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RESEARCH ARTICLE

Bio-absorption of Ni and Cd on *Eichhornia crassipes* root thin film

Souad A. Elfeky · Hisham Imam · Alsayed A. Alsherbini

Abstract Release of heavy metals into waterways without treatment can cause a significant threat to the environment. In this paper, we present a method of improving the removal of heavy metals by using *Eichhornia crassipes* roots (ECR) supported on a polymethyl methacrylate (PMMA) thin film. The functional groups of the synthesized PMMA sample were identified by Fourier transform infrared spectroscopy. ECR roots dried fine powder has a small size and large surface area. They contain many polyfunctional metal-binding sites for both cationic and anionic metal complexes. The results show that using 0.1 g of ECR, about 70 % of Cd present in the water was removed in 4 h; while under the same conditions, about 55 % of Ni was removed. The concentrations of Ni and Cd were measured by laser-induced breakdown spectroscopy, a promising technique for the elemental analysis of heavy metals.

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Introduction

Increasing demand for clean water coupled with a shortage of clean water sources has led to water access becoming an issue worldwide. Treating rural and/or municipal wastewater for reuse in agricultural and industrial activities could constitute a water resource sizeable enough to offset this shortage as well as meet the demand for fresh, clean water (Chong et al. 2010). However, in order to be rendered safe to use, this wastewater needs to be cleaned of hazardous materials, particularly heavy metals.

Heavy metals prove to be phytotoxic at higher concentrations (Tan et al. 2000; Chen and Wong 2006; Llamas et al. 2008). Phytotoxicity results in chlorosis, weak plant growth, yield depression, and disorders of plant metabolism (Sasmaz and Sasmaz 2009). The intentional and incidental disposal of sewage sludge, industrial effluents, etc. into rivers and, consequently, onto agricultural lands results in the accumulation of heavy metals in the soils, leading to contamination of the food chain (Kawatra and Bakhetia 2008).

The presently used techniques for the removal of heavy metals from contaminated waters include reverse osmosis, electrodialysis, ultrafiltration, ion exchange, chemical precipitation, phytoremediation, etc. However, all these methods have disadvantages such as high reagent and energy requirements or generation of toxic sludge or other waste products that require careful disposal (Ahalya et al. 2003). Given the increasing need for water and the severe limitations of treatment current techniques, considerable attention has been focused in recent years upon the field of phytoremediation for the removal of heavy metal ions from aqueous effluents (Alluri et al. 2007; Christian et al. 2012).

The role of aquatic plants in phytoremediation technology is well established (Dushenkov et al. 1995; Rai et al. 1995; Schneider and Rubio 1999). The potential
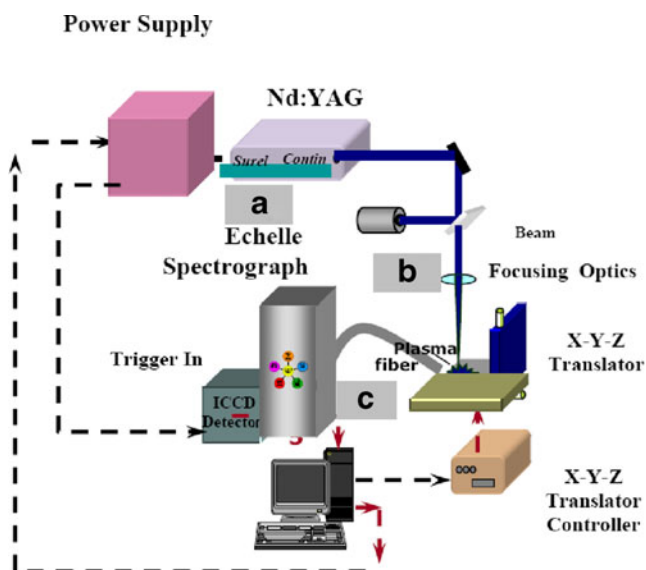
Fig. 1 Schematic representation of LIBS analysis system used for Ni and Cd detection

application of water hyacinth in the removal of heavy metals from water was discovered in the early 1980s (Chigbo et al. 1982).

Dried mass of hyacinth roots has a small size and large surface area. They contain many polyfunctional metal-binding sites for both cationic and anionic metal complexes (Verma et al. 2008).

