgaris*

equilibrium parameter, is used to study the applicability of the Langmuir adsorption isotherm, where, $R_L = 1/(1+bC_o$, C_o – initial concentration and b – the Langmuir constant. R_L value within $0 - 1$ indicates the applicability of isotherm. In the present study, such value of R_L within $0 - 1$ indicates the beneficial adsorption of Cd, Cu and Pb on dead cells of *C. vulgaris*.

On the other side, the Freundlich model was found to provide a better fit to the experimental equilibrium data of cadmium adsorption on *C. vulgaris*, and this observation agrees with those results obtained by LI and CHAMPAGNE (2009) for cadmium adsorption onto crushed mollusk shells and granular activated carbon. Values of b, which related the affinity of the metals to the sorbent surface, indicated that the sorbent had higher affinity with the metal in the order $Pb^{2+} > Cu^{2+} > Cd^{2+}$. This observation was confirmed by the constant $1/n$ values, i.e. the tendency of the adsorbate to be adsorbed (BISHOP
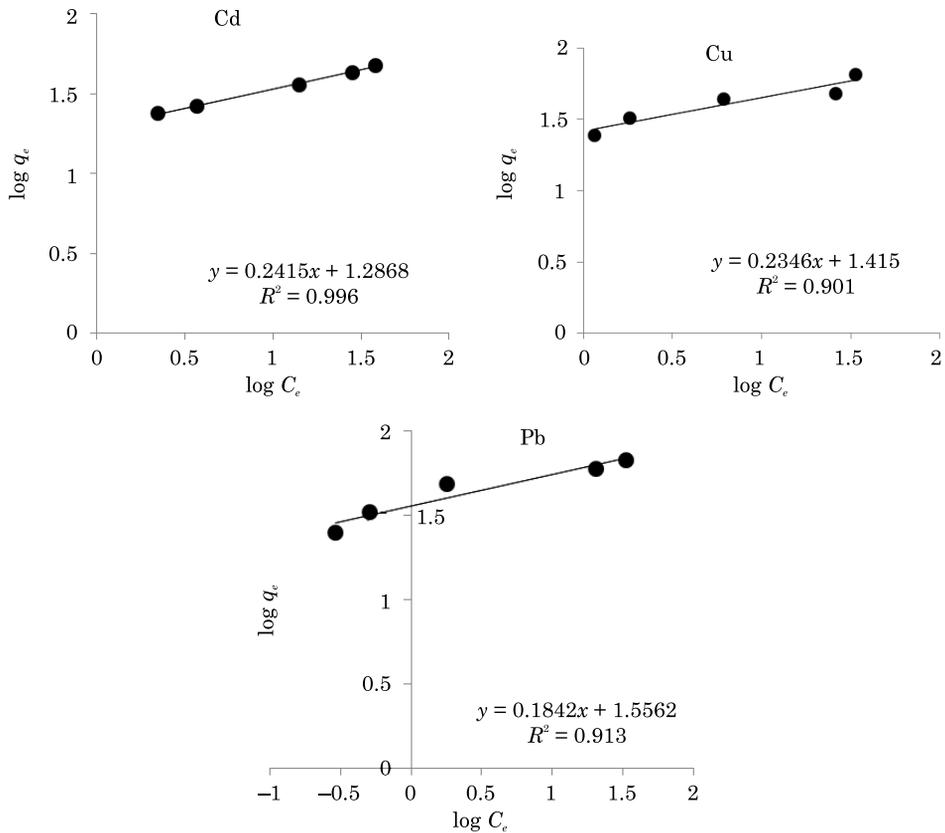
Fig. 2. Freundlich isotherm plot for biosorption of cadmium, copper and lead ions by *Chlorella vulgaris*

2004, GOEL et al. 2005). Where, the Freundlich intensity parameter ($1/n$) is a function of the strength of adsorption in the adsorption process (VOUDRIAS et al. 2002). If $n = 1$, then the partition between the two phases is independent of the concentration. If a value of $1/n$ is below one, it indicates normal adsorption. On the other hand, $1/n$ being above one indicates cooperative adsorption (MOHAN, KARTHIKEYAN 1997). Also the value of $n > 1$ is a favorable adsorption condition (TREYBAL 1998; cited in DABHADE et al. 2009). When $1 < n < 10$, it is beneficial adsorption (ANNADURAI et al. 2000). In the present study, the n value is more than one and less than ten ($1 < n < 10$), which confirms desirable adsorption of Cd, Cu and Pb by powdered *C. vulgaris*.

