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The accumulation of silver and gold in *Lemna gibba* L. exposed to secondary effluents

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ABSTRACT

Aquatic plants are used as a practical and effective method to remove toxic metals from secondary-treated municipal wastewater. In this study, *Lemna gibba* was investigated for its capacity to remove silver (Ag) and gold (Au) from secondary effluents. *L. gibba* was collected from a natural lake and then acclimatized to the effluent *in situ*. The concentration of toxic elements in the plant material was monitored as a function of time over 7 days. *L. gibba* accumulated significant amounts of Ag and Au for six days from initiation of the experimental study. The highest accumulations were 2303% for Ag and 247% for Au. However, after six days, the rate of Ag and Au accumulation in *L. gibba* declined, as saturation levels had been reached in the plant tissues. The metal accumulating property of *L. gibba* can also be commercially exploited to recover Au and Ag from wastewater and mining wastes.

1. Introduction

Toxic elements such as Au and Ag that pollute soils and water are removed with various remediation methods that include chemical, physical, and biological technologies. However, these methods all have different efficiencies for different metals and many can be very expensive, especially if large volumes, low metal concentration, and high standards of cleaning are required.

Aquatic plants are well known to accumulate metals from the environment and to concentrate them within the trophic chains (Outridge and Noller, 1991; Tremp and Kohler, 1995; Miretzky et al., 2004). In other words, using aquatic plants to separate metals from their surrounding waters is extremely efficient, technologically feasible, and cost-effective (Foster, 1976; Raskyn et al., 1997; Chua, 1998; Maine et al., 2001; Prasad et al., 2001; Upadhyay et al., 2007). In this context, plants with a high colonization rate can be viewed as excellent tools for phytoremediation (Prasad et al., 2001).

Duckweed plants are common in the aquatic environment, especially in quiescent water bodies and are divided into four genera: *Spirodela*, *Wolffiella*, *Lemna*, and *Wolffia*. There are approximately 40 species worldwide. Duckweed plants are widely distributed in the world from the tropical to the temperate zones, from fresh-water to brackish estuaries, and throughout a wide range of trophic conditions (Mohan and Hosetti, 1999). Duckweed has been reported to remove various elements (e.g., As, Cd, Cr, Cu, Ni, Pb, Fe, Au, Pt, U, B, Sr, and Zn) (Zhao and Duncan, 1997; Zayed et al., 1998; Fogarty et al., 1999; Antunes et al., 2001; Cossu et al., 2001; Hasar and Öbek, 2001; Cohen-Shoel et al., 2002; Wang et al., 2002; Oporto et al., 2006; Maine et al., 2006; Upadhyay et al., 2007; Obek, 2009; Sasmaz and Öbek, 2009).

Metal accumulation by plants has been extensively investigated using *Lemna gibba* as a model plant from Duckweed plants. *L. gibba* is commonly found in wetlands and is fast growing, adapts easily to various aquatic conditions, and plays an important role in the extraction and accumulation of toxic elements from surface waters (Sasmaz and Öbek, 2009). *L. gibba* has been shown to accumulate high concentrations of a number of different elements (Jain et al., 1988; Ernst et al., 1992; Brooks, 1998; Hasar and Öbek, 2001; Kara et al., 2003; Mkandawire and Dudel, 2005; Mkandawire et al., 2006; Sasmaz and Öbek, 2009; Obek, 2009). The aim of the present research study was to evaluate the capacity of *L. gibba* to remove Ag and Au contaminants from secondary-treated municipal waste water.

2. Materials and methods

Unlike previous studies, our experiments were carried out in a natural environment. Climatic conditions in the study area during this period were: mean daily temperature, 24.9 ± 6.8 °C; mean daily relative humidity, 31.6 ± 2.8%; mean period of sunny days (h), 12.1 ± 0.4; and mean global radiation, 570.4 ± 19 W m^{-2} (information was provided by the Turkish State Meteorological Service).

