BABEȘ-BOLYAI UNIVERSITY
FACULTY OF CHEMISTRY AND CHEMICAL ENGINEERING

ABSTRACT OF THE PhD THESIS

THE REMOVAL OF ORGANIC AND INORGANIC POLLUTANTS USING PHYTOREMEDIATION PROCESSES

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Cluj Napoca

2015

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Keywords: heavy metals, bioremediation, fir cone (abies alba), phytoextraction, marine sediments, aquatic plants

1. INTRODUCTION

With the emergence of industrial revolution and its development, the environmental pollution with heavy metals became a serious problem, disturbing the natural biogeochemical cycles (Khan et al., 2007).

The pollution of water resources due to the disposal of heavy metals has been an increasing worldwide concern for the last few decades. The problem of removing pollutants from water and wastewater became more obvious with rapid industrialization (Gode et al., 2008). Heavy metal pollution has become one of the most serious environmental problems nowadays. Unlike organic pollutants, heavy metals are persistent and non-biodegradable, therefore their removal is extremely important for the health of livings specimens (Peternele et al. 1999; Naiyaa, et al. 2009). The major source of heavy metal contamination is caused by human activities and industrialization, with a direct or indirect discharge of these pollutants in the water bodies.

Bioremediation receives a considerable amount of attention as an alternative process to traditional methods in dyes and heavy metal removal from contaminated waters (Ahluwalia and Goyal, 2007). Bioremediation is a natural process which relies on bacteria, fungi and plants to alter contaminants, as these organisms carry out their normal life functions. During their metabolic processes, these organisms are capable of using chemical contaminants as an energy source, rendering the contaminants harmless or less toxic in most cases. Among the commonly available sorbent materials, biomasses that originate from plants are both economic and ecofriendly, due to their unique chemical composition, availability, renewable capacity, low cost and efficiency. All these qualities make the plant origin biomasses a viable option for the dyes and heavy metal remediation (Sud et al., 2008).

Biosorption is an emerging technology that uses biological materials to remove metals from solution through adsorption. The major advantages of biosorption over conventional treatment methods include: low-cost; high efficiency; minimization of chemical and/or biological sludge; regeneration of biosorbent; no additional nutrient requirement; possibility of metal recovery (Ahalya et al. 2008). The cost advantage of biosorption technology would guarantee a strong penetration of the large market of heavy metal polluting industries (Blázquez et al. 2012).

Phytoremediation represents the use of green plants to remove or degrade contamination from soils and surface waters. It has been proposed as a cheap, sustainable, effective, and environment-friendly alternative to conventional remediation technologies. Plants use solar energy (through photosynthesis) to extract chemicals from the soil and to deposit them in the above-ground part of their bodies, or to convert them to a less toxic form (Raskin and Ensley 2000; Gratão et al. 2005). Aquatic plant biomass, irrespective whether living or dead represents an abundant, cost-effective biological resource that possesses an immense capacity to accumulate organic dyes (Marques et al. 2009; Usman et al. 2013) and hence is exploited worldwide for developing environment-friendly wastewater treatment technologies. Phytoremediation is often referred as botanical bioremediation or green remediation (Chaney et al. 1997) and defined as the use of green plants to remove pollutants from the environment or to render them harmless. It is considered a new highly-promising technology for the remediation of polluted sites (Salt and Kramer 1999) and is currently divided into areas such as phytoextraction, which we used in this study.

Phytoextraction is the uptake of the contaminants from the soil or from aqueous solutions done by the root of the plant.

The theme of this thesis is based focused on the (I) biosorption studies and (II) Characterization, determination and remediation of heavy metals and pesticides found the in marine sediments of the Mediterranean port of Livorno, Italy.

2. INNOVATIVE CONTRIBUTIONS

2.1. Biosorption studies

The present research is set to ellaborate on a phytoremediation method that makes use of some new types of biomasses originating from cellulose. The absorbant material under scrutiny here was obtained from fir cones (*Abies Alba*) in different forms: natural, chemically-treated and imobilised. The biosorbent materials are accessible and friendly with the environment. Cadmium was the heavy metal chosen in this study because of its rare toxicity characteristics.

2.2. Materials and methods

2.2.1 Biomass obtained from cone fir (*Abies Alba*)

a. Natural powder

Fir tree (*Abies Alba*) cones were collected from a botanical garden in Cluj-Napoca, Roumania. The fir cones were washed several times to remove any surface impurities and then dried in an oven at105°C for 24 h. The scales on the cones were then removed and crushed using a bead mill. Prior to being used the fir cone biomass had been washed with distilled water several times until it yielded colorless filtered water. The obtained fir cone powder was then grinded and sieved, particles between 200 and 400 µm were collected and used for analysis.

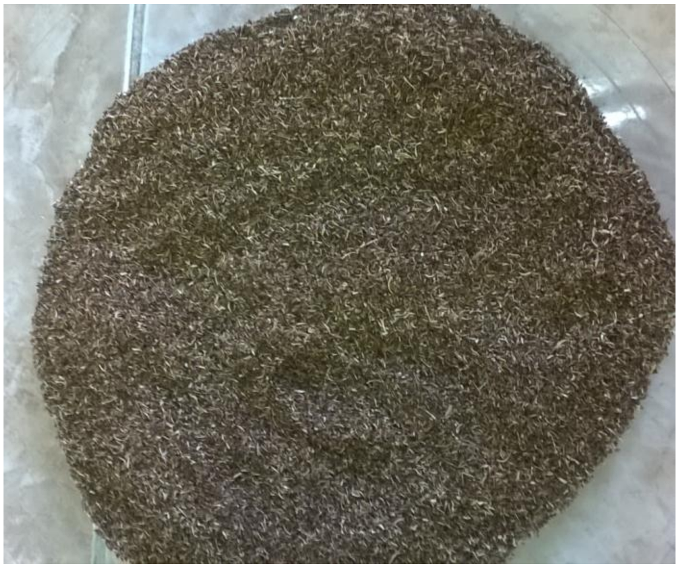

Figure 1. Fir cones (*Abies Alba*)

In order to enhance the biosorption capacity, fir cones powder biomass was subject to NaOH and H_2O_2 treatments. The obtained biomass was used for the removal of heavy metals from aqueous solutions.

2.2.2. Preparations of the Cd (II) and Pb (II) solutions

2.2.2.1 The Preparation of Cd (II) solutions

A stock solution of 1000 mg/L of Cd (II) was prepared by dissolving a weighed amount of $Cd(NO_3)_2 \times 4H2O$ in 1000 ml distilled water. The required concentrations for all the biosorption experiments were obtained by diluting with distilled water to the concentrations ranging between 49-240 mg/L of the stock solution. The initial pH of solution was adjusted using HCl and NaOH solutions. All chemicals were of analytical grade chemicals.

2.2.2. Preparation of Pb(II) solutions

The stock solution of Pb(II) nitrate [$Pb(NO_3)_2$] was prepared by dissolving the accurately-weighed amount of salts in deionized water. The working solutions were prepared by diluting the stock solution with deionized water to give the appropriate concentration of the working solutions. The range of concentrations of metal ions prepared from standard solution varies between 50 and 250 mg/L. Before mixing the adsorbent, the pH of each test solution was adjusted to the required value with 0.1 M KOH or 0.1 M HCl. The reagents used were of analytical grade.

2.2.3 Batch experiments

The biosorption of cadmium onto fir cone powder was studied in batch conditions. Experiments were carried out contacting a known weight of biosorbent (1-4 g) at different stirring rates (200-400-500 rpm), was equilibrated with 100 mL of Cd (II) ions solution of known concentration (49-240 mg/L) in 250 ml of Berzelius glasses at different temperatures using a thermostat water bath (298-326 K). In order to establish the evolution of the removal process, samples of 100 µL were collected at different time intervals (5-240 min). The collected samples at predetermined time intervals were filtered (ME cellulose 0.45µm microfilter) and the remaining concentration in aqueous phase was determined using an Atomic Absorption Spectrometer (SensAA Dual GBS Scientific Equipment, Australia).

The evaluation of the Cd (II) and Pb (II) uptake at equilibrium for the fir cone powder samples was realized using adsorption capacity, q (mg/g) and removal efficiency, E (%) values.

$$E, (\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad (1)$$

$$q_t\,(mg/g) = \frac{(C_i - C_f)\quad V}{m} \qquad (2)$$

where E, (%) represents the efficiency, C_i and C_f the initial and final concentration of lead (mg/L) in the aqueous solution, the q_{max} (mg/g) represents the amount of heavy metals adsorbed onto unit weight of plant, V (L) means the volume of heavy metals aqueous solution and m (g) the plant quantity.

All experiments were conducted in triplicate and mean values were used.

2.2.4. The characterization process of biosorption

The experiments conducted were set to establish the following parameters in order to obtain maximum adsorption capacity. The parameters studied were:

- the influence of initial Cd (II) ions concentration;
- the influence of contact time;
- the influence of agitation speed;
- the influence of the biomass quantity;
- the influence of the initial pH of the solution;
- influence of temperature;
- isotherms models;
- adsorption kinetics

2.2.4.1 The effect of biomass quantity

The effect of biomass quantity on the equilibrium uptake of Cd(II) was investigated with biosorbent masses of 1, 2, 3 and 4 g, results being presented in Fig. 2. The increase in the biomass quantities, from 1 to 4 g, amplifies the removal of Cd(II) ions from 79.59% to 97.76%. Major changes in the removal efficiency can be observed at quantities between 1 and 2 g, then a linear increase takes place from 2 g to 4 g biomass quantity. This effect could be explained by the availability of more adsorption sites on biosorbent surface and by and increase on total functional groups. Higher biomass quantities do not enhance the removal efficiency, thus, optimum biomass quantity of fir cone powder for biosorption of Cd(II) is found to be 4 g.

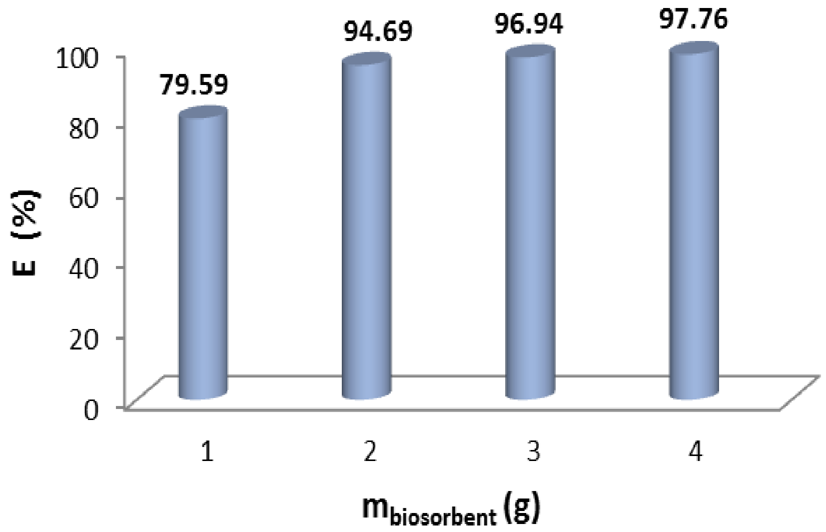

Figure 2. The effect of the fir cone powder quantity on Cd (II) biosorption over the removal efficiency; C_i = 49 mg Cd (II)/L, d = 200-400 µm, 296 K, 5.41 pH and 500 rpm.

2.2.4.2 The effect of initial Cd (II) concentration and contact time

The biosorption of Cd (II) was carried out at different initial ion concentrations ranging from 49 to 240 mg/L contacting 4 g fir cone powder, pH = 5.41, 500 rpm stirring rate at room temperature (23°C) with 240 min of contact time (until equilibrium was reached). The study points out that the higher the initial Cd (II) concentration; the more metal ions were adsorbed per unit weight at equilibrium. The results are presented in Fig. 3. From the experimental studies, it was shown that the adsorption capacity of Cd (II) ion increased from 1.20 mg/g (C_i = 49 mg Cd (II)/L) to 3.91 mg/g (C_i = 240 mg Cd (II)/L) with the increase of initial Cd (II) concentration. The increase in adsorption capacity is due to the higher adsorption rate and the utilization of all available active sites for adsorption at higher Cd (II) concentration. On the other hand, increasing the initial Cd (II) concentration, the adsorption capacity, the amount adsorbed per unit mass of biosorbent will decrease, mainly due to the saturation of adsorption sites during the biosorption process.