Sorption kinetics

The sorption rate is an important parameter used to obtain an image of the sorption process. Kinetics of metal ion biosorption determines the rate, which simultaneously reveals the residence time in batch/continuous mode

operations and efficiency of an adsorbent (KRISHNAN, ANIRUDHAN 2003). The kinetics of the adsorption of Cd, Cu and Pb by *C. vulgaris* was studied for the adsorptive uptake of heavy metals from the aqueous solution at different time intervals. Pseudo-first order and pseudo-second order models were tested on the experimental data (Table 2). The regression correlation coefficient (coefficient of determination) obtained from the pseudo-first order kinetic graph (Figure 3) was observed to be quite low and this implied the non-
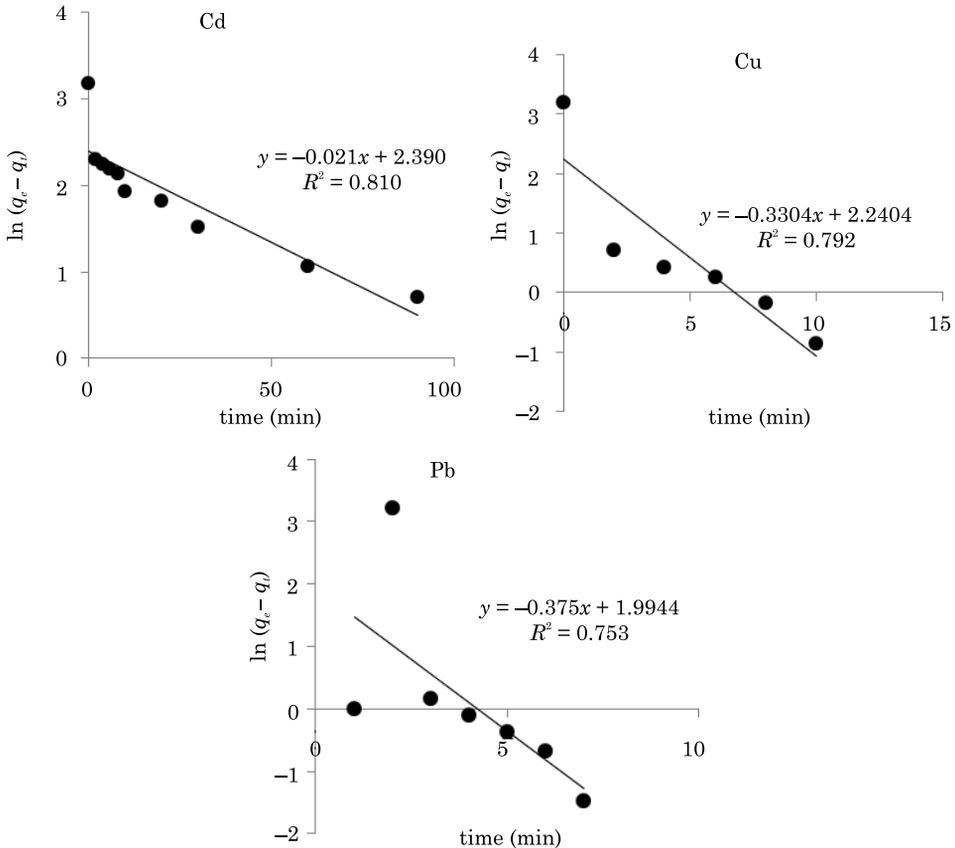
Fig. 3. Pseudo-first-order sorption kinetics for Cd, Cu and Pb adsorbed on *Chlorella vulgaris*

-applicability of the pseudo-first order kinetic model to the experimental data of the adsorption of Cd^{+2}, Cu^{+2} and Pb^{+2} on *C. vulgaris*.

