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Efficiency of removal of cadmium from aqueous solutions by plant leaves and the effects of interaction of combinations of leaves on their removal efficiency

R. Salim*, M. Al-Subu, E. Dawod

Chemistry Department, An-Najah University, Nablus, Palestine

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Abstract

Removal of cadmium from aqueous solutions using 20 species of plant leaves and combinations of these leaves have been studied. Several factors affecting the removal efficiency have been studied. The most efficient types of plant leaves for the removal of cadmium are those of styrax, plum, pomegranate and walnut. The interaction effect of the combined leaf samples on the efficiency of removal of cadmium has been found to be additive in combinations involving styrax plant leaves but seems to be antagonistic in all other combinations. The optimum experimental conditions for removal of cadmium have been found to be at pH 4.1, using high concentrations of naturally dried plant leaves, using ground leaves and to remove cadmium from agitated aqueous solutions. The percentage of metal removed at an initial cadmium concentration of 10 mg/l by the most efficient types of leaves have been found to be 85% for styrax leaves, 85% for plum leaves, 80% for pomegranate leaves, 78% for walnut leaves and 77% for meddler leaves. The presence of foreign ions or complexing agents has been found to reduce the efficiency of removal of cadmium by plant leaves. About 80–85% of the cadmium in charged plant leaves has been released under the influence of changing the pH of the solution, addition of competing ions and the addition of EDTA. The results of removal of cadmium by plant leaves have been found to follow the Freundlich adsorption isotherm, first-order reaction with respect to cadmium and to have intra-pore diffusion as the rate-limiting step.

Keywords: Cadmium; Removal; Plant leaves; Interaction; Efficiency; Kinetics; Aqueous solutions

1. Introduction

Cadmium is one of the most toxic metals affecting man, animals and plants (Friberg et al., 1974; Brooks, 1978; Ormrod, 1984). It was considered one of the "priority pollutants" by the EEC countries (Barbur, 1983). Its excretion from the body is very low (Friberg et al., 1974) and it has synergistic toxicity with other metals, for example, with zinc (Cheremisinoff and Habib, 1972). Thus the removal of cadmium from polluted water is of great importance. Only very few studies have been done on the level of cadmium in the environment of the West Bank, Palestine. One of these studies showed the concentration of cadmium in soil of the highway between Ramallah and Nablus in the West Bank to be 0.45 μg/g (Swaileh et al., 2001a). The concentration of cadmium in the leaves of six common types of roadside plants around the highway of Nablus–Ramallah was reported in the range of 0.3–0.86 μg/g (Swaileh et al., 2001 b). Land snails were reported to magnify cadmium concentration to an average of 19.4 μg/g total dry weight of land snail *Levantina hierosylima* taken from four locations in the West Bank, Palestine (Swaileh et al., 2001b).

Several sorbents have been suggested in the literature for the removal of toxic metals (including cadmium) from water. These include activated carbon (Ferro-Garcia et al., 1988), fly-ash (Yadava et al., 1987), zeolite (Kesraouiouki et al., 1994), ferrites (Navratil, 1994) and limestone (Chen et al., 1999). The most commonly used sorbent is activated

*Corresponding author. Tel.: +972 9 2373762; fax: +972 9 2345589.
E-mail address: radisalim@yahoo.com (R. Salim).

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carbon, which requires regeneration and is costly. Several low-cost sorbents of agricultural and biological origin have been suggested for the removal of toxic metals from polluted waters. Examples of these sorbents are hair (Wilhelm et al., 1989), starch-xanthate (Chaudhari and Tare, 1996), tea-leaves (Singh et al., 1993), apple residues (Lee et al., 1998), hop (Torresdey et al., 2002), moss (Al-Asheh and Duvnjak, 1997), Duckweed (Ornes, 1994), seaweeds (Aderhold et al., 1996), bacteria (Zouboulis et al., 2004), algae (Gin et al., 2002) and fungal biomass (Kapoor and Viraraghavan, 1998).

Due to the availability and low cost, plant leaves were considered as an efficient sorbent for the removal of metal ions from polluted water. Their efficiency was close to the activated carbon results. Examples of reported efficient plant leaves for the removal of metal ions are reed for the removal of cadmium (Sayrafi et al., 1996), sage for cadmium and zinc (Abu-El-Halawa et al., 2003), neem for lead (Bhattacharyya and Sharma, 2004), *Eucalyptus* L. for lead and cadmium (Salim and Abu-El-Halawa, 2002), poplar for the removal of lead (Salim et al., 1994) and copper (Al-Subu et al., 2001), walnut for zinc (Salim et al., 2003), oleander for lead and copper (Abu-El-Halawa et al., 2003), pine for nickel (Salim, 1988) and cypress for aluminum (Salim and Robinson, 1985).

The interaction effects of combinations of cinchona, cypress and pine leaves were studied for the removed of lead from aqueous solutions (Al-Subu, 2002). The interaction effect of plant leaves has been reported to be additive in some combinations, for example, pine and cypress combinations, and antagonistic in other combinations, for example, cinchona with cypress or with pine leaves.

In this study, we compared the efficiency of different types of leaves that are common in Palestine for removing cadmium ions from aqueous solutions. The interaction effect of combinations of the most efficient leaf types has been studied on the removal process of cadmium. Several factors affecting the removal process have been studied. Applicability of adsorption isotherms on the removal process has been tested and a few kinetic parameters of the removal process will be determined. The release of cadmium ions from saturated plant leaves will also be studied.

2. Materials and methods

Samples of 20 common types of plant leaves were gathered from the north areas of the West Bank, Palestine. The various types of plant leaves and their locations are listed in Table 1. Leaves were cleaned thoroughly with deionized water, dried in an oven at 70 °C until constant weight was achieved, after which the leaves were sieved into constant size (0.6–0.7 mm pore radius) and then kept in small bags for further use in the experiments. All experiments were done using oven-dried and ground leaves unless otherwise stated. All types of leaves used were free from cadmium, as indicated from the negligible concentrations of cadmium leached from leaves having about the same leaf-concentrations used in this work after soaking in 1 M HNO_3 for 3 days. Used polyethylene bottles (250 ml) were used in this work. This type of containers was reported by several authors to have minimum adsorption on the container surfaces (King et al., 1974). Only negligible amounts of cadmium were found experimentally adsorbed on the container surfaces under the conditions used in this work. The containers used were decontaminated from metal ions by soaking in 1 M HNO_3 for 3 days and then cleaned thoroughly with deionized water before being used.

