



Removal of toxic metal ions from aqueous solutions using biosorption technique: Review article

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Abstract

The aim of this article is to review the biosorption of metal ions by different biosorbents, such as agriculture waste, fruit peels, industrial waste, fungi and alga. All these types were studied in this work using several parameters.

The maximum uptake of the metals (expressed by mg metal/g biosorbent) has been adopted as a criterion for the metal recovery efficiency. It has been concluded that pH is the most important parameters governing the efficiency of such process. This study is covering the literatures during the last two decades.

Keywords: toxicity, metals, biomass, biosorption, recovery, removal

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INTRODUCTION

The complexes between metal ions and biosorbents are formed due to several suggested mechanisms such as ion exchange, chemisorption and chelation according to the chemical and physical attraction.

Agriculture waste are potent materials as biosorbents due to their contents of starch, cellulose and lignin which contain variety of functional groups containing nitrogen, oxygen, sulfur and other atoms which differ in their ability to form metal complexes according to the related substituents binding with these atoms (Salah 2016). Different types of biomass were studied as biosorbents such as deactivated protonated yeast (Padma 2006), malpighia emarginata seed (Wallas 2018), sugarcane bagasse (Luisa 2019), ginkgo leaf (Yaoyao 2018), combined fruit waste (Ugya 2019), Brassica Campestris stem (Rabia 2018; Rostami, & Balmaki, 2018).sawdust of Picea abies (Urík 2009), rice bran (Muhammad 2007), date palm leaf (Salah 2014), coconut shell powder (Gabriela 2006), tobacco dust (Qi 2008), spent tea and coffee dusts (Syam 2009), chestnut shell (Yao 2010). Heavy metals biosorption by different types of fruit peels were investigated, such as lemon peels (Amit 2010), Pomelo peels (Wanna 2009), grapefruit peels (Meisam 2013), orange peels (Ningchuan 2011). Ponkan mandarin peels (Flavio 2006).

Fungal species are very important in metal biosorption as eco-friendly methods due to their active components in the cell wall, such as glucans, chitins and chitosans. Mechanism of metals biosorption by both live or dead fungal are categorized as metabolism

independent while metabolism dependent mechanism is happened according to the coupling between metals and extracellular metabolites products by transport the metal ion across the membrane of the cell (Ebrahim 2013).

Radioactive isotopes are the most dangerous environmental materials, so theremoval of such isotopes from the areas that relate to people's lives such as the sources of drinking water, is an interesting fact to the scientists working in the nuclear field and the environmental researchers. Some radionuclides were removed by Taraxacum Officinale (Fuks 2016). Different radioisotopes, like ²³³U, ¹⁴⁴Ce, ⁹⁵Zr and transuranium isotopes such as ²³⁹Pu, ²⁴¹Am, ¹⁴⁷Pm were removed by biomass Rhizopus arrhizus (Dhami 1998), radiostrontium and uranium biosorption by alginate beads (Cem 2013, Cem 2009), Radioactive thorium by sargassum filipendula (Martac 2006).

RESULTS AND DISCUSSION

Uptake of metal ion which is expressed by q_e (mg metal / g biosorbent) is considered as the measure of biosorption performance, it could be expressed as Eq. (1).

$$q_e = (C_o - C_e) \times V/m \quad (1)$$

Where:

C_o = initial concentration of metal ion (mg/L).

C_e = final concentration of metal ion (mg/L)

V = solution volume (Litre).

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Table 1. Metal ions uptake using different biosorbents

Biosorbent	Ion	Metal ions uptake mg/gm	Notes	Ref.
Deactivated protonated yeast	Cd(II)	*20 **37.8 ***86.3	pH=6.5 Biosorbent dosage =1g/L * Metal ion conc.=25mg/L ** Metal ion conc.=50mg/L *** Metal ion conc.=100mg/L	Padma 2006
Malpighia emarginata seed	Cd(II) Cr(III) Cu(II) Ni(II) Pb(II) Zn(II)	0.125 0.115 0.090 0.085 0.092 0.125	pH = 8.0 particle size = (105 – 120 mm), stirring (300 rpm), Contact time=60 min Biosorbent dosage = 0.8 g / 100 mL	Wallas 2018
Sugarcane bagasse	Cd(II) Pb(II)	0.146 0.154	pH=5 Metal ion conc.=10 mg/L glass columns, with dimensions of 1.5 cm, height of 50 cm Flow rate through the column of 1.6 mL/ min. Particle size > 0.594 mm (mean fraction), bed height of 28 cm and 7.15 g of biomass for filling	Luisa 2019
Ginkgo leaf	Th ⁴⁺	103.8	pH=4 Contact time, 120 min; Biosorbent dosage = 2 g/ L. Particle size=150-200 mesh Metal ion conc.=100 mg/ L monozite mineral conc. Of Th= 121.6	Yaoyao 2018

m = mass of the biosorbent (gram)