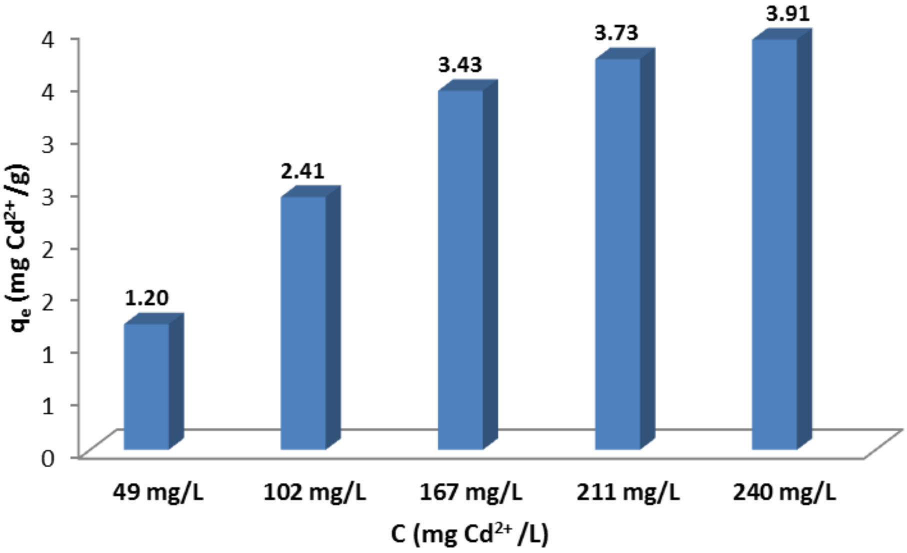

Figure 3. Influence of the initial Cd (II) concentration over the adsorption capacity on fir cone powder; 4g biosorbent, d = 200-400 µm, 296 K, 5.41 pH and 500 rpm.

The biosorption of Cd (II) was studied as a function of contact time and results are presented in Fig. 4. However, the contact time in this study was set to 240 min, where the final equilibrium was attained, thus completing the biosorption process.

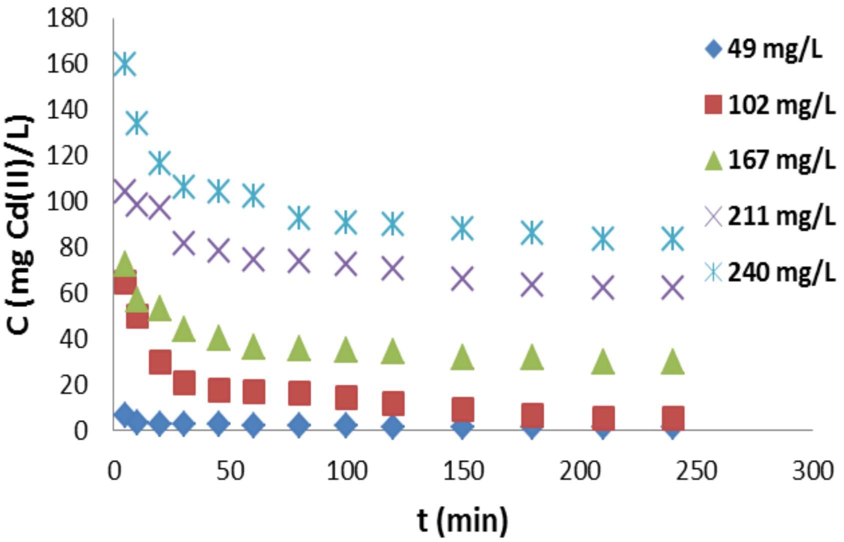

Figure 4. Effect of contact time over and initial concentration on the biosorption of Cd (II) ions on fir cone biosorbent; d = 200-400 µm, 296 K, 5.41pH, 500 rpm.

2.2.4.3 The effect of agitation speed

Three different agitation speeds as 200, 400 and 500 rpm were selected for the biosorption of Cd (II) by the fir cone powder biomass. The adsorption capacity (mg/g) of Cd (II), increased once the increase in agitation speed was amplified. The removal of Cd (II) was found to be 3.48 mg/g, 3.62 mg/g and 3.68 mg/g for 200, 400 and 500 rpm agitation speed, respectively. So, all the subsequent experiments were conducted at an agitation speed of 500 rpm.

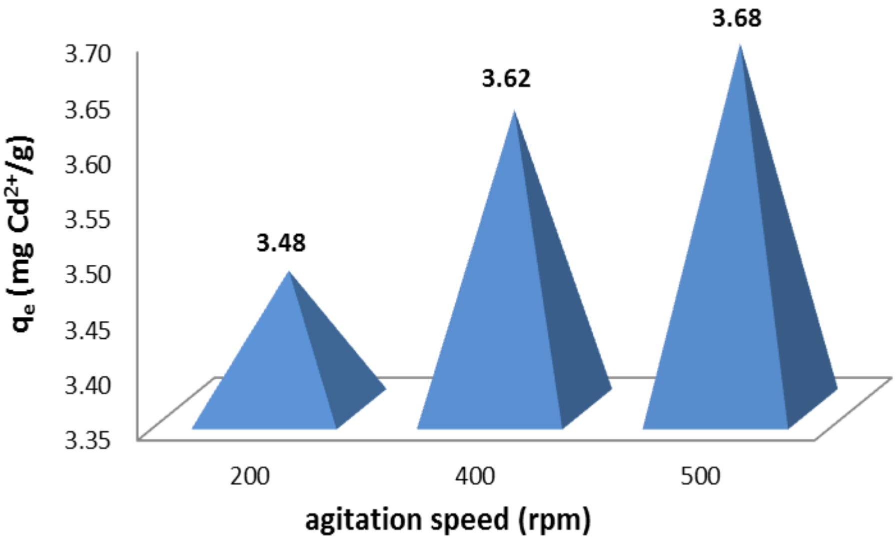

Figure 5. The influence of the initial Cd (II) concentration over the adsorption capacity on the fir cone powder; 4g biosorbent, d = 200-400 µm, 296 K, 5.41 pH and 500 rpm.

2.2.4.4 The effect of the initial pH of solution

The effect of the initial pH of solution onto Cd (II) biosorption from aqueous solution by fir cone powder was investigated over an initial pH ranging between 2.7-8.2. As Fig. 6 shows, at initial pH = 2.7 the amount of cadmium removed from the solution is smaller in comparison with the other initial pH tested. The low removal efficiency value (95.31%) obtained could be attributed to the competition between Cd $^{2+}$ ions and H^+ for active sites on the biosorbent surface. As the initial solution pH increased, an increase in the removal efficiencies is observed, where the maximum removal percent was attained at initial pH = 8.2 (E = 98.65%). It was observed that during the biosorption process, the biosorbent set the initial pH value to 5.5 attained at equilibrium (after around 80 min) for all initial pH of in the solutions studied. However, with increasing of pH, the between protons (H^+) decreases and Cd(II) can be adsorbed on negatively charged sites of the bisosorbent surface. Studies beyond 8.2 were not attempted because precipitation of the hydroxides would have been likely to occur.

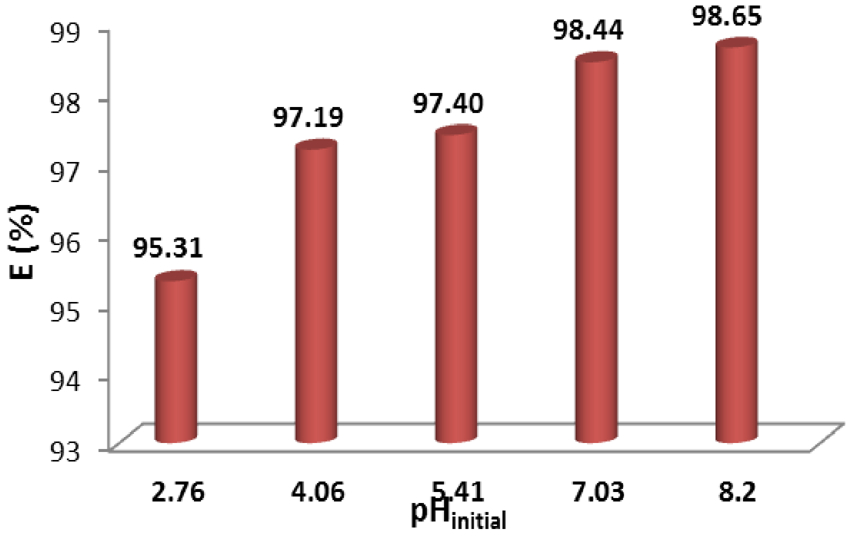

Figure 6. The effect of initial pH values on Cd (II) biosorption using fir cone powder;C_i = 49 mg Cd(II)/L, d = 200-400 µm, 4g biosorbent, 296 K and 500 rpm.

2.2.4.5 The effect of temperature

Similar results were reported for the removal of Cd(II) ions from aqueous solutions using activated fir tree cone with Fenton reagent (Argun et al., 2008) Fig. 7 shows the relationship between temperature and removal efficiency values for Cd(II) biosorption at various temperatures (using a thermostat water bath) from 23°C (296 K) up to 53°C (326 K). The result shows that with the increase of medium temperature from 296 to 326 K, the maximum percentage for Cd (II) removal decrease gradually, which indicates an exothermic process. Recent study showed that the biosorption of Cd (II) using fir tree (*Abies Alba*) sawdust is endothermic in nature, (Nagy et al., 2014) compared with the present study (cones obtained from the same trees) which presents an exothermic process. This can be explained by the differences in the main constituents (cellulose, lignin and hemicellulose) percentage between the two biomasses. It can be concluded that the Cd (II) biosorption is not enhanced by an increase in the medium temperature.

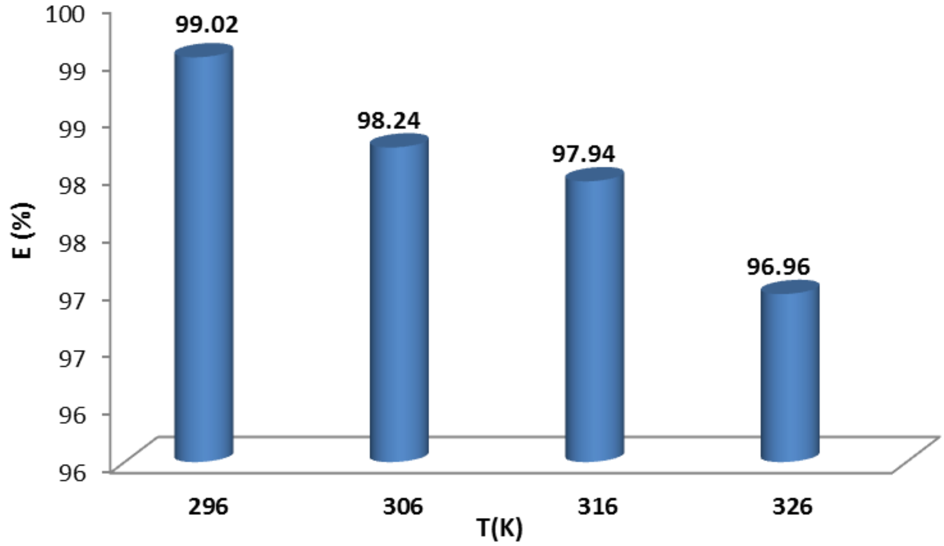

Figure 7. Temperature influence over the removal efficiency of Cd (II) on fir cone powder's C_i=49 mg Cd (II)/L, d = 200-400 µm, 4 g biosorbent, 5.41 pH and 500 rpm.