Table 1
Plant species studied and their collection sites

Scientific name	Common name	Location of collection
Ficus carcia	Fig tree	Jenin
Amygdalus communis	Almond	Jenin
Maspilus japonica	Japanese medlar	Jenin
Prunus armeniaca	Apricot	Jenin
Prunus domestica	Plum	Qalqilia
Morus alba	Mulberry	Jenin
Juglans regia	Walnut	Nablus
Punica granatum	Pomegranate	Jenin
Olea europoea	Olives	Jenin
Malus sylvestris	Apple	Jenin
Ceratonia siliqua	Carob	Jenin
Eucalyptus camaldulensis	Eucalyptus	Jenin
Styrax japonicus	Styrax	Jenin
Quercus calliprinos	Oak	Jenin
Pistacia palastina	Palestine pistachio	Jenin
Vitis vinifera	Vine	Jenin
Pinus halepensis	Pine	Jenin
Citrus sinensis	Orange	Jenin
Citrus limon	Lemon	Jenin
Cupressus semervirenes	Cypress	Jenin

Cadmium solutions used in this work were prepared by dilution from a 1000 mg/l stock solution prepared from analytical grade $Cd(NO_3)_2 \cdot 4H_2O$. All other chemicals used were of high-grade purity.

Removal of cadmium by leaves was measured by following the decrease of concentration of cadmium from 200 ml buffered cadmium solutions on 12 g/l leaves. Concentrations of combinations of leaves used were always divided equally between the types of leaves forming the combined samples of plant leaves. The desired mass of the studied plant leaves was added to a polyethylene bottle containing 200 mL acetate buffer solution. To this suspension of plant leaves, an exact amount of cadmium stock solution (1000 mg/l) was added using Oxford pipette. For the analysis of cadmium concentration in the leaf suspension, an aliquot of 0.5 ml of the sample solution was added to a thermostatic (22 ± 1 °C) cell containing de-aerated 5.0 ml of the acetate buffer. Clear solutions were obtained from the leaf suspensions by using a small glass tube with a sintered glass disk. The removal of cadmium by plant leaves was always followed until equilibrium was attained. The time required for equilibrium was different from one type of leaves to another and was in the range of 48–190 h. The analytical method used for the determination of cadmium concentrations in solution was the differential anodic stripping voltammetry (DPASV) using a Polarographic Analyzer Stripping Voltammeter Model 264 B, EG&G Instrument. The other working conditions of the instrument are listed in Table 2. The concentration of cadmium in solution was calculated by comparing the obtained peak area with peak areas obtained for standards plotted on calibration curves. The standard addition method was used once every 5–7 measurements in order to check the applicability of the calibration curve. The method of DPASV has the advantage of having very high sensitivity and very low detection limits that makes it a good choice for the analysis of dilute solutions of some metals, including cadmium.

Solutions were buffered at pH 4, unless otherwise stated, using acetate buffers. The pH values of solutions were measured using a pH-meter JENWAY, type 3310. The exact pH was obtained by the addition of drops of ~1 M HNO_3 or NaOH, as required.

Three readings were taken for each sample and the average was reported. The relative deviation of the measured values was normally ~5–7%; deviated results of $\geqslant 10\%$ were discarded.

The reliability of the obtained results was tested by applying the MANOVA multi-variate analysis of variance statistical program on five repetitions of removal experiments done using three types of leaves and their combinations (examples of the repetitions taken for the removal of cadmium on plant leaves are shown in Table 3). The results of the statistical analysis indicated no significant difference at $\alpha = 0.05$. The F values obtained for the experimental results (0.201 and 0.230 for the styrax–plum and styrax–plum–walnut leaf combinations) were less than the critical F values (4.000) at $\alpha = 0.05$. The obtained p values were 0.989 for the styrax–plum combination and 0.987 for the styrax–plum–walnut plant leaf combination. The pair-wise comparison of the mean values of the repeated experimental groups indicated no significant difference at $\alpha = 0.05$.

Table 2
Working conditions used for the differential pulse anodic stripping voltammetry

Experimental parameter for low and moderate concentration	
Working electrode	Mercury drop electrode
Drop size	Middle
Reference electrode	Ag/AgCl electrode
Auxiliary electrode	Pt wire
Initial potential	−0.85 V
Final potential	−0.5 V
Deposition potential	−0.85 V
Integration set point	−0.63 V
Purge time	0.5 min
Deposition time	70 s[a]
Equilibrium time	15 s
Scan rate	10 mV/s
Current	1 μA
Pulse amplitude	25 mV
Recorder x-axes scale	500 mV/cm[b]
Recorder y-axes scale	250 mV/cm

[a]Deposition time for high concentrations was 30 s.
[b]Recorder x-axes scale for high concentrations was 100 mV/cm.

3. Results and discussion

3.1. Effect of type of leaves

Removal of cadmium from aqueous solutions was studied using 20 types of plant leaves. The results obtained are shown in Table 4. Activated carbon is also included in the table for the sake of comparison. The obtained results indicate that:

1. The efficiency of plant leaves for the removal of cadmium from aqueous solutions differs highly from one type to another.
2. The efficiency of some types of leaves (e.g. styrax leaves) is high and close to the efficiency of activated carbon for the removal of cadmium.
3. The time required to reach maximum removal of cadmium (i.e. equilibrium time) varies highly from one type of leaves to another. This equilibrium time is probably related to the shape and to the strength of the leaf surface. This equilibrium time is, e.g., 48 h for rough fig leaves but 190 h for the smooth and solid surface of oak leaves.
4. The efficiency for the studied plant leaves and carbon to remove cadmium from aqueous solutions can be arranged in the decreasing order:
   Activated carbon > styrax > plum > pomegranate > walnut > medlar > cypress > mulberry > carob > olive > eucalyptus > pistachio > almond > vine > fig > apricot > oak > pine > apple > orange > lemon leaves. The styrax leaves are the most efficient and the lemon leaves are the least efficient types of plant leaves.

The first five efficient types of leaves have been used to study the effect of most of the factors studied in this work.

The maximum efficiencies, reported in previous studies, for the removal of cadmium from aqueous solutions by plant leaves were ~95% from 1 mg/l Cd solution by 20 g/l reed leaves (Sayrafi et al., 1999), ~99% from 2.2 mg/l Cd solution by 50 g/l sage leaves (Abu-El-Halawa et al., 2003), ~85% from 4.6 mg/l Cd solution by 33.3 g/l eucalyptus leaves (Salim and Abu-El-Halawa, 2002) and ~40% from 1.7 mg/l Cd solution by 5.4 g/l beech leaves (Salim et al., 1992). The results of the present work show a maximum efficiency of removal of 94% of cadmium from 5.0 mg/l cadmium solution by 24 g/l styrax leaves at pH 4.0 (see Section 3.4). This efficiency is competitive with the previously reported maximum efficiencies of plant leaves for the removal of cadmium from aqueous solutions.