Metal uptake depends on the initial concentration of metal ion, the higher the metal concentration, the more the metal uptake (2).

As shown in table-1, different biomass were used with different metal ions, especially those of transition metals such as Cu(II)

Ni(II), Cd(II), Zn(II), Cr(III), Co(II), Hg(II), Fe(II), Au(I), Cr(VI), V(V), and actinides such as U(VI), Th(IV), highly toxic metal such as Pb(II), Hg(II), As(III), As(V), lanthanide such as Ce(III), Eu(III) in addition to Se (VI).

Regarding to the living system, Heavy metals are classified into essential and nonessential metals. Those which contribute in the cellular functions are essential metals such as Ni, Cu, Co, Cr, Fe, Zn, which present at very low concentrations level (nanomolar) in the body, but up of that range, they will be toxic. Nonessential metals such as cadmium, lead and mercury are not required to the cell, so any concentrations of this type of metals, will cause real toxicity (Jan 2018, Rathoure 2016).

Many scientists were interested in the recovery of toxic metal such as (Cr(VI), Pb(II), Hg(II), As(III)), The toxicity of arsenic (As) ion is according to the strong binding between this ion and sulfhydryl groups (SH) present in cysteine which is one of the types of amino acids that make up the final structure of protein by disulfide bond. this binding results in disturb the structure of protein and loss their functions (Benjamin 2018).

Mercury ion is considered as a highly toxic to human, it can damage the brain and kidney, also, neurotoxicity is caused by organic compound such as methyl mercury (Ramesh 2007). Cadmium (Cd²⁺) and lead (Pb²⁺) are very dangerous toxic metals which cause mental retardation encephalopathy. (Cd²⁺), (Pb²⁺) in addition to (Hg²⁺) are classified as soft acids which prefer to bind with soft base (according to HSAB theory) such as thiol

group which is the main component of enzyme leading to disturb their functions (Glen 2012).

Chromium is an essential element in the body and has some functions, but if its concentration is high, then it behaves as very toxic. Cr(VI) is the most toxic form of chromium ions because of its reduction ability to pentavalent ion which damage the deoxyribonucleic acid. Toxic chromium is released by various industries to the environment such as tanning, textile, electroplating, and mining. Hexavalent chromium is genotoxic, it can cause cancer and DNA mutations by damaging genetic information. Biosorption technique can be used to remove Cr(VI) by *Escherichia coli*, *Bacillus subtilis*, *Pseudomonas aeruginosa*, hydrolyzed olive cake, waste crab shells and spent tea coffee dusts as seen in **Table 1**.

Toxic actinide such as uranium and plutonium can be separated by chemical process (Salah 2011, Husam 2011). Uranium is highly toxic element, either as radioactive isotopes or its considerable chemical reactivity. Because uranium emits alpha particles, it is considered as carcinogenic. Kidney is the sensitive target for uranium; it accumulates in the renal tubular causing cellular necrosis in the wall. Several forms of cationic uranium are known especially hexavalent and tetravalent ions and both are toxic but hexavalent is more toxic than the other one. Comparing between ingested and inhaled uranium, the inhaled is more danger to the human body than ingested (Salar 2006). As shown in **Table 1**, biosorbents such as *Pistia stratiotes*, *Lemna*, ginkgo leaf, biocomposite adsorbent, *Zoogloea ramigera* and immobilized *Aspergillus fumigatus* beads are considered as the best biomaterials to resolve the contamination of uranium toxicity.