Previous studies involving water hyacinth have shown that it can absorb or adsorb Zn^{2+}, Cd^{2+}, Hg^{2+}, Cr^{6+}, Cu^{2+}, As, Fe^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cr^{3+}, Pb, Fe, and Zn (Karkhanis et al. 2005; Hassan et al. 2007; Skinner et al. 2007; Abida 2009; Shekar et al. 2011; Shama et al. 2010; Ndimele and Jimoh 2011).

The potential for regeneration of the bio-sorbent provides another advantage since it can reduce the process cost and make possible the recovery of metals extracted from the liquid phase by dilute mineral acids (HCl, H_2SO_4, and HNO_3). For these purposes, it is desirable to desorb the adsorbed metals then regenerate the bio-sorbent material for another cycle of application.

In the present study, the ash of water hyacinth *Eichhornia crassipes* roots (ECR), which are abundantly available as agro waste in tropical countries, was used for removing Ni^{2+} and Cd^{2+} from aqueous solutions. We are reporting their removal by adsorption onto a layer of ECR ash supported in polymethyl methacrylate (PMMA) polymer, a material chosen to facilitate regeneration and reuse of the hyacinth. We performed laser-induced breakdown spectroscopy (LIBS) for detecting the heavy metals because no other technology matches its efficiency in determining trace elements, without complicated sample preparation (Sneddon and Lee 1999). The initial drive for the use and development of LIBS was because of the need for direct and rapid determination of trace elements, particularly metals, in various types of samples. Recently, LIBS technique has been applied for fast qualitative and quantitative analyses of materials. LIBS has several applications in different fields, ranging from cultural heritage studies to industrial process control and bio-medical purposes (Yaroshchyk et al. 2006; Corsi et al. 2001). The advantage of the LIBS technique is that it simplifies the analytical process as it allows the direct vaporization of the sample by interaction with a laser beam of adequate irradiance and, therefore, the preparation of the sample is not necessary. Thus, the LIBS technique can be used to detect quickly polluted areas. Taking into account that cadmium and nickel are toxic elements with significant adverse effects on human and ecosystem health, the minimization of the process for detecting these substances is a relevant issue.

This study aims to assess the ability of water hyacinth root ash to adsorb heavy metals (Cd and Ni) from artificially contaminated water using LIBS technique.

Fig. 2 FTIR spectrum of poly methyl methacrylate
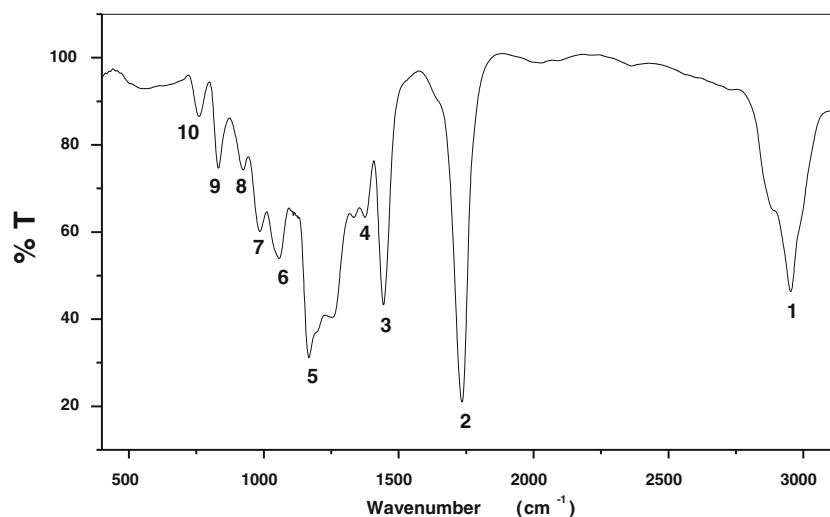
Methodology

Synthesis and spectroscopic analysis of polymethyl methacrylate polymer

About 100 ml of methyl methacrylate monomer, Puriss (Fluka), was degassed by nitrogen in a screw-capped jar. A trace of benzoyl peroxide was then added as initiator. The jar was sealed then degassed by argon and kept undisturbed for 48 h at 55 °C in an oven. The temperature was raised gradually to 90 °C for 5 h in order to remove any remaining traces of unreacted initiator. Before taking the samples out of the oven, we slowly decreased the temperature to 25 °C over a period of 24 h. The Fourier transform infrared spectroscopy (FTIR) spectrum of PMMA was recorded in the solid phase using Bruker IFS 66V FTIR spectrometer in the region 4,000–400 cm^{-1}.