Table 3
Repetitions of results of experiments on the removal of cadmium on samples of combined styrax and plum leaves and of combined styrax, plum and walnut (in equal weight ratio) plant leaves

T/h	C_l	T/h	C_l	T/h	C_l	T/h	C_l	T/h	C_l
Styrax and plum leaves									
0.5	10.42	0.2	10.50	0.5	10.31	0.3	10.01	0.3	11.21
1.0	8.91	0.5	9.01	1.5	8.30	0.5	8.31	1.0	8.51
3.0	8.31	1.0	6.71	3.0	8.12	1.0	7.01	2.0	8.32
5.0	7.61	3.0	6.42	5.0	7.22	3.0	6.82	3.0	7.82
10.0	6.71	5.0	6.62	10.0	6.51	5.0	6.62	5.0	7.31
24.0	6.22	10.0	6.82	15.0	5.90	10.0	7.01	10.0	7.11
48.0	6.40	24.0	7.31	24.0	6.41	15.0	7.11	24.0	6.71
72.0	6.60	48.0	7.31	48.0	6.52	24.0	7.32	48.0	7.02
96.0	6.71	72.0	7.51	53.0	6.80	48.0	7.02	72.0	7.30
120	6.60	95.0	7.20	72.0	6.61	72.0	6.41	96.0	6.90
144	6.50	120	6.70	96.0	6.22	96.0	6.52	120	6.60
168	6.41	144	6.72	120	6.10	120	6.41	144	6.21
196	6.42	168	6.41	144	6.01	144	6.41	168	6.41
216	6.31	192	6.41	192	5.91	196	6.32	216	6.11
240	6.31	240	6.12	240	5.70	240	6.32	240	6.02
Styrax, plum and walnut leaves									
0.5	8.12	0.5	10.80	0.5	10.42	0.5	8.60	0.5	10.31
1.0	7.11	1.0	8.40	1.0	8.31	1.0	7.31	1.0	7.40
1.5	6.41	1.5	6.51	1.5	6.82	1.5	7.01	1.5	7.02
3.0	6.30	3.0	6.31	3.0	6.61	3.0	6.70	3.0	6.82
5.0	6.50	5.0	6.72	5.0	6.40	5.0	6.90	5.0	7.30
15.0	7.10	15.0	7.21	15.0	6.81	15.0	7.20	15.0	7.11
20.0	6.61	20.0	7.32	20.0	7.01	20.0	7.22	20.0	7.21
48.0	6.72	48.0	7.82	48.0	7.11	48.0	7.31	48.0	7.70
51.0	7.11	51.0	7.72	51.0	7.22	51.0	7.51	51.0	8.20
72.0	7.22	72.0	8.00	72.0	7.61	72.0	8.31	72.0	8.42
96.0	7.50	96.0	7.90	96.0	8.10	96.0	8.51	96.0	8.41
120	8.10	120	7.40	120	8.40	120	8.12	120	8.10
144	8.20	144	7.21	144	8.21	144	7.92	144	7.72
196	7.81	196	7.11	196	7.40	196	7.41	196	7.52
240	7.51	—	—	240	7.02	240	7.21	240	7.41

Concentration of Cd = 20 mg/l; concentration of leaves = 15 g/l. C_l; concentration of cadmium ions (mg/l) found in solution after removal process, T/h; time/hour.

3.2. Interaction effects of combinations of plant leaves

Various combinations, in equal weight ratios, of the five most efficient types of plant leaves were used for removing cadmium from aqueous solutions. The results obtained are shown in Table 5. These results indicate that:

1. All combinations involving styrax leaves with other types of leaves showed efficiencies of removal almost the same as the efficiency of removal caused by styrax leaves alone.
2. All other combinations of plant leaves show a small antagonistic effect on the removal of cadmium.
3. None of the combinations studied show synergistic effect on the efficiency of removal of cadmium from aqueous solutions.

3.3. Effect of concentration of cadmium

The effect of concentration of cadmium from its solutions was studied using styrax plant leaves. The results obtained are shown in Fig. 1. These results indicate that:

1. Removal processes of cadmium by plant leaves from the various concentrations of cadmium followed one pattern. In this pattern, the removal of cadmium was somewhat rapid in the first few hours (~50% of the removed cadmium occurs in the first 10 h). The removal process then slows down until it becomes almost steady after a long time (48–190 h, depending on the type of plant leaves used).
2. The time after which the removal rate slows down depends on the concentration of cadmium in solution. This time is shorter from dilute cadmium solutions than from more concentrated ones.

3.4. Effect of concentration of leaves

Removal of cadmium from cadmium solutions, 5.0 mg/l, was studied using several concentrations of the five most efficient types of leaves studied in this work. The results

Table 4
Effect of different plant leaves on the removal of cadmium

Type of leaves	Equilib. time (h)	Initial conc. of Cd (mg/l)					
		1.0	2.0	3.0	4.0	6.0	10.0
		Fraction of Cd removed					
Fig tree	48.0	0.56	0.58	0.58	0.59	0.61	0.63
Almond	72.0	0.60	0.61	0.63	0.63	0.63	0.64
Medlar	96.0	0.72	0.72	0.74	0.74	0.76	0.77
Apricot	72.0	0.56	0.56	0.55	0.57	0.58	0.61
Plum	72.0	0.80	0.81	0.82	0.82	0.84	0.85
Mulberry	48.0	0.66	0.68	0.67	0.70	0.71	0.71
Walnut	96.0	0.75	0.76	0.76	0.76	0.76	0.78
Pomegranate	72.0	0.76	0.78	0.77	0.78	0.79	0.80
Olives	120.0	0.64	0.66	0.67	0.68	0.68	0.72
Apple	72.0	0.48	0.48	0.51	0.51	0.52	0.55
Carob	120.0	0.65	0.67	0.68	0.69	0.70	0.71
Eucalyptus	48.0	0.62	0.64	0.65	0.66	0.67	0.72
Styrax	120.0	0.82	0.82	0.82	0.84	0.84	0.85
Oak	190.0	0.52	0.52	0.55	0.58	0.59	0.61
Pistachio	72.0	0.60	0.61	0.62	0.63	0.64	0.66
Vine	72.0	0.58	0.60	0.61	0.62	0.62	0.64
Pine	48.0	0.52	0.53	0.54	0.53	0.61	0.65
Orange	190.0	0.46	0.46	0.47	0.48	0.49	0.49
Lemon	190.0	0.39	0.40	0.44	0.47	0.49	0.58
Cypress	48.0	0.69	0.70	0.73	0.74	0.75	0.77
Activated carbon	48.0	—	—	—	0.88	—	—

Concentration of leaves = 12.0 g/l; pH = 4.0. Concentration of activated carbon = 12.0 g/l; pH = 4.0.

obtained indicate that the removal efficiency of cadmium is strongly affected by the concentration of leaves in solution. For example, the concentration of cadmium removed from 5 mg/l cadmium solutions, at pH 4.0, was 3.20, 3.35, 3.45, 3.55 and 3.35 by 4 g/l plant leaf suspension of medlar, pomegranate, plum, styrax and walnut leaves, respectively.