Table 1 (continued). Metal ions uptake using different biosorbents

Biosorbent	Ion	Metal ions uptake mg/gm	Notes	Ref.
1-Waste rind of <i>Citrus lanatus</i> 2- Waste peel of <i>Citrus sinensis</i> 3- Their combination	Cr(III) Pb(II)	*5.35 **4.04	pH=2 *Combine Fruit Peel **Citrus lanatus Biosorbent dosage = 5g/100 ml Pb ion conc. =10mg/l Cr ion conc.=15mg/l Contact time=60 min	Ugya 2019
Brassica Campestris stem	Ni(II) Cr(II) Pb(II)	1.1 95 78	pH=4 contact time=60 min Biosorbent dosage = 1 gm/50 ml Pb ion conc.=120 ppm 250 rpm, and at 60 °C)	Rabia 2018
Sawdust of <i>Picea abies</i>	As(V)	9.259	pH=8 120 c time Biosorbent dosage = 0,5 g/50ml metal ion conc. =90 mg/l, sawdust modified with ferric oxyhydroxides	Urik 2009
Protonated rice bran	Ni(II)	*39.76 **66.80 ***68.70	pH=6 *untreated rice bran **HCl treated =4h ***HCl treated =12 h Metal ion conc. =100 mg/L Contact time= 12 h	Muha-mmard 2009
Iraqi palm tree leaves	Cu(II)	25	pH =5 palm leveas ash burned at 300 C° metal ion conc. = 100 mg/l Mixing time = 1 hr. Shaking rate= 300 rpm Particle size = 300µm	Salah 2014
Green coconut shell powder	Cd(II)	285.7	pH =7 Metal ion conc. =100 mg/l. Biosorbent dosage = 5 g/l. pH value: 7. Contact time: 2 h.	Gabrie-la 2006
Tobacco dust	Pb(II), Cu(II), Cd(II), Zn(II) Ni(II)	39.6 36.0 29.6, 25.1 24.5	pH=6.5–7.2 Biosorbent dosage =1g/L	Qi 2008
Spent Tea Coffee Dusts	Cr(VI)	*44.9 **39.0	pH=4. Biosorbent dosage = 3 g/L Metal ion conc. =30mg/l Cr(VI) reduction by both tea and coffee dusts *By tea **By coffee dust	Syam 2009
Chestnut shell	Cu(II)	12.56	pH=5 Metal ion conc.=50mg/l	Yao 2010
lemon peel	Co(II)	22	pH=6 At 25 °C. Biosorbent dosage = 10.0 g/ L 10 h	Amit 2010
Pomelo Peel	Cd(II)	21.83	pH=5 Biosorbent dosage = 0.1 g/ 100 ml Metal ion conc.=50 mg/l At 24 hr	Wanna 2009
Grapefruit peel	Cd(II) Ni(II)	42.09 46.13	pH=5 Biosorbent dosage = 4 g/L Metal ion conc.=50 mg/L	Meisam 2013
Chemically modified orange peel	Pb(II) Cd(II) Ni(II)	476.1 293.3 162.6	pH= 5.5 Metal ion conc.=50mg/L modified orange peel by grafted copolymerization	Ningch-uan 2011
Ponkan mandarin peel	Ni(II) Co(II) Cu(II)	1.92 1.37 1.31	pH=4.8	Flavio 2006
Waste powdered activated sludge biomass	Cu(II) Ni(II)	18.9 13.5	pH=7.0 for Ni(II) and 3.0 for Cu(II) Contact time of 60 min Cu(II) and 120 min Ni(II).	Sukru 2018
Activated sludge.	Cd(II) Zn(II) Cu(II) Ni(II)	18.08 5.71 3.94 4.06	pH=4 At temperature=20°C, Mixing speed=600 rpm, Solution Biosorbent dosage = 1g/250 mL	Addag-alla 2009
Ficus benghalensis L.	Pb(II)	28.6	pH=6. Contact time=20 min, Adsorbent Size=75 micrometer Metal ion conc.=20mg/L Biosorbent dosage = 0.1 g/30mL	Venkates-wara 2013
Phosphorylated dry baker's yeast	Cd(II) Cu(II) Pb(II), Zn(II)	0.88 1.08 0.91 1.17	pH=12 Contact time=10 min Metal ion conc.=100 ppm Biosorbent dosage = 0.5 mg/mL	Yoshih-iro 2019
		In mmol/g		