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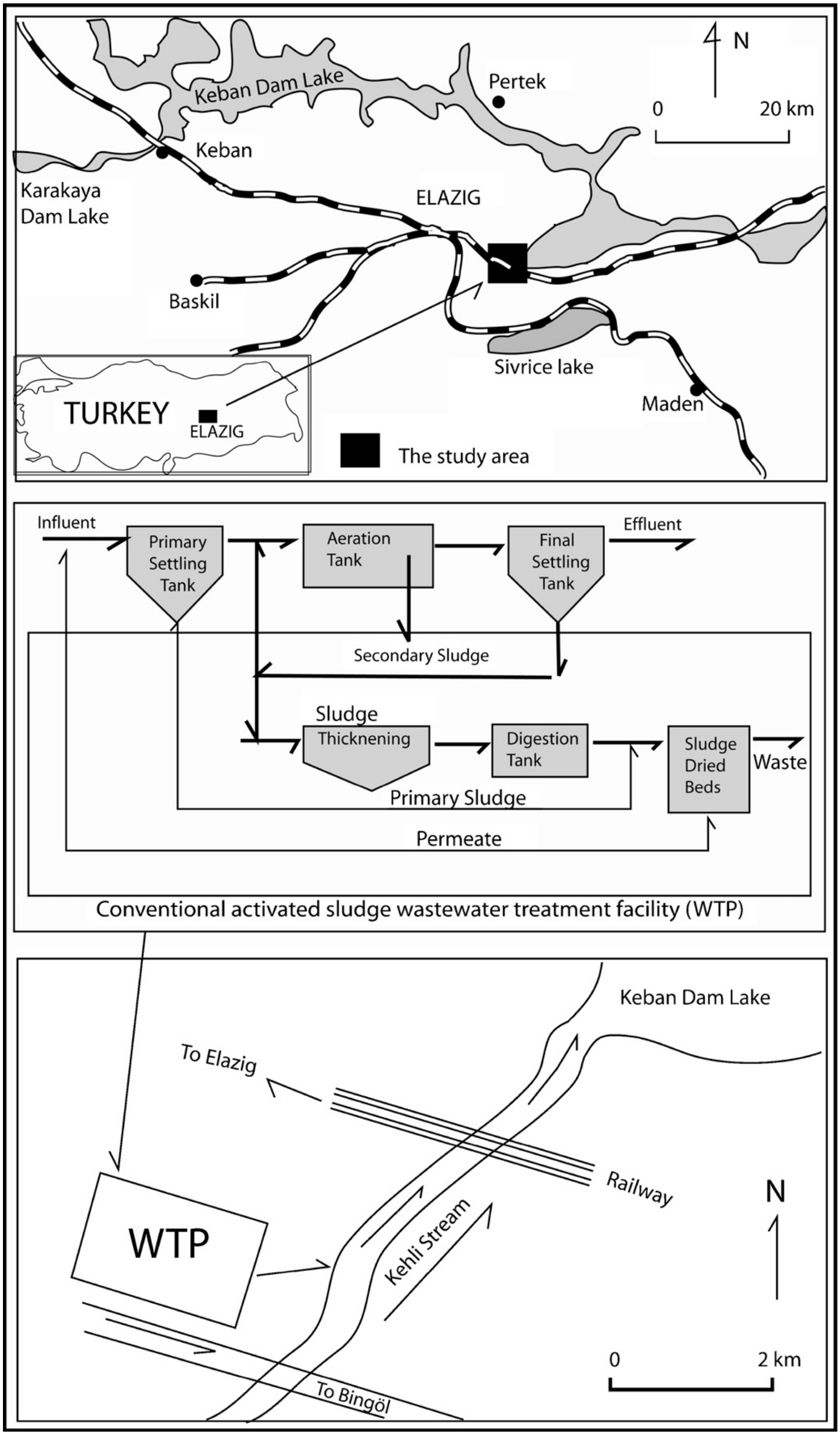

Fig. 1. Map of the study area and flow sheet of the Elazığ Municipality Wastewater Treatment Plant.

2.1. Preparation of samples

The *L. gibba* samples used in the study were collected from a natural lake in Elazığ, Turkey during June and July 2006 (Fig. 1). Within 15–20 min after collecting the plants, selected samples (1120 g) were placed into an open container in the effluent of a final settling tank of the Elazig Municipality Wastewater Treatment Plant (this wastewater treatment plant uses a conventional activated sludge process for treating municipal wastewater). The container (45 cm × 75 cm × 35 cm), with contents consisting of the plant material plus water from the lake, was covered with tulle and then completely immersed in the wastewater. For the next 7 days, approximately 150 g of plant material was removed every day and dried under atmospheric conditions. Water samples were also collected at the same time. All samples were stored at 4.0 °C.