The concentration of cadmium removed from 5 mg/l cadmium solutions, at pH 4.0, was 4.45, 4.60, 4.65, 4.70 and 4.45 by 24 g/l plant leaf suspensions of medlar, pomegranate, plum, styrax and walnut leaves, respectively.

3.5. *Effect of pH*

The removal of cadmium from 2.0 mg/l aqueous cadmium solutions using the five most efficient types of leaves was studied at several pH values ranging between 1 and 10. The pH values of solutions were obtained by the addition of ~1 M HNO_3 or NaOH, as required. The results obtained for the removal of cadmium, after equilibrium is attained, are shown in Fig. 2. These results show a high dependence of the removal process on the pH. The optimum pH value for obtaining the maximum efficiency of removal of cadmium by the studied leaves is pH 4.1. High pH values (>7) also resulted in an increase in the efficiency of removal of cadmium, but to a slightly less extent than from solutions of pH 4.1.

Cadmium is present in solutions of low pH values as free Cd^{2+} ions. At high pH values (>8 according to Cordero et al., 2004) poorly soluble hydroxyl $Cd(OH)_2$ and $Cd(OH)_3^-$ are formed.

The effect of pH on the removal capacity of cadmium below pH 4.1, in the present work, might be attributed to competition between cadmium and hydrogen ions on the adsorption sites of plant leaves. The hydrogen ion is a strong competitor for adsorption because of its small size.

Table 5
Interaction effect of several combinations of plant leaves on the removal of cadmium

Sample	Initial Cd concentration (mg/l)						
	0.5	1.0	1.5	3.0	5.0	7.0	10.0
	Fraction of Cd removed						
Styrax (1)	0.81	0.82	0.83	0.83	0.84	0.85	0.86
Plum (2)	0.79	0.80	0.81	0.82	0.83	0.85	0.85
Pomegranate (3)	0.75	0.76	0.77	0.77	0.78	0.79	0.80
Walnut (4)	0.74	0.74	0.75	0.76	0.77	0.78	0.78
Medlar (5)	0.72	0.73	0.73	0.74	0.75	0.76	0.77
1+2	0.80	0.81	0.82	0.83	0.83	0.84	0.85
1+3	0.76	0.77	0.77	0.78	0.80	0.82	0.83
1+4	0.77	0.77	0.78	0.80	0.81	0.82	0.83
1+5	0.74	0.75	0.76	0.78	0.80	0.81	0.82
2+3	0.76	0.77	0.77	0.78	0.79	0.81	0.82
2+4	0.74	0.75	0.76	0.77	0.78	0.79	0.81
2+5	0.74	0.75	0.76	0.76	0.77	0.78	0.80
3+4	0.73	0.73	0.74	0.75	0.76	0.77	0.78
3+5	0.72	0.73	0.73	0.74	0.76	0.77	0.79
4+5	0.70	0.70	0.70	0.72	0.72	0.73	0.75
1+2+3	0.77	0.80	0.78	0.79	0.81	0.82	0.84
1+2+4	0.74	0.74	0.74	0.76	0.79	0.81	0.82
1+2+5	0.72	0.72	0.72	0.75	0.77	0.78	0.81
1+3+4	0.75	0.76	0.77	0.78	0.80	0.81	0.83
1+3+5	0.71	0.71	0.71	0.73	0.75	0.76	0.79
1+4+5	0.72	0.72	0.72	0.74	0.76	0.78	0.80
2+3+4	0.74	0.75	0.76	0.77	0.78	0.79	0.81
2+3+5	0.70	0.70	0.69	0.72	0.74	0.75	0.79
2+4+5	0.71	0.72	0.72	0.73	0.75	0.76	0.78
3+4+5	0.70	0.70	0.71	0.72	0.75	0.77	0.80
1+2+3+4	0.77	0.78	0.79	0.80	0.82	0.83	0.84

Concentration of leaves = 12.0 g/l; pH = 4.0.

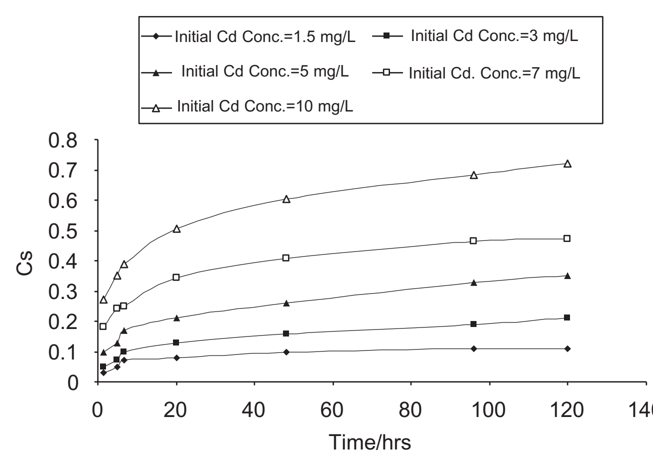

Fig. 1. Effect of concentration of cadmium on its removal from solution by styrax plant leaves. Concentration of leaves = 12.0 g/l, pH = 4.

The reduced capacity of adsorption of cadmium beyond pH 4.1 is probably due to the formation of cadmium complexes with organic components leached from the plant leaves. These complexes have larger sizes than free cadmium ions and thus are weaker competitors for adsorption.

The high removal capacity beyond pH 7 is due to the precipitation of cadmium from solution as cadmium hydroxide.

The maximum biosorption capacity by *Fucus spiralis* nonliving macro-alga was reported at pH ≈4.5 (Cordero et al., 2004). Removal of cadmium, using plant leaves, was recommended to be from aqueous solutions with pH values of ~7 for the removal of cadmium by reed and sage plant leaves (Sayrafi et al., 1999; Salim and Abu-El-Halawa, 2002) and pH 5 using beech leaves (Salim et al., 1992).

3.6. Effect of mode of drying leaves

Removal of cadmium from aqueous solutions having various concentrations of cadmium using oven-dried leaves one time and naturally dried leaves another time was studied on five types of plant leaves. The results obtained are shown in Table 6. These results show little higher efficiency of naturally dried leaves (~18–20 °C) than oven-dried leaves (70 °C). Applying the analysis of variance (ANOVA) statistical test on the results of Table 6 indicated a significant difference between the natural-dried and the oven-dried leaves. The obtained p values were 0.0012, 0.0003, 0.0003, 0.0008 and 0.0000 for styrax, plum, pomegranate, walnut and meddler plant leaves, respectively. This difference in the adsorption capacity might be due to the destruction of some of the adsorption sites of the oven-dried leaves because of the effect of temperature. The order of efficiency of naturally dried leaves also is different from that of the oven-dried leaves. The efficiency of removal of cadmium by naturally dried leaves is arranged in the decreasing order: plum > styrax > medlar > pomegranate > walnut leaves.