Water hyacinth roots polymer thin film preparation

E. crassipes plants were collected from Nile River in Giza, Egypt. The plants were washed with deionized water before being left to air dry. The dried roots were subsequently crushed in a laboratory blender to obtain a fine powder (Al Rmalli et al. 2005). A proportional weight (0, 0.02, 0.04, 0.06, 0.08, and 0.1 g) of water hyacinth roots powder was suspended in 10 ml of the synthesized polymer. The mixture was uniformly distributed in a Pyrex glass Petri dish (100 mm in diameter) and left to dry for 24 h at room temperature.

Removal of heavy metals

Artificially contaminated samples (100 ml double-distilled water, without any change in pH) containing Cd or Ni (10 mg/L for each of the metal ions, a concentration similar to that found in industrial effluents) were kept over ECR-PMMA thin film in a Pyrex glass Petri dish (100 mm in diameter). The control samples containing 10 mg/L from each of the metal ions were kept over PMMA thin film (without ECR) in a Pyrex glass Petri dish (100 mm in diameter). All experiments were repeated three times and the average was presented in the results and figures. Samples were withdrawn each hour for analysis. The samples were measured by LIBS at 60-min intervals. The percentage of heavy metal removal was calculated by applying spectra normalization and plasma modelling. Removal efficiency percentage and removal rate (in Table 3) were calculated according to the following equations $(A_o - A_t / A_o) \times 100$ and $(A_o - A_t)/t$, respectively. Our LIBS analysis system, shown in Fig. 1, was set up as follows: (a) the laser source (Q-switch Nd:YAG laser (Surelite II)); (b) the laser light delivery

Table 1 Observed FTIR frequency for polymethyl methacrylate

Peak no.	FTIR frequency (cm^{-1})	Assignment
1	2,955, ms	C–H asymmetrical stretching in CH$_2$
2	1,733, vs	C=O stretching
3	1,442, ms	CH$_3$ deformation
4	1,376, w	CH$_2$ deformation
5	1,165, s	C–O stretching
6	1,065, m	CH$_3$ twisting
7	984, w	C–C stretching
8	923, w	CH$_3$ rocking
9	830, w	CH$_2$ rocking
10	758, w	C=O out of plane bending

vs very strong, *s* strong *ms* medium strong, *m* medium, *w* weak

and plasma emission collection system; and (c) the system for spectral analysis (echelle spectrometer (PI-Echelle, Princeton Instruments, USA)). Light from the plasma was collected by a 1-m-long wide band fused-silica optical fiber, connected at its other side to an echelle spectrometer. The spectral analysis system consisted of an echelle spectrometer with a gate-intensified charge-coupled device (Princeton Instruments) attached to it. The gate width and delay time had been chosen after performing an optimization procedure for maximizing the spectral line intensity. The choice of gate width and delay time for the spectroscopic data acquisition was made by Princeton Instruments WinSpec software. Data of results were represented using Microcal Origin 8 scientific charting.

Results and discussion

The FTIR spectroscopic analysis of the synthesized PMMA

The functional groups of the synthesized PMMA sample were identified by IR as shown in the spectrum in Fig. 2. The observed frequencies and proposed assignments of the
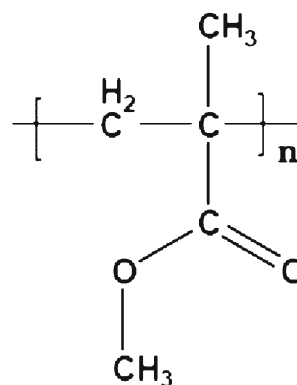

Fig. 3 Structure of polymethyl methacrylate

IR spectral bands of PMMA are summarized in Table 1. Assignments were based on the relative intensities and magnitude of the bands and comparison with literature data for polymers having similar structural features. The strong IR band at 2,955 cm^{-1} is assigned to methylene (CH$_2$) asymmetric stretching vibrations. A sharp, intense characteristic peak appeared at 1,733 cm^{-1} due to the presence of the ester carbonyl group stretching vibration, C=O stretching (Singh and Khanna 2007). The C–O stretching frequency corresponds to one of the intense bands that appear in the fingerprint region. This frequency is quite variable and usually appears within the range of 1,000 to 1,400 cm^{-1} (Harisa et al. 2010). The strong band at 1,165 cm^{-1} is assigned to the C–O stretching modes. The vibrational band at 1,442 is assigned to the deformation modes of the CH$_3$ group (Harisa et al. 2010), whereas the deformation mode of CH$_2$ was observed at 1,376 cm^{-1}. This assignment agrees well with those of Zwarich et al. (1971).