2.2.5. Biosorption kinetics

In order to investigate the mechanism of adsorption, pseudo-first-order and pseudo-second order, intra-particle and liquid film diffusions kinetic were used to test the experimental data. Lagergren proposed the pseudo-first-order kinetic model, which is the most widely used for the adsorption of a solute from a liquid solution (Lagergren. S., 1898)

This model was applied for on the present experimental data as well. Experimental data were also tested using the Ho and McKay pseudo-second order model which based on the assumption that the adsorption follows second-order chemisorption (Ho and McKay., 1999)

A comparison of the pseudo-first-order and pseudo-second-order adsorption rate constant at different initial metal ions concentrations is presented in Table 1. The validity of the used models is verified by the correlation coefficient, R^2. The calculated correlation coefficients are less than 0.9048 for the first-order kinetic model, whereas the values of the correlation coefficient are bigger than 0.9991 for the pseudo-second kinetic order model. Moreover, the theoretical qe,calc values were closer to the experimental theoretical qe,exp values (Table 1). These results suggest that the pseudo-second-order mechanism is predominant and that chemisorption might be the rate-limiting steps that control the adsorption process. Chemisorption is usually restricted to just one layer of molecules on the surface, although it may be followed by additional layers of physically adsorbed molecules (Momcilovic et al ., 2011; Qada et al., 2006).

In order to study the mass transfer process, two diffusion models, intra-particle and liquid film models were applied (Weber W. J and J. C Morris.,1963).

Table 1. The pseudo-first-order and pseudo-second-order rate constants, calculated and experimental q_e values for Cd(II) biosorption on fir cone powder biomass using different initial concentrations; C_i = 49-240 mg/L, 4g biosorbent, d = 0.4 mm, 296 K, pH 5.4, 500 rpm.

C (mg/L)	**q_e (exp) (mg/g)**	**Pseudo-first-order**			**Pseudo-second-order**		
		k_1 (1/min)	**q_e (calc) (mg/g)**	**R^2**	**k_2 (g/mg·min)**	**q_e (calc) (mg/g)**	**R^2**
49	1.20	1.93×10^{-2}	0.12	0.6728	79.07×10^{-2}	1.20	1
102	2.41	$1.96 \times 10^{-}$	0.22	0.9048	42.13×10^{-2}	2.49	0.9992

		2					
167	3.43	1.99×10^{-2}	0.97	0.8498	7.54×10^{-2}	3.47	0.9999
211	3.73	1.94×10^{-2}	1.05	0.8994	4.44×10^{-2}	3.79	0.9991
240	3.91	1.82×10^{-2}	1.34	0.8788	3.74×10^{-2}	4.00	0.9996

The possibility of intra-particle transport in the current study was explored by using the Weber-Morris equation, whereby the intra-particle diffusion is characterized by the relationship between specific sorption (qt) and the square root of time (t1/2). The intra-particle models show that the mass transfer process takes places in three steps, consisting of the boundary layer diffusion (liquid film diffusion), intra-particle diffusion, and the final equilibrium stage (Weber W. J and J. C Morris.,1963; B. Nagy et al., 2014). Plots of t1/2 versus qt are shown in Table 2 for the initial Cd(II) concentrations ranging from 49-240 mg/L. The plots reveal that the intraparticle diffusion line is straight line that does not pass through the origin indicated that intra-particle diffusion in not the only rate the determining mechanism and that some other mechanisms are involved (Dhaouadi et al ., 2010)

Table 2. Intra-particle diffusion rate coefficients for Cd(II) biosorption on fir cone powder biomass using different initial concentrations; C_i = 49-240 mg/L, 4g biosorbent, d = 0.4 mm, 296 K, pH 5.4, 500 rpm.

C (mg/L)	**D (cm^2/s)**	**Region 1, 10-45 minutes**		**Region 2, 45-150 minutes**		**Region 3, 150-240 minutes**	
		k_{ip} (mg/g·min$^{1/2}$)	**R^2**	**k_{ip} (mg/g·min$^{1/2}$)**	**R^2**	**k_{ip} (mg/g·min$^{1/2}$)**	**R^2**
49	7.60×10^{-8}	0.019	0.6561	0.0028	0.8361	1.2×10^{-3}	0.7677
102	8.40×10^{-8}	0.275	0.9361	0.4580	0.9485	1.52×10^{-2}	0.7677
167	2.09×10^{-8}	0.169	0.9176	0.0229	0.8846	1.83×10^{-2}	0.7677
211	1.35×10^{-8}	0.150	0.9149	0.0468	0.8666	1.89×10^{-2}	0.7619

240	1.20×10^{-8}	0.305	0.8837	0.0731	0.7818	0.355×10^{-1}	0.7677
	Intercept:	1.06 – 1.56		1.16 – 2.95		1.18 – 3.40	

The liquid film diffusion model also know external as mass transfer may be a applied to determinate the transport of the solute molecules from the liquid phase up to the solid phase boundary (Dhaouadi et al., 2010; Ioannou and Simitzis., 2008). Liquid film diffusion rate constants -ln(1-F) against t plots intercepts, Table 3, afore determined. The fact that none of the mentioned linear plots exhibit zero intercepts, suggests that the process is not controlled by diffusion through the liquid film surrounding the biosorbent grains.

Table 3. Liquid film diffusion rate coefficients for Cd (II) biosorption on fir cone powder biomass; C_i = 49-240 mg/L, 4g biosorbent, d = 0.4 mm, 296 K, pH 5.4, 500 rpm.

C (mg/L)	**k_{fd} (1/min)**	**Intercept**	**R^2**
49	0.015	- 2.81	0.9058
102	0.018	- 0.85	0.9183
167	0.017	- 1.57	0.9302
211	0.016	- 1.27	0.9463
240	0.018	- 1.13	0.9437

2.2.6. The biosorption isotherm model

The analysis of the isotherm data, by fitting them to different isotherm models is an important step in finding the suitable model that can be used for our purpose. In the present study, the equilibrium data obtained for the biosorption of Cd (II) ions onto fir cone powder were analyzed by considering the Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm models (Nagy et al., 2013; Dubinin et al., 1960; Tempkin and Pyzhev .V., 1940).

Langmuir isotherm represents the equilibrium distribution of cadmium ions between the solid and liquid phases, valid for monolayer adsorption onto specific homogenous sites. The Langmuir constant, q_m, which measures the monolayer adsorption capacity is calculated as 3.74 mg/g and Langmuir constant, K_L, which denotes adsorption energy, is calculated as 0.169 L/mg which confirm favorable Cd (II) biosorption process using fir cone powder (Table 4).

The Freundlich isotherm is used to describe the adsorption characteristics for the heterogeneous surface. The Freundlich constants were calculated along with the coefficient of determination R^2 and these values are given in Table 4. The values for KF and n are 3.8 and 1.31, respectively.

Comparing the coefficient of determination for these two models it can be concluded that the experimental data purported similarities to the Langmuir model ($R^2 = 0.9935$). However striking resemblance to the Freundlich biosorption isotherm model was seen, it was evident from the lower obtained value of R^2 (0.9481). The Dubinin-Radushkevich isotherm expresses the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. The Dubinin-Radushkevich isotherm parameters are shown in the Table 4. If E values are between 8 and 16 kJ mol-1, the biosorption process is chemical and if E < 8 mol-1 the biosorption process is physical (Gîlca et al., 2014; Sari and Tuzen M., 2008).

In our case the mean free energy was 5 mol-1 indicating a physisorption process. Temkin assumes that the heat of adsorption of all molecules the layer would decrease linearly rather than logarithmic with coverage. Taking into consideration the calculated value of the constant related to heat of sorption, B, which has a value smaller than 20 kJ mol^{-1} we concluded that according to this isotherm the sorption process takes place as physisorption (Table 4) (Gîlca et al., 2014; A.U. Itodo, and H.U. Itodo., 2010). This result confirms the result obtained from Dubinin-Radushkevich isotherm.

Table 4. Isotherm constants for Cd(II) biosorption on fir cone powder biomass; C_i = 49-240 mg/L, 4g biosorbent, d = 0.4 mm, 296 K, pH 5.4, 500 rpm.

Dubinin-Radushkevich			**Temkin**		
β (mol^2 kJ^2)	**E (kJ mol^{-1})**	**R^2**	**A_T (L g^{-1})**	**B (J mol^{-1})**	**R^2**
2×10^{-9}	5	0.9705	2.11	7×10^{-5}	0.9923
Langmuir			**Freundlich**		
K_L (L/mg)	**q_{max} (mg/g)**	**R^2**	**n**	**K_f (mg$^{(1-1/n)}$L$^{1/n}$/g)**	**R^2**
0.169	3.74	0.9935	3.8	1.31	0.9481

2.2.7 The biosorptive effect of untreated and chemically modified fir cone powder on Pb(II) removal

2.2.7.1 The effect of contact time

Equilibrium time is one of the most important parameters to design the economical wastewater treatment systems. The experiments were performed to determine the time required to reach equilibrium for the adsorption of lead ions onto fir cone powder.

The adsorption of Pb(II) was studied as a function of contact time and results are presented in Fig. 8. The adsorption increases rapidly with increasing contact time and equilibrium was attained in less than 150 min where a final plateau is observed. Therefore, the contact time selected was of 240 min for further experiments (equilibrium) for all the biomass studied. This tendency was also observed for both treated biomasses.

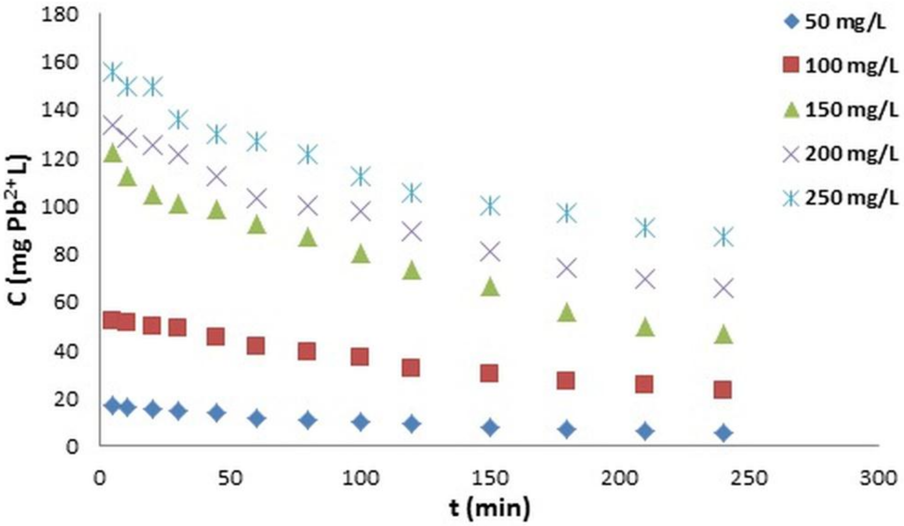

Figure 8. The effect of contact time and initial concentration on the adsorption of Pb(II) over untreated fir cone powder biomass; pH = 5.2, 296 K, 4 g biomass, *d* = 0.2-0.4 mm, 500 rpm.

2.2.7.2 The effect of initial lead ions concentration

The adsorption of Pb(II) (for all types of biomass) was carried out at different initial concentrations ranging from 50 to 250 mg/L contacting 4 g fir cone powder, 500 rpm stirring rate at room temperature 23 ºC (296 K), with 240 min of contact time (until equilibrium was reached). The increase in adsorption capacity occurs due to the higher adsorption rate and the utilization of all the available active sites for adsorption at higher heavy metal concentration. Moreover, a higher initial concentration provides an important initial force to overcome the pollutant mass transfer resistances between aqueous and solid phases. Further increase of the initial metal ion concentration does not lead to further increase in adsorption capacity. These results suggest that the adsorption capacity elevates with the increase of concentration up to a limit.