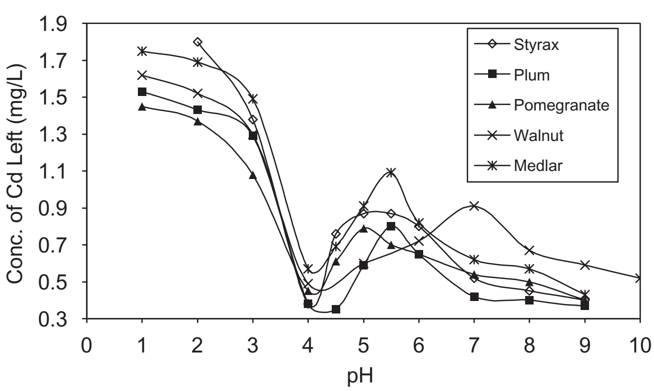

Fig. 2. Effect of pH on the removal of cadmium by several types of leaves. Concentration of Cd = 2.0 mg/l; concentration of leaves = 12.0 g/l.

3.7. Effect of size of leaves

Removal of cadmium from aqueous solutions by five types of plant leaves was studied using three different sizes of each type of plant leaves. These three sizes were (i) normal untouched leaves, (ii) roughly crushed leaves and (iii) ground to 0.6–0.7 mm pore radius. The results obtained indicate a distinct dependence of the efficiency of removal of cadmium on the size of plant leaves. For all types of studied leaves and from all studied concentrations of cadmium, the efficiency of removal of cadmium by plant leaves can be arranged in the decreasing order:

Ground leaves > crushed leaves > untouched leaves.

This arrangement is expected because adsorption of cadmium on leaves is directly related to surface area. This surface area increases with crushing and with grounding leaves.

3.8. Effect of agitation

The effect of casual agitation of leaf suspensions on the efficiency of plant leaves to remove cadmium from aqueous solutions was studied using several types of plant leaves and several combinations of plant leaves. Examples of the results obtained are given in Table 7. A statistical test, ANOVA, was applied on the results of Table 7. This test

Table 6
Effect of mode of drying leaves on their removal of cadmium from solution

Fraction of Cd removed										
Initial Cd conc. (mg/l)	Medlar		Walnut		Pomegranate		Plum		Styrax	
	Naturally dried	Oven dried	Naturally dried	Oven dried	Naturally dried	Oven dried	Naturally dried	Oven dried	Naturally dried	Oven dried
1.0	0.87	0.73	0.82	0.76	0.84	0.76	0.89	0.80	0.88	0.82
3.0	0.88	0.74	0.84	0.76	0.86	0.77	0.91	0.82	0.90	0.83
5.0	0.90	0.75	0.86	0.77	0.88	0.78	0.93	0.83	0.92	0.84
7.0	0.91	0.76	0.87	0.78	0.89	0.79	0.94	0.85	0.93	0.85
10.0	0.92	0.77	0.88	0.78	0.90	0.80	0.95	0.85	0.94	0.86

All readings are taken after equilibrium is attained (120 h for styrax, 96 h for walnut and 72 h for the remaining types of plant leaves). Concentration of leaves = 12.0 g/l; pH = 4.0.

showed a significant difference between the adsorption capacities of cadmium from agitated and non-agitated solutions. The obtained p values were 0.004, 0.004, 0.005 and 0.004 for styrax, plum, walnut and styrax–plum combined plant leaves, respectively.

The effect of agitation of solution is related to the rate-limiting step. This is discussed in Section 3.13.

3.9. Effect of presence of foreign ions and of complexing agents

The effect of the presence of various concentrations of zinc, lead and copper foreign ions and of the EDTA complexing agent on the efficiency of removal of cadmium by plant leaves was studied on five types of plant leaves.

Table 7
Effect of agitation of solution on the removal of cadmium by plant leaves

Time/h	Styrax		Plum	
	Without agitation	With agitation	Without agitation	With agitation
Conc. of Cd adsorbed (mg/g)				
1.5	0.27	0.31	0.25	0.32
5.0	0.35	0.38	0.30	0.35
10.0	0.39	0.44	0.39	0.43
24.0	0.46	0.49	0.48	0.51
48.0	0.52	0.54	0.60	0.66
72.0	—	—	0.71	0.72
96.0	0.69	0.71	—	—
120.0	0.72	0.72	—	—
Leaf type	Walnut		Styrax + Plum	
Conc. of Cd removed (mg/g)				
1.5	0.25	0.33	0.23	0.29
5.0	0.34	0.37	0.29	0.34
10.0	0.37	0.41	0.35	0.39
24.0	0.48	0.50	0.46	0.49
48.0	0.55	0.56	0.54	0.57
96.0	0.65	0.67	0.71	0.72

Concentration of Cd = 10.0 mg/l; concentration of leaves = 12.0 g/l: pH = 4.0.

The results obtained are given in Table 8. These results indicate noticeable effects of the presence of all studied foreign ions and of EDTA on reducing the efficiency of plant leaves to remove cadmium from aqueous solutions. This effect increases with increasing the concentration of the present foreign ion or complexing agent. The effect of the studied chemicals on reducing the efficiency of removal of cadmium by plant leaves can be arranged in the order:

$$\mathrm{EDTA} > Zn^{2+} > Pb^{2+} > Cu^{2+}.$$

The effect of presence of foreign ions was found in some cases to reduce the efficiency of removal of metal ions by plant leaves. For example, the presence of lead and cadmium reduced the removal of copper by poplar leaves (Al-Subu et al., 2001); the presence of copper and cadmium reduced the removal of lead by cypress leaves (Salim et al., 1994); and the presence of copper reduced the removal of cadmium by beech leaves (Salim et al., 1992).

The presence of other ions enhanced the removal efficiency of metal ions by plant leaves. For example, the presence of zinc ions enhanced the removal of copper by poplar leaves (Al-Subu et al., 2001); the presence of magnesium and sodium ions enhanced the removal of lead by cypress leaves (Salim et al., 1994); and the presence of lead ions enhanced the removal of cadmium by beech leaves (Salim et al., 1992).

Wang (1995) concluded that the binding sites on the water hyacinth roots have higher affinity for lead compared to that of cadmium and zinc. Similar results were observed by Low et al. (1994).