2.2. Method

Procedures in the Standard Methods for the Examination of Water and Wastewater (APHA, 1995) were used for the physicochemical analysis of the samples, and the trace elements were quantified by atomic absorption (Perkin–Elmer). The air-dried plant samples were completely dried in a drying oven at 103 °C for 24 h and then ashed at 480 °C for 4 h. These ashed samples (1.21 g of ashed plant material from approximately 3.80 g of dried plant material) were pulverized using hand mortars, labeled, and sent to Canada for analysis.

Ashed samples were digested in HNO_3 for 1 h and then in a mixture of $HCl–HNO_3–H_2O$ (1:1:1, v/v) for 1 h at 95 °C (1.0 g ash per 6 mL). Acid was added to the water samples. The samples were analyzed by inductively coupled plasma mass spectroscopy (ICP/MS; Perkin–Elmer ELAN 9000) at Acme Analytical Laboratories Ltd. in Canada (http://www.acmelab.com/cfm/index.cfm). Acme is currently registered with ISO 9001:2000 accreditation.

3. Results and discussion

Table 1 shows the results of physiochemical analyses of the secondary-treated municipal wastewater and natural water. *L. gibba* accumulated a substantial amount of Ag and Au from the secondary effluents on a daily basis, as shown in Table 2.

L. gibba removed a substantial amount of Ag (Fig. 2) and Au (Fig. 3) from the wastewater and appeared to preferentially take up Ag over Au. As seen in Table 2 and Figs. 2 and 3, the maximum accumulations of Ag and Au from the secondary effluents occurred on the sixth day of the experiment. Considering the previous study by one of the authors (Obek, 2009) and 6-day maximum saturation level determined, a 7-day evaluation was accepted satisfactory.Ag is a nonessential metal and is one of the most toxic of the heavy metals. It shows strong toxicity towards most living organisms, including aquatic plants and animals, even at the trace

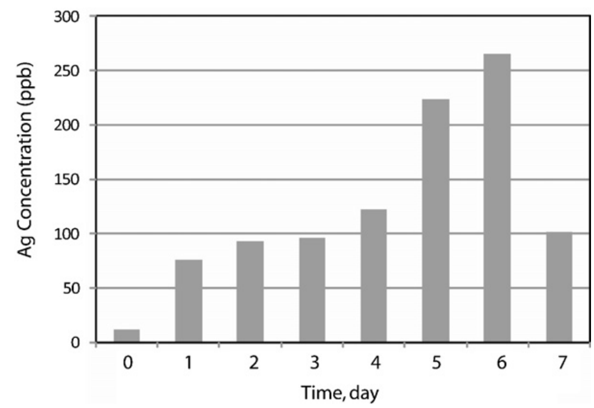

Fig. 2. Silver accumulation by *Lemna gibba*.

levels that arise in aquatic environments from natural and anthropogenic sources (Buhl and Hamilton, 1991; Pais and Jones, 2000; Kabata-Pendias and Pendias, 2001; Jacobson et al., 2005; Xu et al., 2010). Ag content in plant tissue is usually less than 0.01 mg kg^{-1} (Kabata-Pendias and Pendias, 2001).

Au is also toxic to plants, leading to necrosis and wilting by loss of turgidity in leaves (Kabata-Pendias and Pendias, 2001). However, Antunes et al. (2001) reported that the duckweed *Azolla filiculoides* was capable of removing between 86% and 100% of Au from initial metal solutions of 2–10 mg L^{-1}. On a biomass basis, a removal efficiency greater than 95% was observed at all biomass concentrations measured.

Our results provide evidence that *L. gibba* is also an efficient accumulator of Ag and Au. Ag and Au were accumulated from the effluent at high concentrations (2303%, and 247%, respectively) in the natural environment compared with the control sample. On the first and second days, accumulation increases of 739% and 209% were seen for Ag and Au, respectively. However, after six days, the rate of accumulation of Ag and Au in *L. gibba* showed a significant decrease because the metals had reached saturation levels in the tissues. The daily changes in Ag amounts indicated an approximately linear increase up to the saturation level. A fluctuation in the Au accumulation on the fourth day, as seen in Fig. 3, confirms this. However, in a previous study, Obek (2009) indicated that the accumulation values varied from metal to metal for *L. gibba*. For example maximum saturation time for Pb was determined as 5 days in this study. Upadhyay et al. (2007) pointed out that the differences in heavy metal accumulation between plants reflect differences in metabolism and growth activity. This indicates their differential capacities for metal uptake.