On the other hand, application of pseudo-second order kinetic model gave higher values of the regression correlation coefficient for all the studied metals, which implied that the mechanism of adsorption of Cd, Cu and Pb on *C. vulgaris* followed the second order kinetics (Figure 4). The Lagergren rate equation (LAGERGREN 1898; cited in HO 2004) may have been the first rate equation for the sorption in liquid /solid systems based on solid capacity.
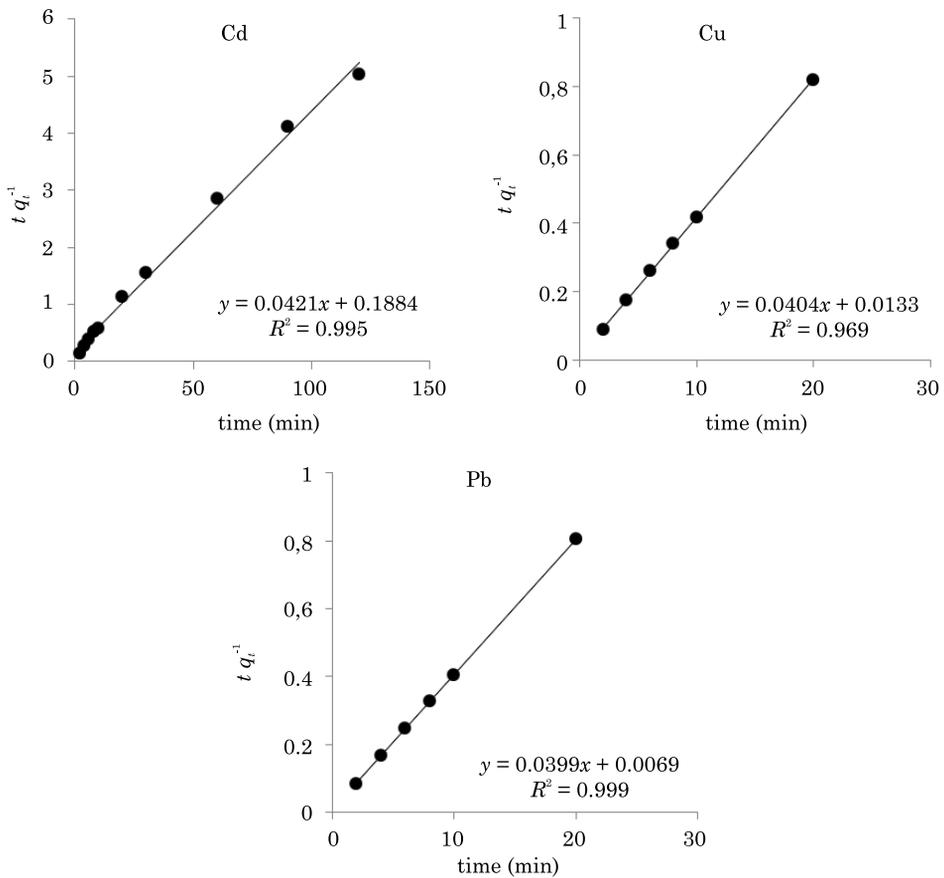
Fig. 4. Pseudo-second-order sorption kinetics for Cd, Cu and Pb adsorbed on *Chlorella vulgaris*

It is the most widely used rate equation for sorption of a solute from a liquid solution (Ho et al. 2000).

The pseudo-first-order model did not fit well (Table 4), as the calculated q_e values do not agree with the experimental q_e values. Conversely, there

Table 4

Comparison of the pseudo-first-order, pseudo-second-order and intraparticle diffusion constants for biosorption of Cd, Cu and Pb on *Chlorella vulgaris*