All above studies indicate that the effect of presence of foreign ions on the removal capacity is complicated. This effect depends on several factors such as:

1. The competition on the adsorption sites between the foreign and the removed ions. This competition is influenced by the charge and size of the hydrated ions involved.
2. Some of the ions present are expected to make complexes with reagents leached from plant leaves into

Table 8
Effect of presence of Cu^{2+}, Zn^{2+}, Pb^{2+} and EDTA in solution on the removal of cadmium using plant leaves

Plant leaves	Fraction of cadmium removed							
	Conc. of Zn (mg/l)		Conc. of Cu (mg/l)		Conc. of Pb (mg/l)		Conc. of EDTA (mg/l)	
	2.0	10.0	2.0	10.0	2.0	10.0	2.0	10.0
Styrax (1)	0.75	0.62	0.77	0.66	0.76	0.64	0.74	0.61
Plum (2)	0.71	0.58	0.76	0.63	0.76	0.64	0.72	0.58
Pomegranate (3)	0.70	0.57	0.70	0.55	0.72	0.61	0.77	0.53
Walnut (4)	0.66	0.51	0.69	0.56	0.70	0.60	0.62	0.51
1 + 2	0.73	0.59	0.75	0.64	0.76	0.64	0.73	0.60
2 + 4	0.69	0.56	0.70	0.58	0.70	0.62	0.65	0.53
1 + 2 + 3	0.70	0.56	0.72	0.62	0.72	0.63	0.68	0.55
1 + 2 + 3 + 4	0.72	0.57	0.73	0.53	0.73	0.64	0.70	0.57

Concentration of Cd = 2.0 mg/l; concentration of leaves = 12.0 g/l; pH = 4.0. All readings are taken after 120 h.

solution. This affects the ability of these ions to compete for adsorption sites.

3. Added ions affect the pH of solution to various degrees. This has great influence on the removal efficiency of metal ions.

The role of EDTA is to change the free cadmium ions into complex ions. The present results suggest that adsorption of complex cadmium ions on plant leaves is less than that of the free cadmium ions. This is probably due to the larger size of the complex ion compared to the free cadmium ion. The large size of the complex ion deprives it from a part of the adsorption sites that can be reached only by the small free cadmium ions.

3.10. Release of cadmium from charged plant leaves

Samples of 12 g/l styrax, plum, walnut and combined styrax–plum plant leaves were saturated with cadmium by soaking each of them in 10 mg/l aqueous cadmium solutions for a long time (1 week). This resulted in the transference of ~85% of cadmium from solution onto leaves. These leaves were then put in solutions having various concentrations of H^+, Zn^{2+}, Cu^{2+} and EDTA, and the release of cadmium from leaves was followed with time. Two values of pH were used for this study, one is more acidic and the other is more basic than the optimum pH chosen for the removal of cadmium (c.f. Fig. 2).

The obtained results are shown in Figs. 3–5 for the release of cadmium under the effects of pH, competing ions and EDTA, respectively. These results indicate that:

1. Cadmium is partially released from plant leaves under the effect of variation of pH, addition of competing ions or the addition of EDTA.
2. About half of the cadmium in leaves is released during the first 1–5 h of the influence of the releasing agent.
3. The release of cadmium from plant leaves is continued for a long time under the influence of the releasing agents. However, a part of cadmium in leaves resists being released after very long times of contact with the releasing agents. This is due to an equilibrium reached between the amount of cadmium released and that linked again to the bound sites. The unreleased part of cadmium in leaves is ~20% under the influence of acidification, ~16–45% under the influence of addition of competing ions and ~ 15–34% under the influence of addition of increasing concentrations of EDTA.
4. The effect of competing ions on the release of cadmium from plant leaves can be arranged in the decreasing order: copper > zinc > lead.

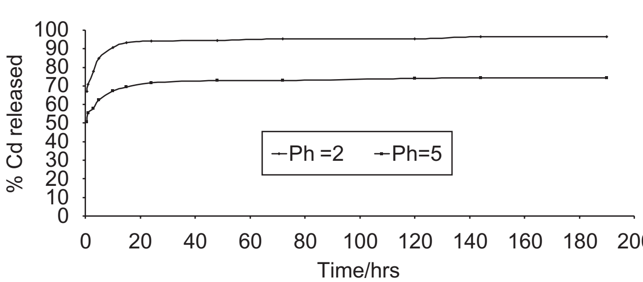

Fig. 3. Release of cadmium from charged styrax plant leaves by changing the pH of the solution.

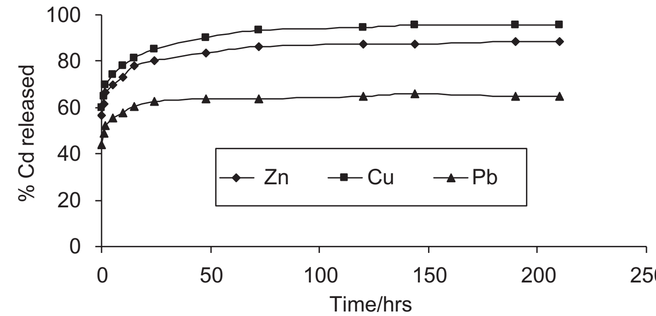

Fig. 4. Release of cadmium from charged styrax plant leaves by the addition of 10 mg/l competing ions at pH 4.0.

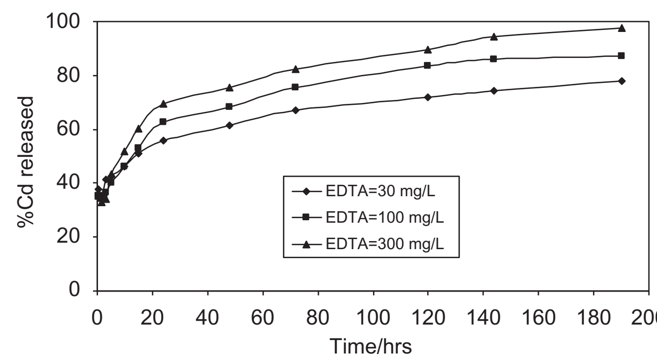

Fig. 5. Release of cadmium from charged styrax plant leaves by the addition of various concentrations of EDTA.

3.11. Application of adsorption isotherms

The Freundlich and the Langmuir adsorption isotherms are the most widely applied isotherms for the adsorption of metal ions on a wide variety of adsorbents.

The Freundlich isotherm is an empirical one appropriate for the adsorption processes where non-uniformity of the surface of adsorbent is expected. An appropriate formula of the Freundlich adsorption isotherm is:

$$\log C_s = \log K + 1/n \log C_l,$$

where C_s is the concentration of metal ion adsorbed (mg/g), C_l the concentration of metal ion remaining in solution (mg/l), K the constant indicating the adsorption capacity of the adsorbent and n the constant indicating the adsorption intensity of the adsorbent.