Table 2 Statistical analysis of the bioabsorption rate of Cd and Ni

Time	M	SD	P
Cd			
0	1	0	0
60	96	3.694203	0.020149
120	78	17.2675	0.01347
180	65	24.67766	0.008823
240	6	27.68875	0.008558
Ni			
0	1	0	0
60	88	8.823997	0.008961
120	75	16.58073	0.006586
180	71	18.5753	0.00623
240	68	20.49115	0.006216

M mean, *SD* standard deviation, *P* P value

Fig. 4 Percentage of adsorption of **a** Cd at $\lambda_{ex}=$ 636.3 nm and **b** Ni at $\lambda_{ex}=$ 352.2 nm. I/I_0 represents the optical density at any time divided by the optical density at zero time
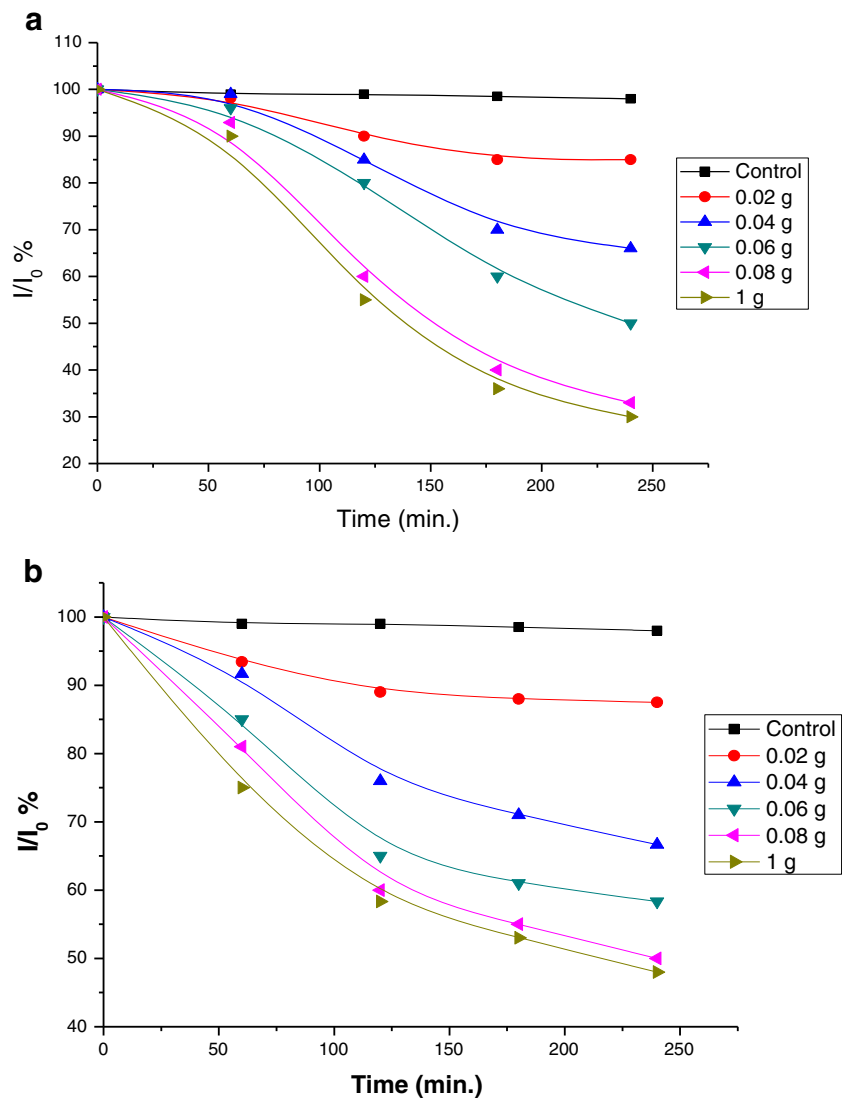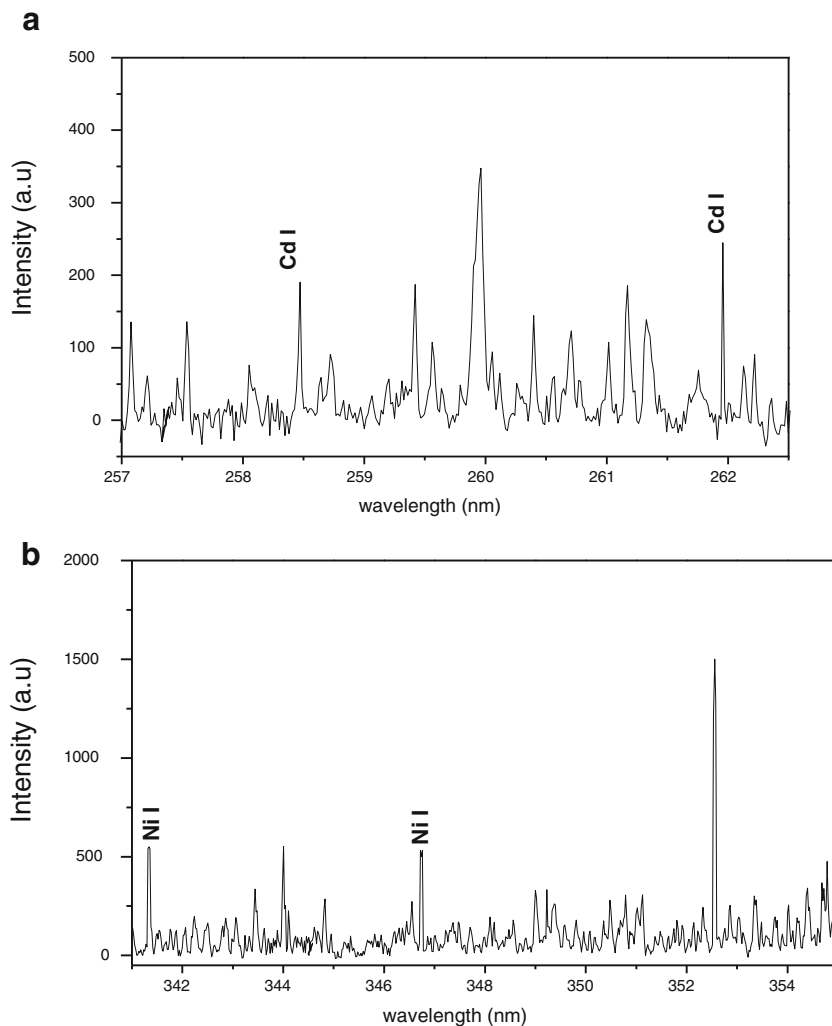
Fig. 5 LIBS emission spectra of **a** Cd(I) and **b** Ni(I) lines