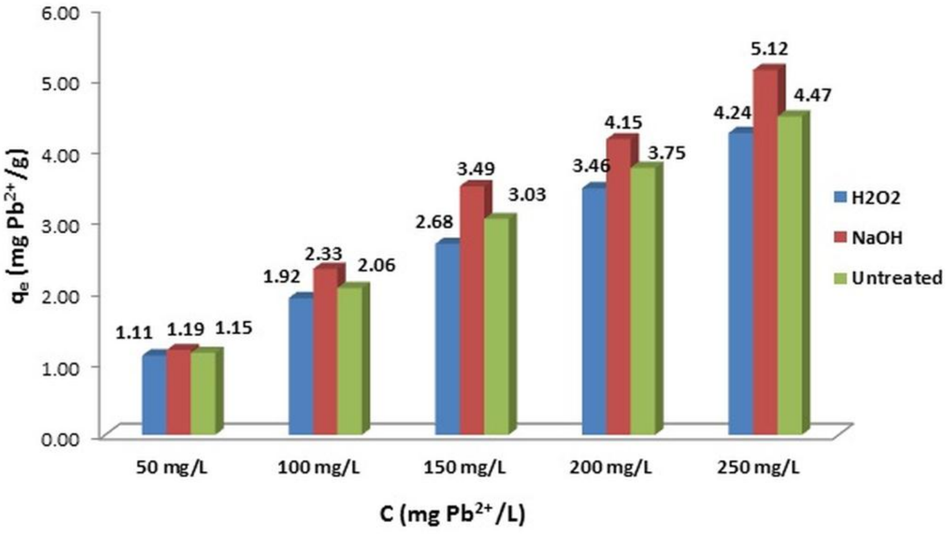

Figure 9. Influence of the initial Pb(II) concentration over the adsorption capacity onto fir cone powder; C_i = 50-250 mg Pb(II)/L, 4 g biomass, *d* = 0.2-0.4 mm, 296 K, pH 5.2, 500 rpm.

2.2.7.3 The effect of initial pH

The pH of the initial heavy metal solution plays an important role, particularly on the adsorption capacity by influencing the chemistry of heavy metal molecule and adsorbents in aqueous solutions. It is directly related to the competitive ability of proton ions with metal ions to active sites on the biomass surface (Hernainz et al., 2008). In order to study the effect of this parameter on metal adsorption on untreated and treated fir cone powder, the initial pH of solution varied within the range of 2.0–7.0. This pH range is chosen in order to avoid metal solid hydroxide precipitation (above pH 7.0, Pb ion precipitates as $Pb(OH)_2$).

The results indicate that the maximum uptake capacity of the lead ions is obtained at pH 5.2, in all cases (Fig. 10). At low pH values, there is an excessive protonation of the biomass surface resulting in a decrease in the sorption of Pb(II) ions. Acidic sites are protonated in acidic conditions explaining the low adsorption of lead by fir cone powder untreated and treated at low pH. A decrease in the adsorption capacity at higher pH (pH >5.2) is not only related to the formation of soluble hydroxylated complexes of the lead ions in the form of $Pb(OH)_2$, but also to the ionized nature of the cell wall surface of the biomass under the studied pH (Amini et al., 2008). Chemical treatments also affect the main groups responsible for the metal adsorption;

therefore, these two types of treatment show different effects/impacts over the fir cone powder surface.

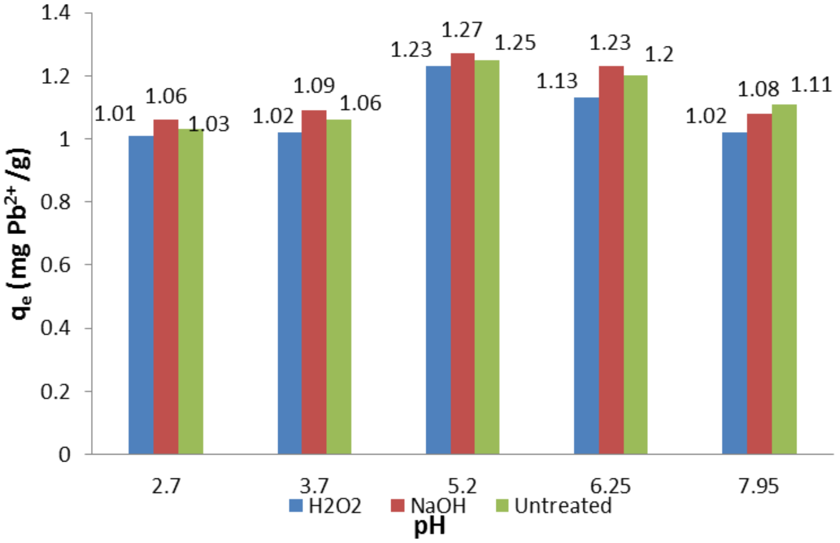

Figure 10. The effect of initial pH values on Pb(II) adsorption capacity using fir cone powder; C_i = 50 mg Pb(II)/L, 4 g biomass, *d* = 0.2-0.4 mm, 296 K, 500 rpm.

2.2.7.4 The effect of temperature

Temperature is an important parameter for the adsorption process. Experiments were performed at different temperatures (296, 303, 316, 326, and 336 K) using a thermostat water bath in the following conditions: initial concentration of lead ions 50 mg/L, adsorbent dose 4 g/L, agitation time 240 min, agitation speed 500 rpm. The result shows that with increase of medium temperature from 296 to 336 K, the maximum percentage for Pb(II) removal decrease gradually, which indicates an exothermic process. The temperature increase may produce a swelling effect within the internal structure of the fir cone enabling large heavy metal molecules to penetrate further. A decrease in adsorption of Pb(II) ion with the rise in temperature may be due to increasing metal desorption tendency from the interface to the solution (Sari et al. 2007). Optimum temperature was selected as (296K) for the future adsorption experiments. Similar results were reported for the biosorption of Cd (II) ions onto sodium hydroxide treated sawdust (Nagy et al., 2014).

2.2.8 Adsorption kinetics

2.2.8.1 The pseudo-first order kinetic model

The pseudo-first- order and pseudo-second-order model were applied to the experimental data to clarify the adsorption kinetics of Pb(II) onto fir cone powder biomass.

The obtained regression coefficient (R^2) values indicated that the adsorption mechanisms of Pb(II) onto the fir cone powder biomass does not follow the pseudo-first-order kinetic model (Table 1). It can be also seen that the experimental values of $q_{e,exp}$ are not in good agreement with the theoretical values calculated ($q_{e,cal}$) from Eq. (3). Therefore, the pseudo-first-order model is not suitable for modelling the Pb(II) adsorption process onto the fir cone powder.

2.2.8.2 The Pseudo second order kinetic model

The adsorption process, with chemisorption being the rate control followings pseudo second order model, the sorption kinetics may be represented by pseudo second order model.

This model is more likely to predict kinetic behaviour of adsorption with chemical sorption being the rate-controlling step (Ho et al., 1999). A comparison of the pseudo-first-order and pseudo-second-order adsorption rate constant at different initial metal ions concentrations is presented in Table 5. As the table shows, the linearized pseudo-second-order kinetic model provides much higher R^2 values than those for the pseudo-first-order model for all types of biomass. In addition, the theoretical qe,cal values were closer to the experimental qe,exp values. In view of these results, on can assert that the pseudo-second-order kinetic model provided a good correlation for the untreated and treated fir tree powder in the removal of Pb(II), in contrast to the pseudo-first-order model.

Table 5. Pseudo-first-order and pseudo-second-order rate constants, calculated and experimental q_e values for Pb(II) adsorption on fir cone powder biomass using different initial concentrations C_i = 50-250 mg/L, 4g biomass, d = 0.4 mm, 296 K, pH 5.2, 500 rpm.

C (mg/L)	***$q_e(exp)$* (mg/g)**	**Pseudo-first-order**			**Pseudo-second-order**		
		***k_1* (1/min)**	***$q_e(calc)$* (mg/g)**	***R^2***	***k_2* (g/mg·min)**	***$q_e(calc)$* (mg/g)**	***R^2***
				Untreated			
50	1.15	1.41×10^{-2}	0.34	0.8475	7.90×10^{-1}	1.13	0.9928
100	2.06	0.99×10^{-3}	0.45	0.8427	4.21×10^{-1}	2.10	0.9974
150	3.03	2.24×10^{-2}	0.89	0.7801	7.54×10^{-3}	3.64	0.9951
200	3.75	1.11×10^{-2}	1.34	0.8708	4.44×10^{-2}	3.95	0.9871
250	3.91	0.88×10^{-2}	2.78	0.8651	3.74×10^{-2}	4.31	0.9905
				NaOH			
50	1.20	2.19×10^{-2}	0.28	0.7382	7.92×10^{-1}	1.18	0.9998
100	2.34	1.09×10^{-2}	2.20	0.8321	1.82×10^{-1}	2.39	0.9992
150	3.49	1.31×10^{-2}	2.29	0.9370	1.48×10^{-2}	3.44	0.9820
200	3.28	1.31×10^{-2}	1.68	0.9112	1.15×10^{-2}	4.37	0.9957
250	5.13	1.27×10^{-2}	2.79	0.9152	2.12×10^{-2}	5.06	0.9970
				H_2O_2			
50	1.11	1.93×10^{-2}	0.125	0.6728	7.97×10^{-1}	1.10	0.9973
100	1.92	1.96×10^{-2}	1.216	0.9048	4.21×10^{-1}	2.02	0.9931
150	2.68	1.99×10^{-2}	0.972	0.8498	7.54×10^{-2}	3.24	0.9651
200	3.46	1.94×10^{-2}	1.047	0.8994	4.44×10^{-2}	3.80	0.9849
250	4.24	1.82×10^{-2}	1.343	0.8788	3.77×10^{-2}	4.05	0.9880

2.2.9 The adsorption isotherm models

Adsorption isotherm is fundamentally important to describe the interaction of solute with adsorbent, and is critical in optimizing the use of adsorbent. The Langmuir, Freundlich, Temkin and Dubinin-Radushkevich competitive adsorption isotherm models were tested in the present study.

2.2.9.1 The Langmuir and Freundlich isotherm models

The Langmuir sorption isotherm has been successfully applied to the adsorption processes of heavy metal ions. The basic assumption of the Langmuir theory is that adsorption takes place at specific homogeneous sites within the sorbent.

The Freundlich isotherm model emphasizes the relationship between equilibrium liquid and solid phase capacity based on the multilayer adsorption (heterogeneous surface).
The one closest to linearity could be considered as describing better the adsorption equilibrium in a certain system (Kamari et al. 2009).

The isotherm parameters for the adsorption of Pb(II) onto untreated and chemically treated biomass are given in Table 6. From the linearity of the two plots, expressed in R^2 the Langmuir adsorption model provides the best match, with experimentally-obtained data for all the studied adsorbents. Maximum adsorption capacities $q_{\max}$ were calculated to be 3.7 mg/g for untreated and 4.8 and 2.9 mg/g for NaOH and H_2O_2, respectively. As $q_{\max}$ value showed, the NaOH treatments exhibit the highest adsorption. Moreover, the calculated adsorption capacity for the H_2O_2 treatment (2.9 mg/g) is much smaller in comparison with the untreated (3.7 mg/g) one. Therefore, it can be concluded that H_2O_2 treatment has a negative impact over the fir cone uptake capacity and specificity of Pb(II).

2.2.9.2 Temkin and Dubinin-Radushkevich isotherm models

The Temkin isotherm equation assumes that the decrease in heat of adsorption of all the molecules in the layer would decrease linearly rather than logarithmically with coverage (Temkin and Pyzhev 1940). Taking into consideration the calculated value of the constant related to the heat of sorption, which has a smaller value smaller than 20 kJ mol^{-1} (Table 6), we concluded that, according to this isotherm, the sorption process for the untreated and both treated biomass takes place as physisorption.

The D–R isotherm model was also performed on the equilibrium data in order to determine the nature of the adsorption processes as physical or chemical. The D–R sorption isotherm is more general than the Langmuir isotherm as its derivation is not based on ideal assumptions such as equipotent of the sorption sites, absence of stoic hindrance between sorbed and incoming particles and surface homogeneity at a microscopic level (Malik et al. 2005).

If E values are between 8 and 16 kJ/mol, the adsorption process takes place chemically, while, $E < 8$ kJ/mol, the sorption process proceeds physically. In our case, the mean free energy obtained for all types of biomass was smaller than 8 kJ/mol, indicating a physisorption process. This result confirms the one obtained from the Temkin isotherm.