The Langmuir adsorption isotherm is commonly applied to monolayer chemisorption of gases. However, several authors have applied this isotherm for the adsorption of metal ions on sorbents. This isotherm is mainly applied when no strong adsorption is expected and when the adsorption surface is uniform. A commonly used formula of the Langmuir adsorption isotherm is

$$1/C_s = 1/b + 1/ab(1/C_l),$$

where C_s and C_l are as defined in the Freundlich isotherm, a is the constant indicative of the bonding energy between the adsorbent and the adsorbed species and b the constant indicative of the mass of the adsorbed species required for a monolayer coverage of a unit mass of adsorbent.

The applicability of the above isotherms on the present results was tested on a representative group of results of Table 4 containing plant leaves having high, medium and low efficiencies of removal of cadmium from aqueous solutions. Both the Freundlich and the Langmuir adsorption isotherms showed linear relationships on the present results (shown in Figs. 6 and 7 for the Freundlich and the Langmuir adsorption isotherms, respectively). The parameters of the Freundlich adsorption isotherm were calculated from the results of Fig. 6. The values of the parameter n are 1.09, 0.93, 0.87 and 0.78 for n values of styrax, walnut, olive, vine and lemon leaves, respectively. The values of the parameter K are 358.8, 166.4, 67.0, 41.7 and 25.9 for styrax, walnut, olive, vine and lemon leaves, respectively. The parameter n for all studied types of leaves is ~1, indicating low coverage of cadmium on leaves. The values of this parameter show also the decrease of the intensity of adsorption of cadmium with decreasing efficiency of removal of cadmium by plant leaves. The values of the parameter K also indicate decreasing capacity of adsorption of cadmium with decreasing efficiency of removal of cadmium by plant leaves. The values of the parameters n and K obtained in this work are close to the values obtained from previous works on the removal of cadmium by plant leaves (Sayrafi et al., 1996; Salim and Abu-El-Halawa, 2002; Salim et al., 1992).

The parameters of the Langmuir adsorption isotherm, a and b, were found to be erroneous and with negative values for most of the present results. This suggests the unsuitability of this isotherm for application on the present results. Such negative values of the Langmuir parameters were reported in a previous work on the removal of lead on pine leaves (Al-Subu, 2002). The negative values of the Langmuir parameters were attributed to the non-uniformity of plant-leaf surfaces and to the high strength of adsorption of lead on pine leaves (Al-Subu, 2002). These same reasons are probably the cause of the negative values of the Langmuir parameters found for the present results.

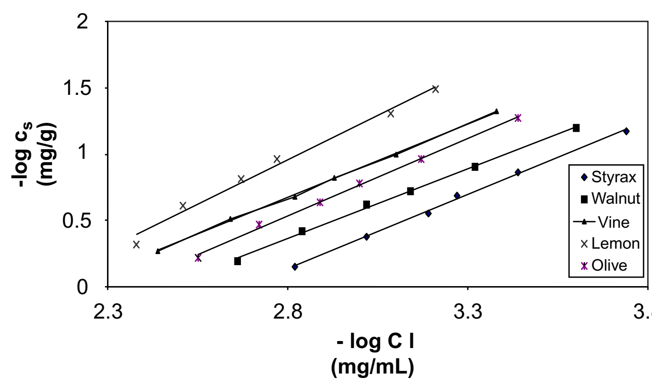

Fig. 6. Linear relations of adsorption of cadmium on plant leaves according to the Freundlich adsorption isotherm.

3.12. Order of reaction

For each initial concentration of cadmium, in the results presented in Fig. 1, the values of C_s were plotted against the square root of time $t^{1/2}$. These plots gave straight lines (examples of the obtained lines are shown in Fig. 8). The slopes of these lines were used to obtain the rates of reaction:

$$(\mathrm{d}C_s/\mathrm{d}t) = 1/2t^{1/2}(\mathrm{d}C_s/\mathrm{d}t^{1/2}).$$

The obtained rates of reaction were found to be linearly related to C_l (examples of the obtained lines are shown in Fig. 9). This indicates a first-order reaction, with respect to cadmium, for the process of the removal of cadmium on plant leaves. This conclusion was tested and found true for several types of leaves and leaf combinations. The tested

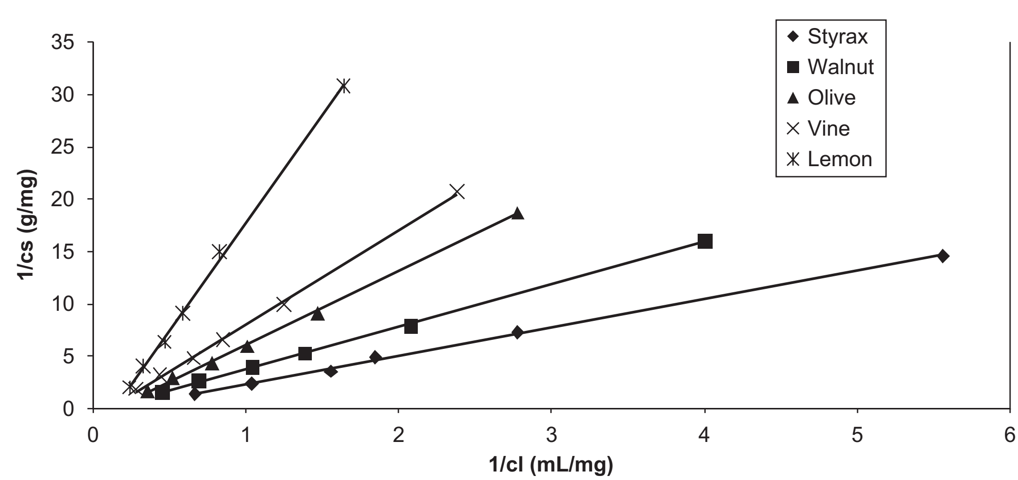

Fig. 7. Linear relations of adsorption of cadmium on plant leaves according to the Langmuir adsorption isotherm.