The band at 1,075 cm^{-1} is assigned to CH$_3$ twisting, and the CH$_3$ rocking mode is observed at 923 cm^{-1}. The weak band

appearing at 830 cm^{-1} has been identified as the CH$_2$ rocking vibration, which is consistent with the assignment proposed by Srivastava et al. (2007) and Nallasamy et al.

Table 3 Removal efficiency and rate of Ni and Cd (10 mg/L) measured by LIBS techniques after a time of 240 min

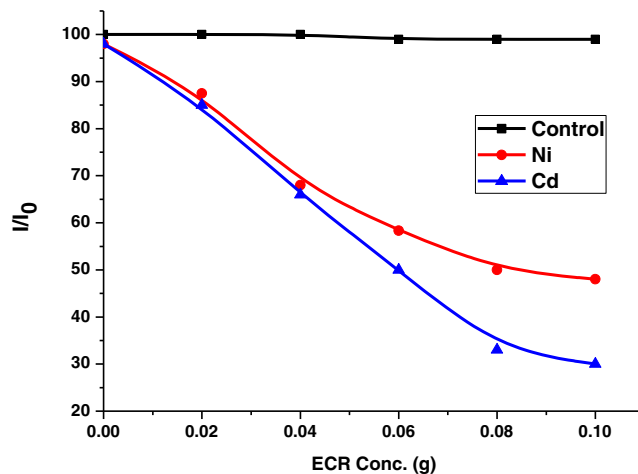| Heavy metal	Water hyacinth concentration (g)	Removal efficiency (%)	Removal rate
Cd	0	2	1.39×10^{-6}
	0.02	15	1.04×10^{-5}
	0.04	34	2.4×10^{-5}
	0.06	50	3.5×10^{-5}
	0.08	67	4.7×10^{-5}
	0.1	70	4.9×10^{-5}
Ni	0	2	1.39×10^{-6}
	0.02	12.5	8.7×10^{-6}
	0.04	33.4	2.3×10^{-5}
	0.06	42	2.9×10^{-5}
	0.08	50	3.4×10^{-5}
	0.1	52	3.6×10^{-5}

Fig. 6 The rate of Cd and Ni removal versus ECR concentration

(2002). The IR band at 758 cm^{-1} is assigned to the C=O out of plane bending mode (Fig. 3).