Metal		Pseudo-first order			Pseudo-second order				Weber and Morris diffusion		
Symbol	q_e (mg g^{-1})	K_1 (Lmin^{-1})	q_e (cal)	R^2	K_2 (g mg^{-1} min^{-1})	q_e (cal)	R^2	$K_2 q_e^2$	K_{1d} (mg g^{-1} min$^{-1/2}$)	C (mg g^{-1})	R^2
Cd	23.885	-0.021	10.913	0.8098	0.0094	23.753	0.9952	5.31	1.0159	12.88	0.9742
Cu	24.423	-0.330	9.397	0.7916	0.1664	24.390	0.9995	99.01	0.8894	21.096	0.9806
Pb	24.855	-0.375	7.348	0.753	0.2307	25.063	0.9999	144.93	0.5197	22.927	0.9866

was a consensus between the calculated q_e and q_e experimental values for the pseudo-second-order (Table 4). Therefore, the pseudo-second-order model reflected the best the adsorption kinetics of Cd, Cu and Pb ions on *C. vulgaris*. Comparable result of previous studies confirm the outcome obtained herein (NCIBI et al. 2007, HAMEED et al. 2008).

Mechanism of sorption

The experimental adsorption kinetics of Cd, Cu and Pb, on *C. vulgaris* showed a sharp increase in the adsorbed concentration during the first minutes, followed by a lower uptake rate (Table 2), which can be described by the WEBER and MORRIS model (1963), $q_t = Ki_d t^{1/2} + C$. The intercept C reflects the boundary layer effect. The larger the intercept, the greater the contribution of the surface sorption in the rate controlling step (HAMEED et al. 2008). The initial part is connected to faster mass transfer through the boundary layer and/or adsorption on the solid surface, followed by slow diffusion inside the particles. According to WEBER and MORRIS (1963), if the rate limiting step is intraparticle diffusion, a plot of solute sorbed against the square root of contact time should yield a straight line passing through the origin. However, numerous studies report that intraparticle diffusion is not the only rate controlling step for the sorption of metal ions using biosorbents (HO et al. 2000), and adsorption kinetics may be controlled by film diffusion and intraparticle diffusion simultaneously (QIU et al. 2009). Figure 5 showed that the linear plot does not pass through the organ, which indicates that the intraparticle diffusion was not a sole rate controlling step. On the other hand, a higher value of k_{id} illustrates an enhanced rate of adsorption, whereas a larger k_{id} values illustrates better adsorption which is related to improved bonding between the sorbate and sorbent particles (ERHAN et al. 2004). Our results gave a good fit plot with a determination coefficient of R^2 equal 0.974, 0.980 and 0.987 for Cd, Cu and Pb, respectively. According to ITODO et al. (2012), the intraparticle diffusion is a transport process involving some movement of species from the bulk of the solution to the solid phase. An adsorbent may be in the form of porous barriers and thesolute moves by diffusion from one fluid body to the other by virtue of a concentration gradient.