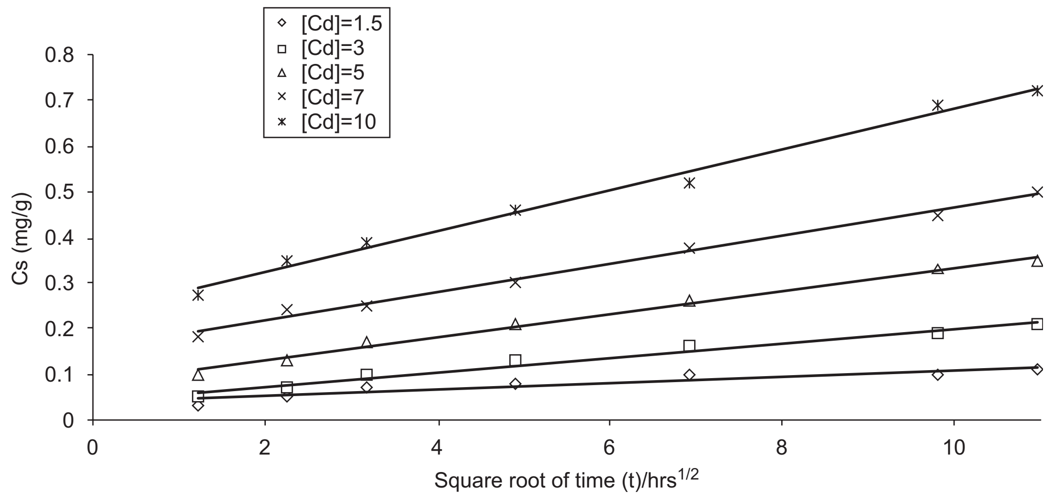

Fig. 8. Relations of C_s and $t^{1/2}$ for the removal of cadmium from aqueous solutions having various concentrations of cadmium.

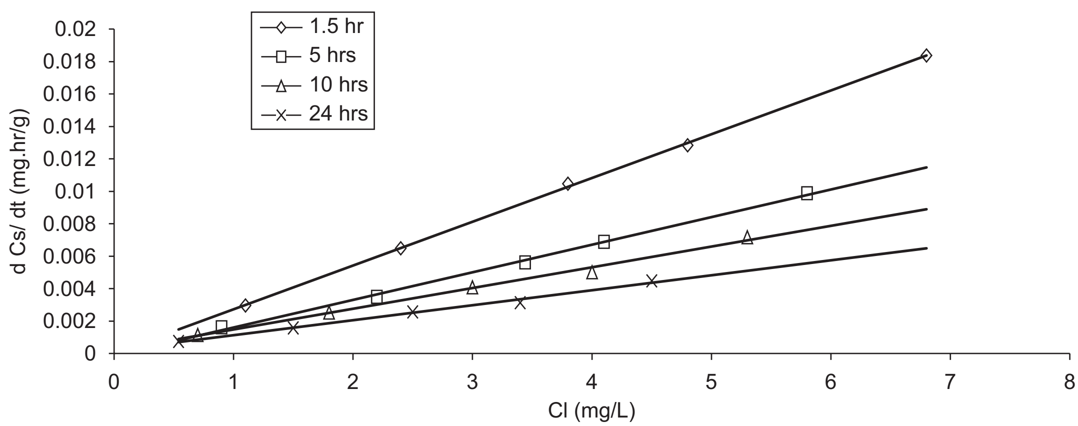

Fig. 9. Relations between the rate of removal of cadmium on styrax plant leaves from solutions having various concentrations of cadmium and after several times of contact between solutions and plant leaves.

leaves were styrax, plum and walnut plant leaves. The tested combinations of plant leaves (in equal weight ratios) were styrax + plum, styrax + walnut, plum + walnut, and styrax + plum + walnut leaves.

3.13. Rate-limiting step

Adsorption of metal ions on plant leaves follows a three-step process (Salim et al., 1992):

1. Film diffusion: in which metal ions reach by diffusion, driven by a concentration gradient, the surface of leaves.
2. Intra-pore diffusion: in which most of the adsorbed metal ions have to enter the pores of the leaves in order to reach the internal adsorption sites.
3. Adsorption: in which the metal ions become adsorbed on the adsorption sites.

The straight-line relations found between C_s and $t^{1/2}$ (c.f. Fig. 8) suggests that diffusion is the rate-limiting step (Helfferich, 1962; Weber et al., 1963). The small effect of agitation (c.f. Table 7) suggests that intra-pore diffusion is the rate-limiting step for the removal of cadmium by plant leaves. The same conclusion was also suggested for the uptake of cadmium on beech leaves (Salim et al., 1992).

4. Conclusions

Plant leaves are capable of removing cadmium from aqueous solutions. The efficiency of removal varies widely from one type of plant leaves to another. The efficiencies of removal of cadmium by the studied species can be arranged in the decreasing order:

Activated carbon > styrax > plum > pomegranate > walnut > medlar > cypress > mulberry > carob > olive > eucalyptus > pistachio > almond > vine > fig > apricot > oak > pine > apple > orange > lemon leaves.

All combinations of styrax with other types of plant leaves result in additive effects on the efficiency of removal of cadmium; all other combinations of plant leaves result in antagonistic effects on the efficiency of removal of cadmium.

The maximum removal efficiency of cadmium by plant leaves is not affected by cadmium concentration in aqueous solutions. However, the range of concentration studied in this work is not wide. It is probable that by using a wide range of initial cadmium concentrations, the differences in sorption capacity would be more appreciable. The pH of solution affects highly the removal efficiency of cadmium; the maximum efficiency is obtained at pH 4.1. The efficiency of removal of cadmium increases with the increase in the concentration of plant leaves used for the removal of cadmium from aqueous solutions. The naturally dried plant leaves are more efficient than oven-dried leaves for removing cadmium from solution. Ground plant leaves have higher efficiency than untouched or roughly crushed leaves for removing cadmium from aqueous solutions. Agitation of solution increased slightly the efficiency of removal of cadmium by plant leaves.

The presence of foreign ions and of the complexing agent, EDTA, reduced the efficiency of removal of cadmium by plant leaves. The effect of the studied chemicals on reducing the efficiency of removal of cadmium can be arranged in the decreasing order: $EDTA > Zn^{2+} > Pb^{2+} > Cu^{2+}$.

Cadmium ions can be released from plant leaves, charged with cadmium, by changing the pH of solution, by the addition of a competing ion or by the addition of EDTA. However, a part of the cadmium adsorbed by plant leaves resists being released by all used releasing agents.

The present results of removal of cadmium by plant leaves and by combined plant leaves follow the Freundlich adsorption isotherm. Parameters of this isotherm indicate the variations in the adsorption capacity and adsorption intensity of cadmium on the studied plant leaves according to their various efficiencies of removal. The results give straight lines according to the Langmuir adsorption isotherm. However, the parameters obtained from the present results, according to this isotherm, are negative and meaningless.

The results of the present work suggest a first-order reaction, with respect to cadmium, for the removal process of cadmium by plant leaves. There are indications that the rate-limiting step for the removal process is intra-pore diffusion.

The method presented in this work might be of interest for industrial and for environmental applications for the removal of toxic metal ions from the environment. Using plant leaves for the removal of metal ions have the advantages of being available, cheap and efficient. The contaminated plant leaves are expected to precipitate and become a part of the sediment. However, using this method for treatment of industrial effluents might require finding a way for a proper disposal of the leaves.

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