LIBS analysis of Cd and Ni

The spectrum obtained using the LIBS technique can be regarded as a "fingerprint" of the material being analyzed. By comparing the differences in the intensities of the Cd and Ni lines versus those in the spectrum of the control samples, the removal ratio of these elements could be determined.

Figure 4a, b illustrates the average removal rate of Cd and Ni from water in the presence of 0.02–0.1 g of the ECR in PMMA thin film. The data shown in these figures demonstrate the insignificant adsorption in the case of the control samples. The adsorption increased relative to that of the control when 0.02 g of dry roots was used. Increasing the concentration of the roots from 0.02 to 0.1 g further increased the rate of adsorption. Maximum removal percentages of 70 % for Cd and 52 % in the case of Ni were achieved using 0.1 g of roots after 4 h of adsorption. The removal mechanism may be physical adsorption as a result of van der Waals interactions between the metal ions and ash particles. Ash contains negatively charged carbon particles, whereas the metal ions are positively charged. Consequently, electrostatic attraction arises between the negatively charged ash particles and positively charged heavy metals.

Furthermore, the ECR ash contains oxides of Na, K, Ca, and Mg (Matai and Bagchi 1980). These oxides undergo phenomena such as precipitation, adhesion, adsorption, and ion exchange (Vengaris et al. 2001; Gupta and Bhattacharyya 2008). Precipitation and ion exchange may be responsible for chemisorptions (Alluri et al. 2007).

As seen in Fig. 4a, b, Cd removal was higher than that of Ni. This may be due to saturation of the available active sites on the hyacinth thin film for interaction with Cd at 70 % and with Ni at 52 %. Saturation limits the amount of metal that can be adsorbed regardless of the concentration of the metal in solution. It can be concluded that metal adsorption of the roots was not a simple process and that it was affected by the chemical organization of the hyacinth roots. Similar results have been reported for the adsorption of Cu(II) and Zn(II) ions by water hyacinth (Buasri et al. 2012).

Statistical analysis of the data in Table 2 (Cd and Ni) shows mean, *P* value, and standard deviation between different ECR concentrations at the same time of adsorption compared with the control. In all treatments, a *P* value less than 0.05 means that the mean difference is significant at 0.05 levels.

Figure 5a, b represents the LIBS spectra of the Cd and Ni lines, respectively. The Cd(I) integrated line intensities occur at 258.4870 and 261.8979 nm. The Ni(I)-integrated line intensities of the $3d^8(^3F)4s^2$–$3d^9(^2D)4p$ transition occur at 341.3476 nm and those of $3d^8(^3F)4s^2$–$3d^8(^3F)4s4p(^3P^0)$ are observed at 346.7501 nm. The detected peaks of both Cd(I) and Ni(I) are in agreement with the spectroscopic data from the National Institute of Standard and Technology (Farooq et al. 2012).

Table 3 illustrates the removal efficiency and rate equations as considered herein in the photooxidation of Rhodamine 6G and trypan blue via TiO_2 and Au/TiO_2 thin films (Souad and Al-Sayed 2011a, b). The ECR removal efficiency for Cd was 70 % and that for Ni was 52 % at a time of 240 min. Further, the ECR removal rate for Cd (4.9×10^{-5}) was greater than that for Ni (3.6×10^{-5}) after the same time; therefore, the ion selectivity for ECR was greater for Cd than for Ni, as illustrated in Fig. 6.

Figure 6 represents the water hyacinth sorption for Cd and Ni. The maximum rate of removal for both elements separately was obtained with 0.1 g ECR after 240 min.

Conclusions

This study introduces an economic method for removing heavy metal contaminants from water by hyacinth thin film. Hyacinth shows high ability to remove Cd and Ni from artificially contaminated water. LIBS technique was successfully used for detecting and identifying Cd and Ni. The average removal efficiency for the plant species water hyacinth was 70 %, for Cd, and 52 %, for Ni after 240 min.

Conflict of interest The authors declare no conflict of interest.

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