The experimental results (Tables 1, 2) demonstrated that the preference of *C. vulgaris* was greater for Pb and Cu than Cd under the competitive sorption system. This indicates the higher tendency of Cd to remain in solution compared to Pb and Cu. This observation was confirmed by the isotherm constants and kinetic studies for the affinity of metals ion to sorbate on the surface of *C. vulgaris*, which was in the order of Pb > Cu > Cd. ABDEL-ATY et al. (2013) revealed that blue green alga *Anabaena sphaerica* Born. & Flah. was more effective also for Pb biosorption than Cd. According to SHAHEEN et al. (2012) Pb is a better candidate than Cu and Cd for electrostatic and inner-sphere surface complexation reactions. This finding may be attributed to differences in metal characteristics (Table 5) and resultant affinity for
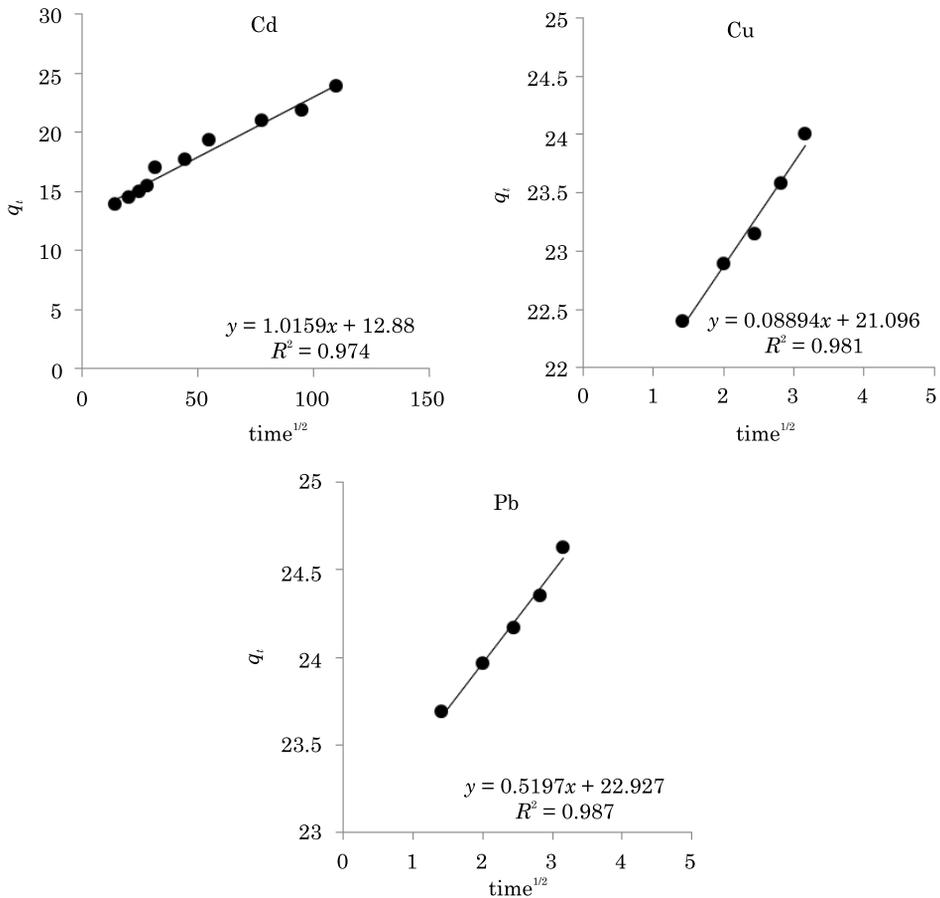
Fig. 5. Intraparticle diffusion plots for biosorption of Cd, Cu and Pb on surface of *Chlorella vulgaris*

Table 5

Some physicochemical characteristics of the studied metal ions

Properties	Cd	Cu	Pb
Atomic weight	112.414	63.546	207.2
pK_h	10.1	7.9	7.71
Ionic radius (Å)	0.97	0.73	1.19
Hydrated radius (Å)	4.26	4.19	4.01
Electronegativity	1.69	1.91	2.33
Misono parameter	0.303	0.284	0.393
Solubility product (Ksp) at 25°C	7.2×10^{-15}	4.8×10^{-20}	1.42×10^{-20}

sorption sites. The important overlapping factors, which influence the relative selectivity of cations, could be summarized as follows:

1. higher electronegativity and greater hydrolysis constant, these factors favour Pb for inner-sphere surface sorption/complexation reactions compared to Cu and Cd;

2. higher atomic weight;

3. higher ionic radius, and subsequently smaller hydrated radius, favouring coulombic interactions of Pb with exchange sites – which is consistent with the theory according to SELVARANI (2000, cited in ARIVOLI et al. 2008) about the ions with smaller hydrated radii;

4. greater solubility product;

5. the Pearson's hard and soft acids and bases theory (Pb and Cu are borderline acids while Cd is included into soft acids),

6. a larger Misono softness value – according to SPOSITO (1980) the index of Misono softness explains the tendency to form covalent bonds between heavy metals and colloids (sorbents).

CONCLUSION

The experimental results indicated that the Langmuir and Freundlich isotherm models were well fitted for lead, copper and cadmium adsorbed onto *C. vulgaris*, which was confirmed by very high determination coefficients. Considering the experimental adsorption kinetics, the pseudo-second order model reflected the best the adsorption of Cd, Cu and Pb ions onto this biosorbent. A sharp increase was shown in the adsorbed concentration during the first minutes, followed by a lower uptake rate described by the Weber and Morris model. Furthermore, intraparticle diffusion was not the only rate controlling step. These studies suggest that non-living *C. vulgaris* cells appear to be an effective and innovative biosorbent in the removal of heavy metals, in the order of Pb > Cu > Cd, from aqueous solution.

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