Table 1
Physicochemical characteristics of wastewater in the secondary clarifier and in natural water.

Parameter	Unit	Wastewater	Natural water
Temperature	(°C)	17.60 ± 0.50	19.30 ± 0.01
pH		7.67 ± 0.10	7.10 ± .0.10
DO	(mg L^{-1})	3.75 ± 0.1	6.42 ± 0.1
COD	(mg L^{-1})	35.00 ± 3.00	8.30 ± 2.00
NO_2^--N	(mg L^{-1})	0.08 ± 0.01	0.20 ± 0.01
NO_3^--N	(mg L^{-1})	0.60 ± 0.01	2.70 ± 0.01
PO_4^{3-}-P	(mg L^{-1})	>5.00	0.16
NH_4^+-N	(mg L^{-1})	<0.04	0.93 ± 0.30
Ag	(ppb)	<0.5	<0.05
Au	(ppb)	<0.5	<0.05

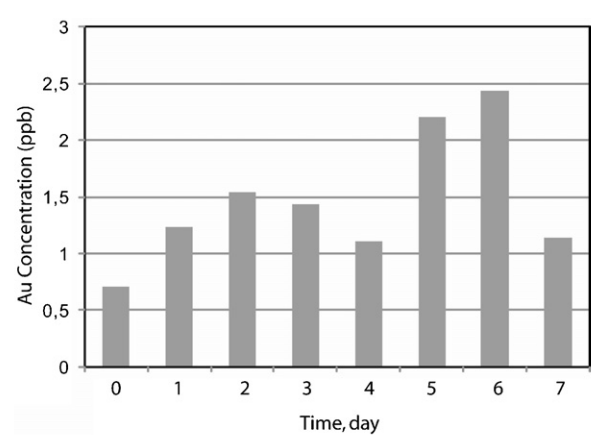

Fig. 3. Gold accumulation by *Lemna gibba*.

Table 2
Chemical composition per day by *Lemna gibba*.

Parameter	Before study	After study						
		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
P (%)	0.66	0.53	0.61	0.54	0.68	0.74	0.74	0.63
Ca (%)	3.66	3.41	4.3	3.57	4.01	4.27	4.02	3.84
K (%)	2.43	1.89	2.03	1.66	1.87	1.66	1.86	1.81
Mg (%)	0.38	0.30	0.36	0.31	0.38	0.38	0.37	0.35
Fe (%)	0.03	0.09	0.11	0.09	0.10	0.13	0.11	0.09
Ag (ppb)	11	75.6	92.3	96	121	223.3	264.3	100.7
Au (ppb)	0.7	1.23	1.53	1.43	1.10	2.20	2.43	1.13.

L. gibba's biomass polluted by different contaminants can be utilized for biogas production and papermaking. For the biofiltration of heavy metals from secondary treated municipal wastewater, *L. gibba* discussed here performed excellently and can be recommended for recovery of mining areas like gold and silver. This technique is highly recommendable for recovery of contaminants in all effluents.

From Table 2, it is seen that P, Ca and Fe accumulation in *L. gibba* were not affected the accumulation of Au and Ag and the accumulation of these elements in *L. gibba* also increased for six days contrary to the study by Moral et al. (1995) in which they reported that concentrations of the nutrient elements N, P, K, Na, Ca, and Mg in stems and branches were significantly affected by Cr treatments (50 and 100 mg L^{-1}) in tomato.

4. Conclusion

The aquatic plant *L. gibba* was used to investigate the accumulation of Ag and Au from a secondary wastewater effluent as a potential alternative method for removal of metal ions from wastewater. Both Ag and Au were quickly absorbed by *L. gibba* for six days after exposure to effluent. However, after day 6, accumulation of these elements began to vary, most likely due to reaching a saturation level in the plant material. The preferential sequence of accumulation was Ag > Au. The removal of heavy metals and toxic trace elements in wastewater by *L. gibba* is environmentally nondestructive and cost-effective.

Harvesting time for absorption level is also important. The longer harvesting time the more metal the plant absorbs up to a certain day. But more frequent harvesting could increase the total metal absorption efficiency.

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