Table 6. Langmuir, Freundlich, Dubinin-Radushkevich and Temkin calculated coefficients using linear regression analysis for Pb(II) removal using fir cone powder, C_i = 50-250 mg/L, 4g biosorbent, d = 0.4 mm, 296 K, pH 5.2, 500 rpm.

	Langmuir			**Freundlich**			**Dubinin-Radushkevich**			**Temkin**		
	K_L (L/mg)	**q_{max} (mg/g)**	**R^2**	**n**	**K_f (mg$^{(1-1/n)}$ L$^{1/n}$/g)**	**R^2**	**β (mol^2 kJ^2)**	**E (kJ/mol)**	**R^2**	**A_T (L/g)**	**B (J/mol)**	**R^2**
Untreated	0.168	3.7	0.993	3.79	1.30	0.948	7×10^{-6}	4.51	0.976	2.36	3×10^{-5}	0.907
NaOH	0.267	4.8	0.987	2.31	1.07	0.977	9×10^{-7}	4	0.960	2.71	5×10^{-6}	0.939
H_2O_2	0.954	2.93	0.981	0.27	1.83	0.939	4×10^{-6}	5	0.995	2.20	4×10^{-6}	0.992

3. Crystal violet dye biosorption and phytoextraction using living *Salvinia natans* and *Salvinia natans* powder: A comparative study

3.1. Living *Salvinia natans*

*S. natans L. (*family of *Salviniaceae)* a free-floating aquatic fern, was the plant chosen for the phytoextraction process. The *S. natans* growth were performed in a hydroponic greenhouse system (at University of Agricultural Sciences and Veterinary Medicine in Cluj-Napoca, Romania), with an addition of fertilizer (Complex 3, 0.5 %). The plants that aged 30 days were selected for the phytoremediation experiments.

3.2. *Salvinia natans* powder

Prior to its utilization, *S. natans* was washed several times with deionized water and dried at 80°C for 48 hours. The dried samples were grinded and sieved, 200 and 400 µm mesh size was further used in all experiments. The biomass was washed again with 0.01 M HCl to remove any soluble biomolecules that might have caused interference, and then cleaned with sterile distilled water. The samples were filtered and dried at 80°C for 48 h.

3.3. Chemicals

The Crystal violet salt was used as pollutant in the phytoremediation experiments. The cationic Crystal violet dye (Tris (4-(dimethylamino) phenyl) methylium chloride, chemical formula = $C_{25}N_3H_{30}Cl$, molecular weight = 407.9788 g/mol. Wavelength maximum (λmax = 590 nm). All chemicals and reagents used in the study were of analytical grade (purity $\geq$ 99 %) and supplied by Merck (Germany).

3.4 Phytoextraction experiments with living *Salvinia natans*

The phytoremediation experiments were carried out in controlled conditions (at room temperature 21 - 23ºC, using with a lamp with the 14/10 h light/dark photoperiod), in 250 mL Beaker glass containing 200 mL synthetic wastewater and 5 g fresh aquatic plants along with the macro- and micronutrients. The plants were kept in laboratory conditions for an acclimatization period of 4 days in modified Hoagland nutrient solution with the following chemical composition: 1 mM KNO_3; 1 mM $Ca(NO_3)_2 2.4H_2O$; 1 mM $NH_4H_2PO_4$; 1 mM $MgSO_4 \times 7H_2O$; 25 mMKCl; 12.5 mM H_3BO_3; 1 mM $MnSO_4 \times H_2O$; 1 mM $ZnSO_4 \times 7H_2O$; 0.25 mM $CuSO_4 \times 5H_2O$; 0.25 mM H_2MoO_4 (85% MoO_3) with Fe(III) citrate (36). Samples were withdrawn from the aqueous solution every day for monitoring the plant's removal efficiency.

3.5. The biosorption experiments with *Salvinia natans* powder

The adsorption experiments were performed in batch condition, contacting 0.4 g powder obtained from 5 g fresh plant with 200 mL of CV at different initial concentrations (20 - 90 mg/L), under stirring (150 rpm), room temperature 23ºC ± 2ºC (296±2 K). In order to establish the evolution of the removal process, samples of 500 μL were collected at different time intervals up to 240 min. The collected samples at predetermined time intervals were centrifuged (10 min) and the dye concentration in aqueous phase was determined on a daily basis. The concentrations were determined using the double beam UV-visible spectrophotometer (GBC Cintra 202, Australia).

3.6. Characterizations of the process

For both processes, biosorption and phytoextraction, the same parameters and conditions were studied: a) effect of plant quantity: m_{plant} =1-5 g fresh plant; b) effect of initial concentration of CV: C_i =20 - 90 mg/L, c) effect of initial pH = 3.0-10; d) effect of temperature: t_1 = 10ºC, t_2 = 23ºC, t_3 = 35ºC (283-308 K).

The pH of the solution was initially adjusted by adding a small amount of 0.1 M HCl or 0.1 M. NaOH solutions and then measured using a pH meter.

In order to evaluate the amount of CV retained per unit mass of biomass, the biosorption and phytoextraction capacity was calculated using the following equations (37):

$$E,(\%) = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

$$q_{\max}(mg/g) = \frac{(C_i - C_f)V}{m} \tag{2}$$

where E, (%) represents the removal, C_i and C_f the initial and final concentration of Crystal violet (mg/L) in the aqueous solution, q_{max} (mg/g) represents the amount of CV adsorbed onto unit weight of plant, V (L) means the volume of dye aqueous solution and m (g) the plant quantity. The experiments were conducted simultaneously both for living and powder-form plant, following the same parameters.

3.6 Results and Discussion

3.6.1. The effects of initial CV concentration

The biosorption of CV was carried out at different initial dye concentrations ranging from 20 to 90 mg/L contacting 0.4 g *S. natans* powder obtained from 5 g fresh biomass, pH initial = 5.4, 150 rpm stirring rate at room temperature 23ºC (296 K), with 240 min of contact time (until equilibrium was reached). Experiments with living biomass were carried out at the same initial dye concentrations ranging from 20 to 90 mg/L containing 5 g fresh biomass, at room temperature 23ºC (296 K), pH initial = 5.4 and 200 mL synthetic dye solution.

The results are presented in (Fig. 11). In both cases, the adsorption capacity augments with the increase of the initial concentration. The increase in adsorption capacity occurs due to the higher adsorption rate and the utilization of all the available active sites for adsorption at higher CV concentration. According to the results, it can be observed that the aquatic plants highest removal efficiency was attained at the smallest initial concentration and that the removal capacity of aquatic plants depended on the initial dye concentrations. Also the plant phytoextraction capacity is influenced by the plant’s surface active sites and by the plant’s uptake abilities and saturation.

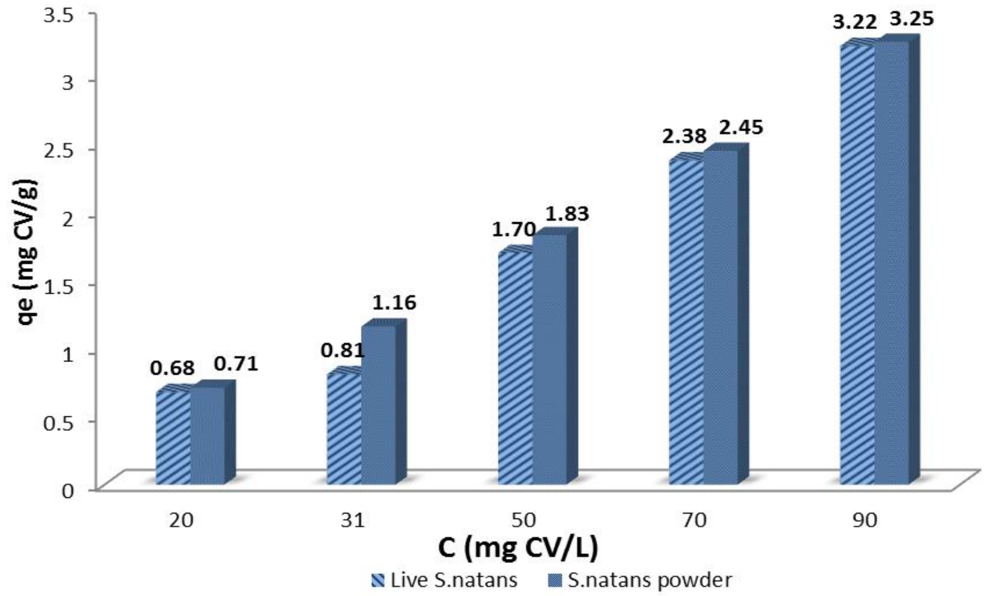

Figure 11. Influence of the initial dye concentration over the adsorption capacity for CV phytoextraction and biosorption; C_i = 20-90 mg/L, 0.4 g biomass, 296 K, pH 5.4, 150 rpm (biosorption).

3.6.2 The effect of pH

The pH parameter has been identified as one of the most important parameter that effective on dye phytoextraction. The pH of the aqueous medium is an important factor, which affects directly the living system biological and biochemical functions and it is directly related to the competitive ability of hydrogen ions with dye ions to active sites on the biosorbent surface. The effect of the solution pH onto CV biosorption and phytoextraction was studied within pH 3.0 - 10 range. The highest removal efficiency for both processes was determined at the initial pH value of 5.4.

At lower pH, the H^+ ions compete effectively with dye captions, showing a decrease in the dye removal efficiency. At higher pH, the plant surface becomes negatively charged, and this can intensify electrostatic force of attraction of the positively charged CV cautions, increasing the phytoremediation efficiency. The aquatic plants can tolerate a wide range of initial pH from acidic to alkaline. Their dye removal efficiency was notable in various cases and the hydrophytes possess characteristic properties to equilibrate the pH, which may present the plants' responses to the induced water stress. These results can be explained by the plant metabolic reactions involving consumption, production or transfer of protons during the processes (Bligny et al., 1997):

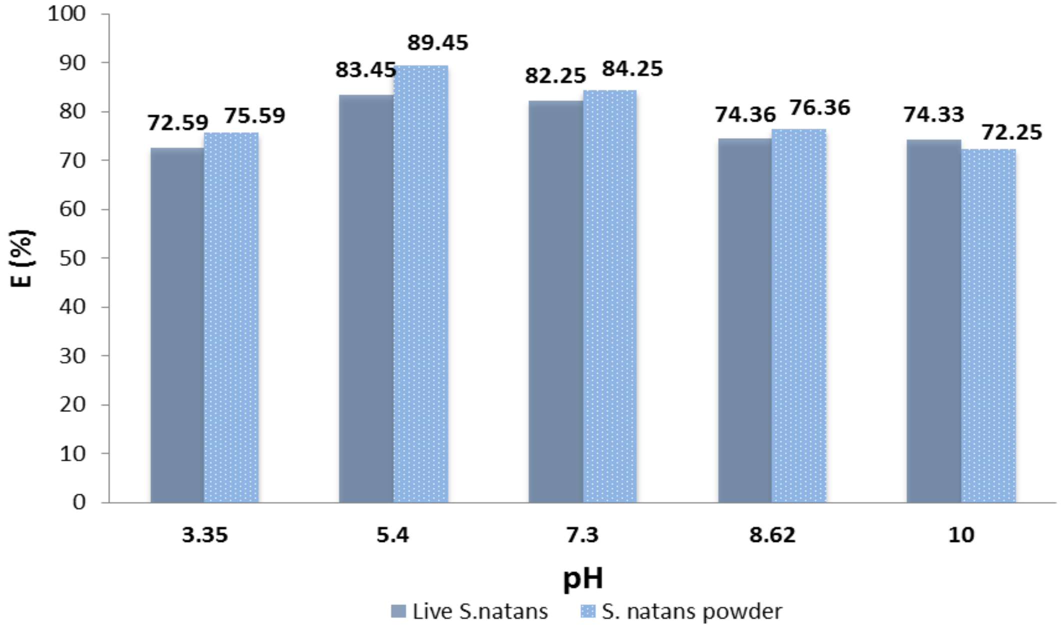

Figure 12. The effect of initial pH values on the removal efficiency for CV phytoextraction and biosorption; C_i = 50 mg/L, 0.4 g biomass, 296 K, 150 rpm (biosorption).

