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Pb(II) biosorption by selected waste biomass

ABSTRACT

Global concerns regarding environmental issues have required the evaluation of the waste biomass as potential biosorbents of heavy metals. This paper provides a review on using aquatic weed Myriophyllum spicatum and its compost and selected agricultural wastes: corn silk, peach and apricot stones as biosorbents of lead ions. These biomasses were characterized by Scanning electron microscopy (SEM). The results of the studies on adsorbent efficiency of these bio wastes show that they apart from their wide availabilities are enriched with appreciable biosorption capacities. The paper also provides a critical view concerning future applications of this kind waste biosorbents in treatment of heavy metal contaminated water.

***Keywords**: lead, biosorption, waste biomass.*

1. INTRODUCTION

The occurrence of heavy metals in water causes hazards to humans and other living organisms. Heavy metals pollution has turn into a global problem therefore different organization such as: World Health Organization (WHO), U.S. Environmental Protection Agency (USEPA) and many government environmental protection agencies have set the Maximum Contaminant Levels (MCLs) for the heavy metals in drinking water along with trade effluent [1].

Lead can be found to industrial discharges from a variety of sources, like: batteries, paints, pigments, ammunition, petrol, electroplating, cables, alloys and steels, plastics and glass industry [2]. The toxicological effects of lead in humans include: anemia, sterility, hypertension, learning disabilities, mental deficiency, abortion, kidney damage, behavioral disturbances, vomiting and malaise [3]. Hence lead removal is of utmost importance.

Different physico-chemical and biological processes are usually utilized to remove pollutants (including lead) from industrial wastewaters before discharge into the environment [4]. These separation processes are not entirely economically achievable because of the high cost of performance. For that reason, it is important to find new processes, which are more efficient and cost-effective [5]. Application of biosorption can considerably reduce capital, operational and total treatment costs compared with the conventional processes [6].

The application of low-cost biosorbents made from agricultural wastes and weeds can not only reduce a large quantity of solid waste but also be very attractive. Their benefits include low investment cost, simplicity of design and operation, notable performance even with very low concentration solutions [7].

Requirements Directive 1999/31/EC require that biowaste with more than 3% organic content is no longer accepted for landfilling as the directive is proposed to prevent or entirely reduce the adverse effects of waste landfilling on the environment by introducing strict technical requirements [8].

On this basis we entered on a review of the literature entailing the collection and analysis of data on biosorption of lead with selected agricultural wastes: corn silk, peach and apricot stones and aquatic weed *Myriophyllum spicatum* and its compost.

2. CHARACTERISTIC OF SELECTED BIOSORBENTS

Physical and chemical characteristics of biosorbents are significant to recognize adsorption mechanism as well as potential application of the materials [9]. Thus, this section discusses the characterization of selected waste biomasses.

Corn silk was gathered from the local cornfields near Belgrade (Serbia). Collected biomass was washed several times with deionized water to

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remove impurities, dried at 353 K, milled and sieved into particle size less than 0.2 mm [10].

Apricot and peach stones were from the juice factory “Vino Župa” Aleksandrovac in Serbia.

According to the data from this factory, 500 to 1,000 t apricot stones and 1,500 t peach stones as waste are generated per month during the summer season. Apricot stones were air dried, milled (KHD Humbolt Wedag AG) and < 1 mm fraction was used. Samples were washed with deionized water to remove impurities, dried at 60 °C [11].

Peach stones were separated from soft fruit residues, washed in water, dried at room temperature for several days, milled ((Siebtechnik GmbH, Germany) and sieved through aperture size less than 1mm. In order to eliminate surface impurities, the samples were washed several times in 0.001 M HCl and then in distilled water. The samples were dried at 60 ^{o}C to a constant weight and kept in desiccator before use.

Myriophyllum spicatum is aquatic weed which grows on every continent except Antarctica [12]. In many countries, as well as in Serbia, *M. spicatum* presents an undesirable aquatic weed which needs to be continuously take away from water and disposed [13].

Samples of freshly harvested (with a mechanical underwater harvester) aquatic weed *M. Spicatum* were taken from the artificial Sava Lake, Belgrade, Serbia. With mowing, the amount of unwanted aquatic weed from lake is being significantly reduced (approximately 350-400 m^3 per harvesting cycle) The harvested plant material is placed in an open landfill used specifically for this purpose without turning. Samples of compost were taken from the landfill surface (1 year old) [13].

SEM analyses were done with the dried samples coated with gold using the JEOL JSM-6610LV SEM model.

Scanning electro-micrographs of instigated waste biomass are shown on Figure 1. The same figure shows the chemical composition of these waste materials.