3.6.3. The effect of temperature

During the phytoextraction processes, temperature has a major effect on the plant biochemical processes affecting the enzyme activity, the translocation of nutrients and photosynthesis of plants (Zhaoet al., 2005). The effect of temperature on the phytoremediation efficiency of CV dye was tested at the range of 10 - 35ºC. Results showed the removal efficiency of dye CV increase with increase in temperature from 10 to 35ºC (Fig. 13), for both processes. The observed increase in adsorption and biosorption of CV with a rise in temperature is indicative of the fact that the adsorption process is endothermic in nature. The increase in the temperature of the system affects the solubility and particularly the chemical potential of the dye, which is known to be a controlling factor in the process of adsorption. A temperature increase minimizes the solubility of dye, hence adsorption accentuates. An increasing number of molecules may acquire sufficient energy to undergo an interaction with the active site at the surface (Ho et al., 1999).

The results indicated that the two types of phytoremediation processes have the ability to remove CV from the aqueous solutions.

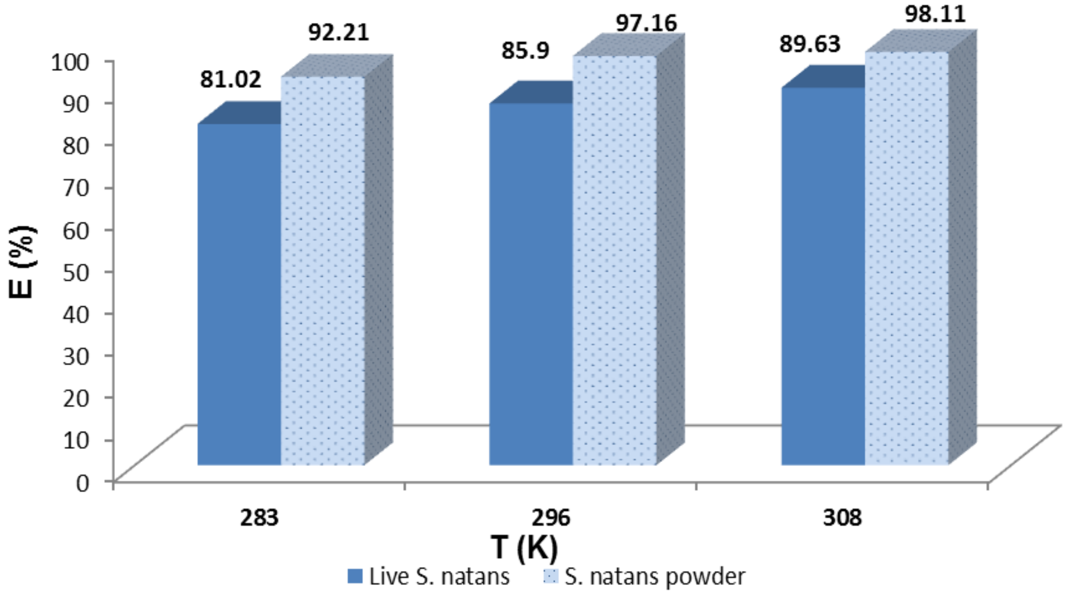

Figure 13. Temperature influence over the removal efficiency of CV on living *S. natans* and *S. natans* powder; $C_i = 50$ mg/L, 0.4 g biomass, pH 5.4, 150 rpm (biosorption).

3.7. Biosorption and phytoextraction kinetics

The prediction of the biosorption rates gives important information for designing batch biosorption systems. Lagergren's pseudo- first-order and pseudo-second-order model were performed for the experimental data to clarify the biosorption and phytoextraction kinetics of CV onto *S. natans* biomass. The linear form of the pseudo-first-order rate equation, by Lagergren (Nagy et al. 2015) is given as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (3)$$

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \qquad (4)(4)$$

where qt and qe (mg/g) are the amounts of the crystal violet adsorbed at equilibrium, time (mg/g) and t (min), k_2 (g mg^{-1} min^{-1}) is the rate constant of the second-order equation respectively and k_1 is the rate constant of the equation (min−1).

In addition, the theoretical q_{e2}, cal values were closer to the experimental qe,exp values. In view of these results, it can be said that the pseudo-second-order kinetic model provided a good correlation for the biosorption and phytoextraction of crystal violet onto *S. natans* contrasted to the pseudo-first-order model.

Table 7. Pseudo-first-order and pseudo-second-order rate constants, calculated and experimental q_e values for CV removal using living *S. natans* and *S. natans* powder at different initial concentrations; C_i = 20-90 mg/L, 0.4 g (biosorption)/ 5 g (phytoextraction) biomass, 296 K, pH 5.4.

C (mg/L)	**q_e (exp) (mg/g)**	**Pseudo-first-order**			**Pseudo-second-order**		
		k_1 (1/min)	**q_e (calc) (mg/g)**	**R^2**	**k_2 (g/mg·min)**	**q_e (calc) (mg/g)**	**R^2**
Living *S. natans*							
20	0.70	5.96×10^{-2}	0.65	0.986	1.06×10^{-2}	0.81	0.994
31	0.81	2.25×10^{-2}	0.54	0.886	8.88×10^{-2}	1.87	0.972
50	1.70	5.76×10^{-2}	1.14	0.859	1.18×10^{-2}	1.81	0.983
70	2.39	6.22×10^{-2}	2.18	0.931	2.57×10^{-2}	2.82	0.985
90	3.22	6.96×10^{-2}	3.32	0.978	2.60×10^{-2}	3.69	0.991
***S. natans* powder**							
20	0.71	1.02×10^{-3}	0.87	0.905	4.29×10^{-2}	0.71	0.990
31	1.16	0.06×10^{-3}	0.42	0.609	1.03×10^{-2}	1.09	0.988
50	1.83	1.29×10^{-2}	0.68	0.853	0.07×10^{-3}	1.83	0.997
70	2.45	1.70×10^{-2}	1.39	0.910	0.02×10^{-3}	2.59	0.999
90	3.25	1.38×10^{-2}	2.90	0.943	0.06×10^{-4}	3.74	0.983

3.8 The biosorption and phytoextraction isotherm models

In this study, the biosorption and the phytoextraction isotherm were investigated using four equilibrium models, namely the Langmuir, Freundlich Temkin and Dubinin–Radushkevich (D–R).

The Langmuir isotherm linear equation is expressed as follows:

$$\frac{1}{q_e} = \frac{1}{q_m b} \times \frac{1}{C_e} + \frac{1}{q_m} \tag{5}$$

Where q_e is the solid-phase adsorbate concentration at equilibrium (mg/g), q_{max} is the maximum adsorption capacity corresponding to the monolayer adsorption capacity (mg/g), C_e is the concentration of crystal violet solution at equilibrium (mg/L), and b is the adsorption equilibrium constant that is related to the apparent energy of adsorption.

The Freundlich isotherm linear equation is expressed as:

$$\log q_e = \log K_F + \frac{1}{n} \times \log C_e \tag{6}$$

where k is related to adsorption capacity and n is related to intensity of adsorption. The lnq_e versus lnC_e plot allows the determination of the Freundlich constants.

The monolayer saturation capacity of Crystal violet q_m was calculated to be 12.74 mg/g, while the Langmuir constant, which is related to adsorption energy, was determined to be 0.226 mg/L. Freundlich isotherm constants were also calculated. The linearity of the two plots, expressed by $R^{2,}$ can give information about the fitting between the experimental data and the isotherm model. The one closest to linearity could be considered as describing better the adsorption equilibrium in a certain system (Kamari et al., 2009).

When comparing the determination coefficient for these two models it can be concluded that the experimental data were the most suitable for the Langmuir model ($R^2 = 0.972$) for biosorption and ($R^2 = 0.958$) phytoextraction, respectively.

The linear presentation of the D–R isotherm equation (Dubinin–Radushkevich et al. 1947) is expressed by:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \tag{7}$$

where, qe is the mole amount of metal ions an dyes adsorbed on per unit weight of biomass (mol/g), qm is the maximum biosorption capacity (mol/g), β is the activity coefficient related to biosorption mean free energy (mol^2/J^2) and ε is the Polanyi potential, where, R is the universal gas constant (8.314 J/mol K) and T is the absolute temperature (K).

Free energy E per molecule, of adsorbate, which helps to distinguish between the physical and chemical adsorption of metal ions is given below:

$$E = \frac{1}{\sqrt{-2\beta}} \tag{8}$$

The isotherm constants qm and β were obtained from the intercept and the slope of the plot lnqe vs. ε2. If E values are between 8 and 16 kJ mol-1, the biosorption process is chemical and if E < 8 mol-1 the biosorption process is physical (Gîlca et al. 2014; Sari and Tuzen 2008).

In our case, the mean free energy was 5 mol^{-1} indicating a physical process for biosorption and phytoextraction.

Temkin isotherm equation contains a factor that takes into account the adsorbent-adsorbate interactions (Temkin and Pyzhev 1940). It is based on the fact that the heat of adsorption of all the molecules in the layer decreases linearly with the coverage of molecules due to the adsorbate-adsorbent repulsions and the adsorption of CV uniformly realised on the surface.

The equation of this model is given below:

$$Q_e = B \ln \times A_t + B \ln \times C_e \tag{9}$$

$$B = \frac{RT}{bT} \tag{10}$$

where T is the absolute temperature in Kelvin and R is the universal gas constant, AT is the Temkin isotherm equilibrium constant (L/g), bT is Temkin isotherm constant and B is a constant related to the heat of adsorption (J/mol). From the qe vs. lnCe plot, AT and B constants were determined. Taking into consideration the calculated value of the constant related to heat of sorption, B, which has a value smaller than 20 kJ mol-1, we concluded that according to this isotherm, the sorption process takes place as physisorption (Table 8).

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Table 8. Langmuir, Freundlich, Dubinin-Radushkevich and Temkin calculated coefficients using linear regression analysis for Crystal violet removal using living *S. natans* and *S. natans* powder; C_i = 20-90 mg/L, 0.4 g (biosorption)/ 5 g (phytoextraction) biomass, 296 K, pH 5.4.

	Langmuir			**Freundlich**			**Dubinin-Radushkevich**			**Temkin**		
	K_L (L/mg)	**q_{max} (mg/g)**	**R^2**	**n**	**K_f ($mg^{(1-1/n)}$ $L^{1/n}$/g)**	**R^2**	**β (mol^2 kJ^2)**	**E (kJ/mol)**	**R^2**	**A_T (L/g)**	**B (J/mol)**	**R^2**
Living *S. natans*	0.417	2.07	0.958	1.15	3.04	0.930	2×10^{-6}	5	0.914	2.50	3×10^{-6}	0.886
***S. natans* powder**	0.226	12.74	0.972	1.03	3.13	0.967	2×10^{-6}	5	0.870	2.50	4×10^{-6}	0.862

3.9. The biosorption and phytoextraction thermodynamics

The thermodynamic parameters, the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of the biosorption process for the adsorption of CV onto *S. natans* powder at different temperatures 10–35 °C (283-308 K) by Eqs. (11)– (12)

$$\ln K_d = \frac{\Delta H^{o}}{RT} + \frac{\Delta S^{o}}{R} \tag{11}$$

$$\Delta G^{o} = RT \ln K_d \tag{12}$$

where ΔH°, ΔS°, ΔG°, and T are the enthalpy, entropy, Gibbs free energy, and absolute temperature and R the universal gas constant. The ΔH° and ΔS° parameters were found from the slope and intercept of the plots of ln KD against 1/T. Experimental results were used to calculate the thermodynamic parameters and are presented in (Table 9).