SEM micrograph of *M. spicatum* shows that the plant material has porous structure (wavy surface with square openings). This surface permits the binding of heavy metal towards the center of the particles.The structure and look of the surface of the compost *M. spicatum* is significantly different from the surface of *M. spicatum*. Breakdown of organic matter significantly transformed the structure of the material. There is evident particle structure of compost, and the surface is layered and swollen. The morphology and the nature of the surface of the ground peach shell particles is presented on the at 1000 x magnification. Surface nature can be denoted as multilayer porous surface with an average macro pore diameter of about 1μm, which may be beneficial to metal ions diffusion and later metal adsorption. SEM micrograph showed quite smooth surface of apricot shells with occasional pores on it, (diameter of 1 μm) and some random cracks. This raw material has poor and negligible surface area. The corn silk has coarse surface with a large number of cavities and channels on the outer wall. Surface morphology like this might provide better diffusion of solution and improve interaction between metal ions in active sites on corn silk surface.

The chemical composition data of tested biosorbents are also shown in Figure 1 and their values are presented in papers [11,13,14]. Cellulose content ranged from 58% up to 16.5% and the highest percentages have stones and the lowest corn silk. Compost *M. spicatum* and stones have the most lignine while *M. spicatum* and corn silk obtain the highest percentage of proteins compared to other waste biomass.

Biological material is complex and different structural components are present in biomass, so many functional groups are able to interact with metal species, like: carboxyl, hydroxyl, amino, thiol, phosphate, to changeable degrees and influenced by physico-chemical factors. Biosorption is a complicated process considering given conditions and system [4,15].

Fouriertransform infrared (FTIR) spectrophotometry determines biosorbent active sites [16]. The functional groups that might participate in the biosorption process of lead removing are listed in Table 1.

Table 1 - FTIR determined functional groups with ligand atoms as possible active sites for biosorption of lead(II) ions from aqueous solution by selected waste biomass

Biosorbent	Name of functional group	Functional group	Ligand atom	Reference
M. spicatum	Carbonyl	>C=O	O	[13]
	Carboxyl	-COOH	O	
	Hydroxyl	-OH	O	
Compost *M. spicatum*	Carbonyl	>C=O	O	[13]
	Hydroxyl	-OH	O	
Peach stones	Hydroxyl	-OH	O	
	Carboxyl	-COOH	O	
Apricot stones	Carbonyl	>C=O	O	
	Hydroxyl	-OH	O	
Corn silk	Hydroxyl	-OH	O	[10]