The negative values of ΔG° indicated the feasibility and spontaneity of CV biosorption and phytoextraction onto *S. natans*. The decrease in ΔG° values shows a decline in the feasibility of biosorption as temperature is increased. The ΔG° parameter was found to be -0.0099 J/mol K for biosorption and for phytoextraction to be -0.0116 J/mol K. The negative ΔS° value means a decrease in the randomness at the solid/solution interface during the biosorption process. The positive value of ΔH° indicated the endothermic nature of the biosorption of CV onto *S. natans* (Eren et al., 2013). The endothermic process shows that the diffusion from bulk solution to adsorbent surface may require energy to overcome interaction of dissolved ions with solvation molecules (Nagy et al., 2013).

Table 9. Termodynamic parameters for the removal of CV on living *S. natans* and *S. natans* powder at various temperatures; C_i = 50 mg/L, 0.4 g (biosorption)/ 5 g (phytoextraction) biomass, pH 5.4.

	ΔS°	**ΔH°**	**ΔG°, (kJ/mol)**		
	(kJ/K·mol)	**(kJ/mol)**	**283 K**	**296 K**	**308 K**
Living *S. natans*	-0.12×10^{-2}	0.012	-3.29	-3.45	-3.58
***S. natans* powder**	-0.09×10^{-2}	0.010	-2.81	-2.94	-3.06

4. Characterization, determination and remediation of heavy metals and pesticides found in the marine sediments of the Mediterranean port of Livorno, Italy.

4.1. Description of study areas

Sediment samples were collected from the Leghorn harbor (Italy) on the Mediterranean Sea. Polluted marine sediments were dredged in February, 2014 from the sea bottom of approximately 7 m to depth (43°33´2´´N; 10°17´39´´E), (Fig. 14). The climate in the studied area belongs to the Mediterranean climate, which is characterized by warm to hot, dry summers and mild to cool, wet winters. (Doni et al., 2015).

Figure 14. Map of the study location and sampling sites in the Leghorn area of Italy

4.2. Organochloride pesticides, polychlorinated biphenyls, polyciclic aromatic hydrocarbons and heavy metals analysis

4.2.1. Sample extraction for GC/MS analysis

A quantity of 2 g of dried sediment was extracted by adding 3 mL of acetone and was placed in an ultrasound bath for 10 minutes, followed by the addition of 3ml hexane and subjected afterwards to another 10 minutes of ultrasound treatment. The extraction procedure was repeated two times to improve the efficiency of recovery. The organic extracts were combined, added 2 mL of trimethylpentane and concentrated by a nitrogen stream for the elimination of acetone and hexane. In order to remove the sulphur compounds, trimethylpentane solution was shaken with 1 mL of 2-propanol and 1 mL of TBA-sulfite reagent for 1 min. Afterwards, 5 mL of water was added and the test tube was shaken for another minute, followed by centrifugation, and the trimethylpentane phase was transferred to a test tube (Jensen et al., 1977). The trimethylpentane phase was finally concentrated to 1 mL and purified on activated silica stationary phase. The repeatability of the method was assessed on the basis of 3 parallel determinations of pesticides.

4.2.2 Heavy metals from dredged marine sediments

The concentration levels of heavy metals (Cu, Cr, Ni, Pb, Zn and Cd) was detected in sediments samples by extraction, using the following extracting solutions: HCl (1M), double distilled water, NaCl (36‰) and concentrate HNO3 (67 %). The sediment contains most studied forms of heavy metals in oxidative status 0, in order to determine the amount of heavy metals; their existence was passed in the salt form by treatment with acids, order to be able to determine the amount of heavy metals.

In particular, 200 g of sediment was stirred for 6 hours in 200 mL of extracting solutions (each in separate solution). At the end of the predetermined time, the suspension was filtered and the resulting solution was analysed by inductively coupled plasma optical emission spectrometer (ICP–OES, Optima 5300 DV, Perkin–Elmer, USA). The measured heavy metal concentrations are summarized in (Table 10). Heavy metals (Cu, Cd, Zn) detected in sediment samples were below the limit of detection, except lead and copper, which were in higher concentrations.

Table 10. Heavy metals concentrations in the four extracting solutions

Sample	Cu mg/L	Pb mg/L	Zn mg/L	Ni mg/L	Cd mg/L	Cr mg/L
HCl 1M	ND	3.5	0.51	1.8	0.20	0.42

H_2O	ND	0.57	0.038	0.26	0.055	0.028
NaCl *36* ‰	ND	2.52	0.040	1.99	0.33	0.33
HNO_3 67 %	0.48	2.35	2.74	2.48	0.44	2.274

4.3. Organochloride pesticides, polychlorinated biphenyls, polyciclic aromatic hydrocarbons and heavy metals analysis

4.3.1. Reagents and standards

Reagents used in the research comprised the following: n-hexane, n-acetone, trimethylpentane, methanol, anhydrous sodium sulfate. They were of analytical grade and were obtained from Sigma Aldrich (Germany) and de-ionized water.

In order to determine the organochloride pesticides and polyciclic aromatic hydrocarbons content, the sediment was dried at room temperature for 48 h. All the OCP standards acenaphthene, acenaphthylene, acenaphthylene-D8, anthracene, anthracene-D10, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chlordane, chlorpyrifos, crysene, p-p'DDD, p-p'DDE, p-p'DDT, dibenzo(ah)anthracene, dibenzo(ah)anthracene-D14, dieldrin, endosulfan sulfate, phenanthrene, fluoranthene, fluorene, naphthalene, PCB052, PCB101, PCB 118, PCB128, PCB138, PCB170, PCB180, PCB187, PCB194, PCB206, pyrene, indeno(1,2,3-cd)pyrene, simazine and trifluralin were purchased from O2SI Smart Solution, (USA).

Standard solutions were prepared in acetone at a concentration of 100 µg/mL and diluted with acetone when necessary. The entire glassware was cleaned with laboratory detergent, sequentially rinsed with de-ionized water, acetone, and methanol and heated in an oven at 300 ˚C for 12 h.

4.4. Plant material and growing conditions for phytoextraction studies

Three submerged aquatic plants species were used in the present study: fanwort (*Cabomba aquatica*), tape grass (*Vallisneria spiralis*), and floating fern (*Salvinia natans*). The plants' growth experiments were performed in a hydroponic greenhouse system (at University of Agricultural Sciences and Veterinary Medicine in Cluj-Napoca, Romania), with an addition of fertilizer (Complex 3, 0.5 %). Plants aged 30 days, were selected for the phytoremediation experiments. The plants were kept under laboratory conditions for an acclimatization period of 4 days in modified Hoagland nutrient solution with the following chemical composition: 1 mM KNO_3; 1 mM $Ca(NO_3)2\times4H_2O$; 1 mM $NH_4H_2PO_4$; 1 mM $MgSO_4\times7H_2O$; 25 mM KCl; 12.5 mM H_3BO_3; 1 mM $MnSO_4\times H_2O$; 1 mM $ZnSO_4\times7H_2O$; 0.25 mM $CuSO_4\times5H_2O$; 0.25 mM H_2MoO_4 (85% MoO_3) with Fe(III) citrate (Taiz and Zeiger, 2002) as iron source, at room temperature (21-23°C) with a 14/10 h (light/dark) photoperiod. The plants were cultivated in 250 mL Erlenmeyer flasks (5 g), containing 100 mL of lead solution of sediment and 100 mL Hoagland solution.

The phytoremediation experiments were carried out for 10 days. The sediments resulted from the solution´s heavy metal content were checked using the Atomic Absorption Spectrometer (SensAA Dual GBC Scientific Equipment, Australia).

4.5. Digestion of plant material and determination of heavy metal content

At the end of the experiment, plant samples were dried for 12 h at 60ºC in a forcedly – drought oven. The dried plant samples (approximately 0.2 g) were digested in 8 mL of concentrated nitric acid (Merck, Germany) at 40°C for 8 h. After digestion, the solutions were filled up to volume with distilled water to 50 mL. Determinations of heavy metal concentrations in all samples were carried out using the Atomic Absorption Spectrometer.

4.6. Metal accumulation in the aquatic plants tissues

In the phytoextraction studies, the bioaccumulation of lead and copper in aquatic plants was monitored. Relatively high amounts of accumulated Pb and Cu is observed in the order *Salvinia natans* > *Vallisneria spiralis* > *Cabomba aquatica*. The highest concentrations of Pb in the aquatic plants are associated with the high concentrations in the surrounding sediments. In some cases, copper had not been detected.

As table 11 shows, all the plants accumulated copper only from the solution with HNO_3 in Hoagland. However the highest removal amount (2.641±0.014 mg/kg) was obtained at *Salvinia natans*. Rahman and Hasegawa (2008) reported that the highest concentrations of arsenic in this aquatic plant (*Salvinia natans*) were 2.400 ±0.02 µmol (g dry weight)-1 respectively, over 5 days.

The concentrations of lead in the sediments have an initial concentration of 3.5 mg/L, and can be detected from all solutions. The measured Pb concentrations varied between 3 mg/kg and 0.250 mg/kg DW at different experimental solutions, where the highest concentration of lead was accumulated by *Salvinia natans* (3.328 ±0.032 mg/kg DW), and using sodium chloride with Hoagland nutrient solution. Aquatic plants *Vallisneria spiralis* and *Cabomba aquatica* had a very low rate of accumulation, demonstrating a decreased survival in this experimental condition.

Marques et al. (2009) observed maximum Pb concentrations of 1178 mg/kg in the roots and 149 mg/kg dry weight in the leaves of *Rubus. ulmifolius*, over 16 days. According to the literature, a lower concentration of heavy metals is proving to be more easily accumulated in the plant and opposite (Dhir, 2009).

The above results indicate that these aquatic plants might accumulate large amounts of lead and copper in their tissues. These results are similar to the findings of Dhir (2004) who reported that *Salvinia natans* is a metal hyperaccumulator plant which was able to tolerate and bioconcencentrate high quantities of Fe^{2+}, Cr^{6+} and Ni^{2+} metals (Chorom et al., 2012).

Plants can uptake the heavy metals via their roots and in certain cases, such as submerged plants, by their leaves. The metal uptake occurred by two pathways: first step extracellular (apoplastically), which is a fast one followed by intracellular (simplistically), which is a slow level. The heavy metals' uptake in the fast stage was possible by physical and chemical sorption (adsorption) as well by ion exchange processes. The slower stage is the intracellular uptake and transport of the metals into the cells (Raskin et al., 1994).

Table. 11 The amount of Pb and Cu accumulated by aquatic plants during the 10-day exposure.

Aquatic plant species	Heavy metal concentration	Experimental solutions		
			Pb content in plant (mg/kg DW)	Cu content in plant (mg/kg DW)
Salvinia natans	3 mg/L Pb	NaCl with Hoagland	3.328 ±0.032	ND
	3 mg/L Pb	NaCl without Hoagland	3.247±0.020	ND
	2.8 mg/L Pb 0.8 mg/L Cu	HNO_3 with Hoagland	2.852 ±0.013	2.641±0.014
	3.5 mg/L Pb	HCl with Hoagland	1. 938±0.013	ND
Vallisneria spiralis	3 mg/L Pb	NaCl with Hoagland	3.107 ±0.034	ND
	3.5 mg/L Pb	NaCl without Hoagland	3.061±0.028	ND
	2.8 mg/L Pb 0.8 mg/L Cu	HNO_3 with Hoagland	2.640 ±0.034	2.409±0.048
	3.5 mg/L Pb	HCl with Hoagland	1.935 ±0.048	ND
Cabomba aquatica	3 mgL Pb	NaCl with Hoagland	2.400 ±0.029	ND
	3 mg/L Pb	NaCl without Hoagland	1.965 ±0.183	ND
	2.8 mg/L Pb 0.8 mg/L Cu	HNO_3 with Hoagland	0.205 ±0.003	1.941±0.028
	3.5 mg/L	HCl with Hoagland	1.780±0.005	ND

ND- non-detected concentration (mg/L)

DW- dry weight (mg/Kg)

4.7. Organochlorine pesticides polyciclic aromatic hydrocarbons and polychlorinated biphenyls

Unlike heavy metals, all chlorinated hydrocarbons are anthropogenic in origin. Non-persistent pesticides are unlikely to contaminate the marine environment significantly, since they will be degraded before reaching it (Michael, 1978). The highly chlorinated hydrocarbons are found in the deeper sediments and are more readily adsorbed by sediment particles. On the other hand, the less-chlorinated hydrocarbons are more easily decomposed.