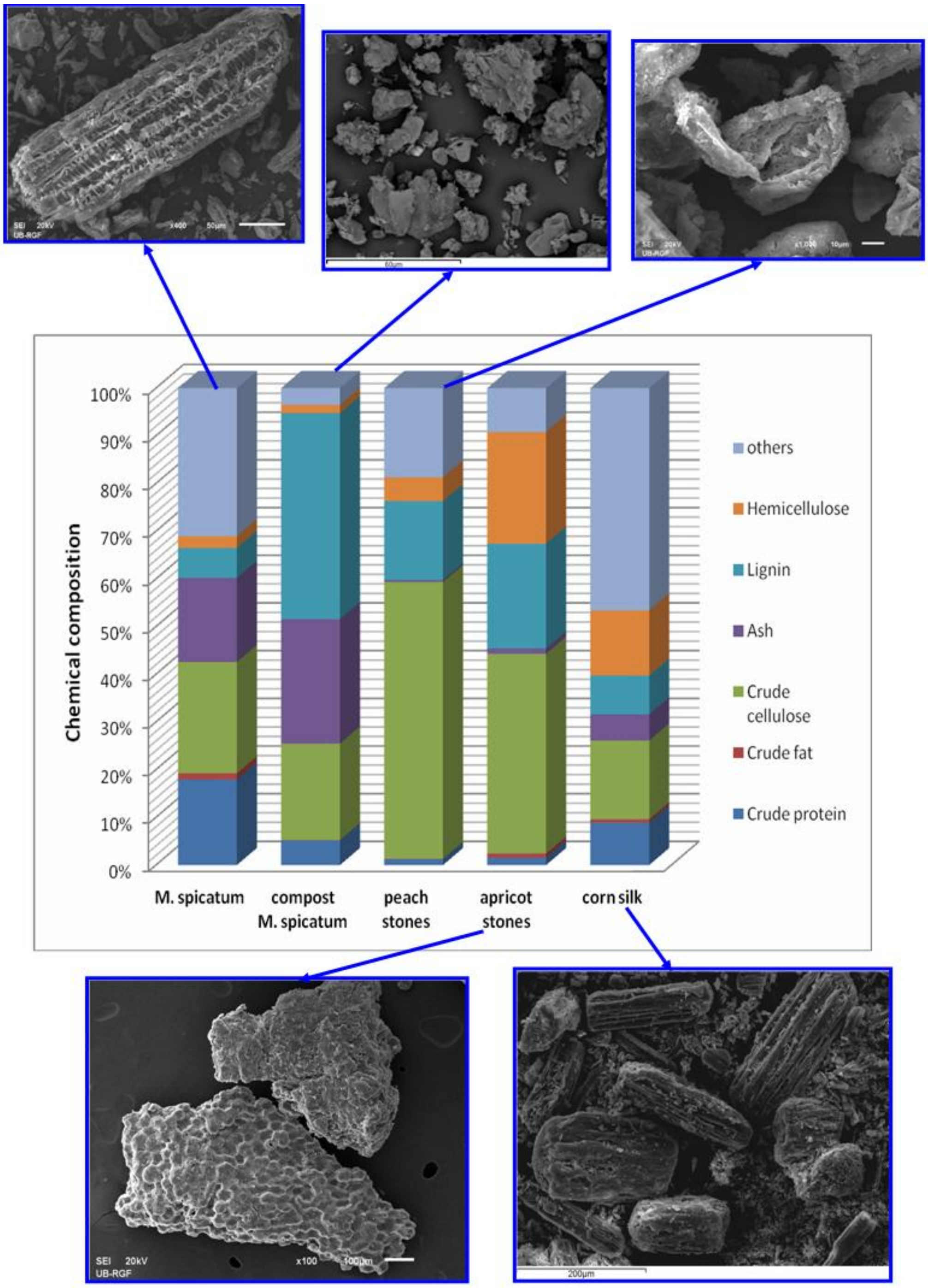

Figure 1 - SEM micrographs of waste biomass and their average chemical composition

From FTIR data presented in Table 1 some surface functional groups such as: hydroxyl, carboxyl, carbonyl, might be involved in lead removal with specified biosorbents. The identified organic functional groups are compounds of polysaccharides, lignin, amino acids of waste biomass which chemical composition is shown in Figure 1.

pH value at which adsorbent surface charge has a zero value is point of zero charge (pH_{PZC}). At pH value greater than pH_{PZC} adsorbent surface charge is negative and might interact with cations, accordingly at pH value lower than pH_{PZC} adsorbent surface charge is positive and could interact with anions [17,18]. The information about of pHPZC could indicate the possible electrostatic interactions between adsorbent and metal ions in solution [18].

Table 2 - Point of zero charge characterized biosorbents and intervals of pH value with different surface charge

Biosorbent	point of zero charge (pH_{PZC})	References	surface (pH range)		
			positive	neutral	negative
M. spicatum	7	[13]	1,0-2,0	2,0-12,0	>12,0
Compost *M. spicatum*	6,1	[13]	1,0-2,0	2,0-12,0	>12,0
Peach stones	4,75		2,0-4,0	4,0-9,5	9,5-11
Apricot stones	4,9		2,0-4,8	5,0-9,0	>9,0
Corn silk	6	[10]	<4,0	4,0-10,0	>10,0

The Table 2 shows the value of the point of zero charge represented biosorbents and intervals of pH value when their surface is positive and intervals when it is negative. Based on the data in table the biggest pH range where surface is neutral have: *M. spicatum* and its compost, then corn silk, peach and apricot stones. The lowest value of the point of zero charge, which is in this case in the acidic range have stones and the greatest value has surface of aquatic weeds.

Figure 2 shows the capacity of biosorbents which are the subject of this review. The largest lead binding capacity *q* showed corn silk and the smallest apricot stones