PAHs are included in the organic compound class containing two or more benzene rings. PAHs in the marine environment may be of different origins: pyrolytic (forest fires, volcanic eruptions, waste incineration and combustion of fossil fuels), petrogenic (from petroleum and its fractionation products), or diagenetic (diagenetic transformation of biogenic precursors on marine sediment) (Nikolaou et al., 2009).

They are characterized by high toxicity, persistence and the ability to bioaccumulation in the environment. Due to their molecular weights, they can be divided into low molecular weight compounds (LMW), e.g., naphthalene, acenaphthylene, fluorene, phenanthrene, and pyrene, and high molecular weight compounds (HMW), e.g., benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene, and coronene (Boonyatumanond et al., 2007).

The distribution of various pesticides in the sediment from the three locations sampled is summarized in Fig. 15.

Only seven PAHs compounds (4–6 aromatic ring specie), benzo(a)anthracene, benzo(a) fluoranthene, benzo(b)fluoranthene benzo(k)fluoranthene benezo(a)pyrene, benzo(g,h,i) perylene, dibenzo(a,h)anthracene) were detected above the determination limits.

Benzo(b)fluoranthene was present in the highest concentration in sediment samples, in all studied pesticides average levels of up to 0.2633 ng/g. Benzo(a)anthracene, benzo(a) fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benezo(a)pyrene, benzo(g,h,i) perylene, dibenzo(a,h)anthracene concentrations was however lower than benzo (b)fluoranthene ranging in all sediments samples studied.

In the present study, however, the concentration of detected dieldrin was much higher while aldrin was lower than the one in the study. Another study by Darko et al. (2008) reported lower concentrations of aldrin and dieldrin - 0.65 ng g1 (lg kg-1) and 0.072 ng g1 (lg kg-1) in Lake

Bosomtwi in the Ashanti region of Ghana. The absence of aldrin in the analyzed sediments samples may be attributed to a cessation of their use in the area and also to their decomposition in the environment. The import of aldrin pesticides, widely used in the 1950's and 1960's, has been banned in Morocco since the 1984 National implementation plan for Stockholm Convention on Persistent Organic Pollutants (POPs).

Endosulfan sulfate concentrations detected in the sediment samples were relatively low, as compared with those reported by Mensah (2012), wherein the measured endosulfan sulfate concentration in sediment was of 0.06 ng/g. Endosulfan sulfate concentration was relatively low and the absence of alpha-endosulfan indicated a high rate of degradation of the compound.

From the sediment samples studied, p-p'DDD, p-p' DDE and p-p'DDT levels were significantly lower than p,p-DDT. The concentration of p-p'DDD, p-p' DDE and p-p'DDT ranged from 0.0015 ng/g to 0.0053 ng/g to 0.0018 ng/g, among the studied samples with the highest mean concentration being p-p'DDE. Some p-p´DDT metabolites were detected in sediments but did not exceed permissible limits. In this research pp´-DDT concentrations in sediment are lower, in comparison with other years, when the DDT concentration was much higher, indicating a slow degradation process for DDT. DDT has been banned from agricultural use and restricted for public health purposes, under the Stockholm convention in which Ghana is a signatory. The present investigation therefore gives an indication on the restricted use of DDT for agricultural and vector control purposes in Ghana (Mensah et al., 2012).

Usually the lower chlorinated (tri and tetrachlorobiphenyls) are the ones with the highest removal rates from contaminated soils (Erickson, M.D., 1997). It was also observed an increase in the concentration of PCB101 (20 %), PCB 138 (40 %), PCB170 (41 %), PCB 180 (45 %) and PCB 194 (64 %). In this sediment samples most of the PCB was below the detection limit. PCB has very low water solubility (0.0027–0.42 ng/L-1) and is very hydrophobic (Gomes et al., 2014).

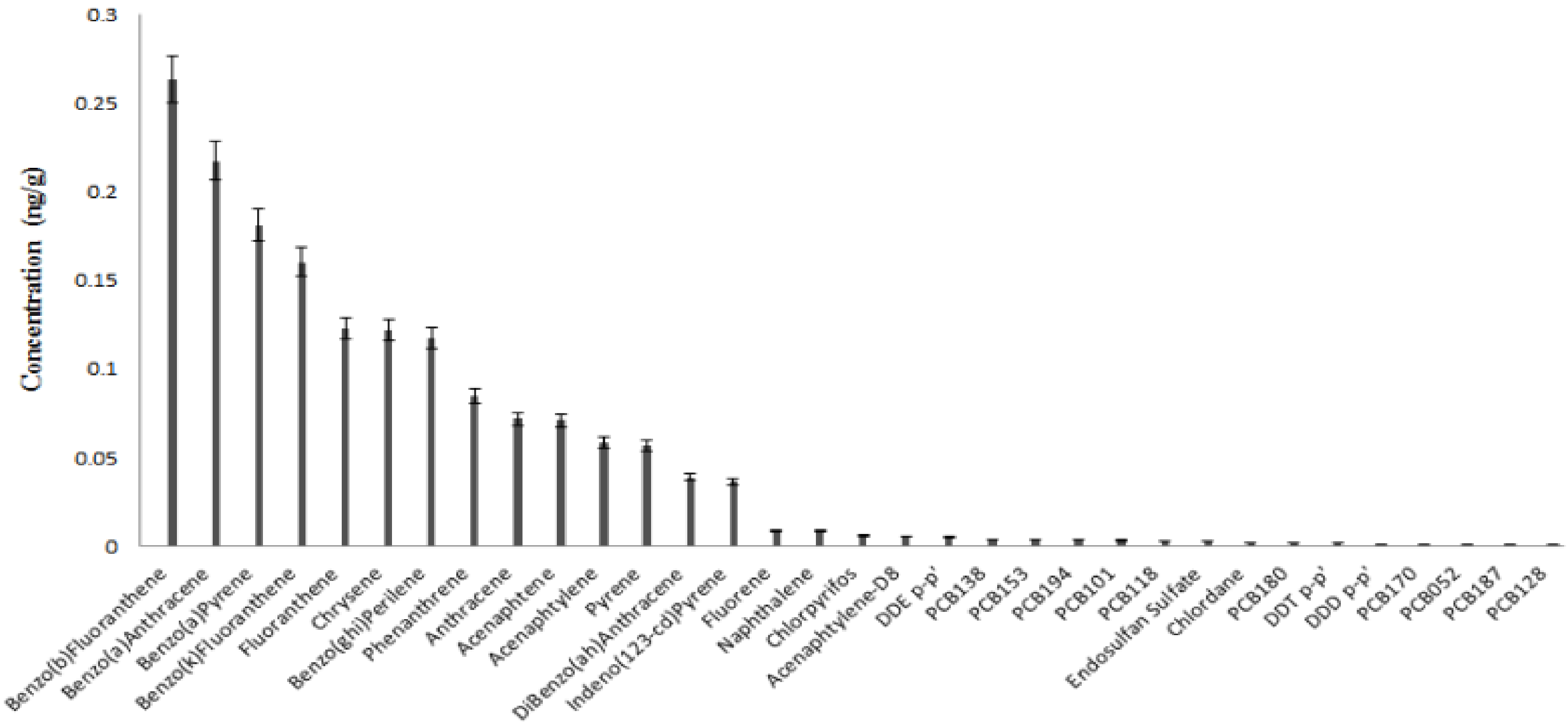

Figure 15. The distribution of various pesticides in the sediment from the three locations sampled

General Conclusions

The biosorption study of untreated fir tree (*Abies Alba*) cones biomass has proven to be a highly effective and promising adsorbent for the removal of cadmium ions from aqueous solutions. This biosorbent is widely available as a natural material, is mechanically stable, and most importantly it is ecofriendly. Cd (II) and Pb (II) biosorptions and removal efficiency can be influenced by a number of factors, such as effective particle size, biomass quantity, agitation speed, initial solution pH, temperature, contact time, and initial Cd (II) concentration. It was found that Cd (II) biosorption by fir cone powder is highly pH dependent, the favorable initial pH of solution being attained at value of 8.2 where a removal efficiency of 98.65% was achieved.

This research present the results of a detailed study on the Pb(II) ions removal process from the aqueous solution, using untreated and chemically treated (NaOH and H_2O_2) Romanian fir (*Abies alba*) cone as adsorbent. The fir cone powder was characterized in detail using SEM analysis, where the obtained images showed morphological modifications on the surface after treatment and Pb(II) adsorption by comparison with the untreated sample. The highest adsorption capacity was attained at initial pH values of 5.2 for all the studied biomass (untreated and both treated adsorbent). Equilibrium (Langmuir, Freundlich, Dubinin- Radushkevich and Temkin) isotherm models and kinetics (pseudo-first-, pseudo-second models and intra-particle and liquid film diffusion) of the considered biosorption process were discussed in details, for both processes.

It can be concluded that the studied adsorption process at pseudo-second-order model indicates a chemisorption mechanism, where the chemisorption is usually restricted to just one layer of molecules on the surface, and it may be followed by additional layers of physically adsorbed molecules. The Langmuir model proved to be a better match to the data than the Freaundlich, for the both processes. As a result, this fact is provend by the Dubinin-Radushkevich and Temkin isotherm models, where the values obtained at mean free energy (Dubinin-Radushkevich) and the constant related to the heat of sorption (Temkin) indicates a physisorption process.

In conclusion that the NaOH treatment increased the adsorption capacity of fir cone powder, with the alkaline treatment being the most effective. In addition, the H_2O_2 treatment did not cause an enhancement on the adsorption capacity in comparison to the untreated biomass, leading us to the conclusion that this oxidative treatment is less effective on fir cone powder.

Results obtained from the present investigation revealed that NaOH modified fir cone powder was an effective, green adsorbent for removing the Pb(II) ions from aqueous solutions.

In this research was tested for the removal of CV from aqueous solutions, the use of *S. natans*, living and powder form. The removal capacity depends on the initial dye concentration, biomass quantity, initial pH and temperature. Findings suggest similarities between the two processes for *S.natans*, in both living and powder form.

Our results demonstrate that for both processes the adsorption on the plant surface is determinant. Kinetics (pseudo-first- and pseudo-second-order) equilibrium (Langmuir and Freundlich isotherm), and thermodynamics of the considered biosorption process were discussed in detail. According to the isotherm models (Dubinin-Radushkevich and Temkin), the adsorbtion of CV on living *S.natans* and powder *S. natans* was physical in nature. Equilibrium was best described by the Langmuir isotherm, while the kinetic of the process was best described by the pseudo-second-order model for both. Thermodynamic parameters showed that the CV biosorption and phytoextraction processes on *S. natans* are endothermic.

The purpose of this research was to analyze the concentration of heavy metal pollutants, and organic compound levels in the sediments collected from the Leghorn harbor (Italy) on the Mediterranean Sea. The phytoextraction possibility was studied in order to asses a new alternative method for multimetal remediation purposes. Three plants, namely *Salvinia natans*, *Vallisneria spiralis* and *Cabomba aquatica* were tested for the removal of lead and copper from the sediment. These three plants proved to be highly effective in absorbing Pb at different concentrations. The correlation between the final metal concentration in the water and the metal concentration in the plant indicated that these plants can be used effectively for the removal of heavy metals from a solution with various concentrations. In the present investigation there were not registered changes in the levels for the DDT because it was taken out of use. Only specific classes of pesticides show the changes. However benzo(a)anthracene, benzo(a)fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benezo(a)pyrene, benzo(g,h,i) perylene, dibenzo(a,h)anthracene concentrations were lower than benzo(b)fluoranthene ranging in all the studied sediments samples. In addition, the results of this study revealed that *Salvinia natans* was a good candidate for removing Pb and Cu from the polluted aquatic environments.

ACKNOWLEDGEMENTS

This work was possible due to the financial support of the Sectorial Operational Program for Human Resources Development 2007-2013, co-financed by the European Social Fund, under the project number POSDRU/159/1.5/S/132400 with the title „Young successful researchers – professional development in an international and interdisciplinary environment”.

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