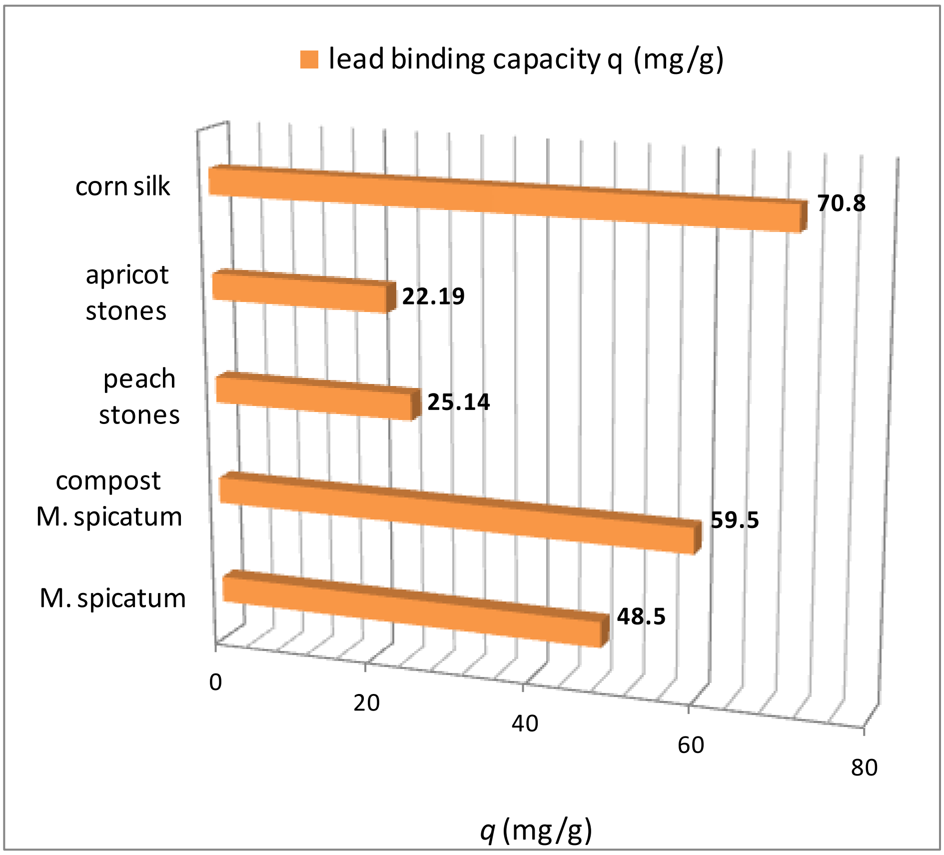

Figure 2 - Lead binding capacity of selected waste biomass

3. CONCLUSION AND FUTURE PROSPECTS

Each year in the European Union 3 billion tonnes of waste biomass is been made. These wet waste biomasses are plentifully available in Europe, while their disposal and recycling becomes increasingly difficult as energy efficient, environmentally sound and economically viable processes barely exist. The existing treatment methods for these materials are mainly incineration or landfilling. A small amount is composted, digested anaerobically or used as animal feed [8].

Directive 1999/31/EC limits further legal ways for biowaste disposal and sets the basis for progressing new technologies for its reuse. By

2020 the EU Member States could be generating 45% more waste than in 1995 [8].

Biosorption capacities and mechanisms are determined by the nature of contaminants, characterization and modification methods. Therefore, selectivity of appropriate biosorbents and their modification is essential and need more considerations [9].

Further investigations of biosorption can create pilot-scale or industrial-scale implications sustainable reality[19]. Biosorbents are usually in the form of powder. For applications in pilot-scale, from "active biomass powder" biosorbents should be in the suitable form of pellets or granules. The pellets should have certain characteristic: mechanical properties (strength, hardness), low mass transfer resistance for the metal ionic species in solution [20]. The primary purpose of immobilization is to increase the mechanical strength using a minimum quantity of matrix material, and it might provide advantages such as ability to reuse and separation of solid biomass from the bulk fluid. The process will become cost effective by reusing the biomass after regeneration [21]. Immobilization of biomass is achieved by bringing into a matrix of the natural polymers such as alginate, chitosan, chitin and cellulose derivatives [22,23]. Furthermore, the possibility of application combined biosorbents and adsorbens should be investigated [24].

Future investigation will include combining different biosorbents with higher capacities and the synergistic effect. These biosorbents will be in the form of granules and created by immobilization with natural polymers.

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IZVOD

BIOSORPCIJA Pb(II) ODABRANOM OTPADNOM BIOMASOM

Zaštita životne sredine na globalnom nivou zahteva evaluaciju otpadne biomase kao potencijalnog biosorbenta teških metala. Ovaj rad daje pregled korišćenja vodenog korova Miriophillum spicatum i njegovog komposta kao i odabranog poljoprivrednog otpada: kukuruzne svile, koštica breskve i kajsije kao biosorbenata jona olova. Ove biomase su okarakterisane Skenirajućom elektronskom mikroskopijom (SEM). Rezultati studija o efikasnosti ovog bio-otpada pokazuju da pored široke dostupnosti ova otpadna biomasa poseduje i značajne biosorpcione kapacite. Ovaj rad pruža kritički stav za buduće primene ovakve vrste biosorbenata otpadnog porekla, u tretmanu otpadnih voda zagađenih teškim metalima.

Ključne reči *: olovo , biosorpcija , otpadna biomasa.*

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