Table 1 (continued). Metal ions uptake using different biosorbents

Biosorbent	Ion	Metal ions uptake mg/gm	Notes	Ref.
Pseudomonas species	Cd(II) Cr(VI) Cu(II) Ni(II)	500 111 164 556	pH=5	Hany 2004
Waste brewery yeast	Cd(II)	*12.1 **17.97	pH = 5.6 Metal ion conc.=45 mg/L Biosorbent dosage=0.1 g/100 ml Temp.= 23 °C, Shaking rate =150 rpm. *Untreated biomass **Treated biomass with NaOH	Szende 2015
Alga Spirogyra hyalina	Cd(II) Hg(II), Pb(II), As(III) Co(II)	9.832 39.212 15.471 8.719 7.856	Cd(II) ion conc.=40 mg/L in 90 min. Hg(II) ion conc.=40 mg/L in 120 min. Pb(II) ion conc.=80 mg/L in 120 min. As(III) ion conc.=40 mg/L in 120 min. Co(II) ion conc.=80 mg/L in 120 min.	Nirmal 2012
Biomass of fungus <i>Aspergillus niger</i>	Cu(II) Ni(II)	20.82 20.50	pH=5.0 Biomass pretreated with Na ₂ CO ₃ (0.2N) Shaking=150 rpm Contact time=3 hr.	Amna 2011
Hydrolyzed olive cake	Zn(II) Cr(VI) Cu(II) Pb(II)	5.51 3.38 5.17 13.21	pH=4.5-5 Continuous Biosorption (Fixed-Bed Columns) Metal ion conc.=200mg/L (except for Cr which equal 100mg/L).	Rafael 2019
Bacillus subtilis	Fe(II)	7.25	pH= 4.5. Metal ion conc.=100 mg/l Biosorbent Biosorbent dosage =1 g/l Temp.= 30°C Contact time= 24 hrs, the	Srilaks-hmi 2019
Pistia stratiotes Lemna sp	U(VI)	0.0286 0.681 In mmol/g	pH=4 Contact ime = 60 min Uranium ion conc.= 0.63 mmol/L	Ludmi-la 2019
Zoogloea ramigera	U	49.7	pH= 3.5 Biosorbent dosage =0.15 g/l Equilibrium time=60 min. Temp = 30 °C	Vijayaraghavan 2008
Waste crab shells	Au(I) Se(VI) Cr(VI) V(V)	0.17 0.15 0.54 0.79 In mmol/g	Au=(pH =3.4) Se (pH =3.0) Cr (pH =2.0) V (pH =2.5) Biosorbent dosage 40 mg / 20 ml Au concentration = 2.2 mmol / L Se concentration = 6.2 mmol/L. Cr concentration = 7.7 mmol/L. At 24hr at room temperature	Hui 2003
Penicillium Brevicompactum	Cu(II) Co(II) *Cu(II) **Co(II)	25.32 54.64 17.39 30.96	pH 5.0 At 30 C Contact time of 1 hour Mixing rate=220 rpm Biosorbent dosage=1g/ 100mL * Binary Cu (Co) ** Binary Co (Cu)	Kolish-ka 2007
Brown Seaweed Biomass	Cr(III)	24.1	pH=4 Metal ion conc.=100 mg/L, 24 h of contact time	Yeoung 2001
Crab shell particles	Cu(II) Co(II)	243.9 322.6	pH=6 Biosorbent dosage=5 g/l	Vijayaraghavan 2006
Biocomposite adsorbent	UO ₂ ⁺²	43.2	pH=4 Metal ion conc.=100 mg/L. Contact time =120 min of	Sule 2011
Immobilized Aspergillus fumigatus beads	UO ₂ ⁺²	98.4	pH=5.0 Dose of wet beads, 2.0% (w/v); Contact time= 60 min Temperature,=30 Metal ion conc.=200 mg/L.	Jing 2010
Crab shell particles	Ce(III) Eu(III)	144.9 49.5	pH = 6 Biosorbent dosage = 5 g/L	Vijayaraghavana 2010
Live and dead strain Rhodococcus	Pb(II)	*88.74 **125.5	pH = 5.0, Biosorbent dose= 0.75 g/L. Temp.=30° C for live and 20° C for dead biosorbents Contact time=7.5 min Metal ion conc.=200 mg/L. *For live *for dead	Xin 2020

CONCLUSION

1- Biosorption technique is classified as eco-friendly because it does not need to use environment harmful detergents.

2- It is considered as cheap and easy method.
3- Agricultural and industrial waste can be invested by biosorption technique as the aim of materials decontamination.

4- Increasing the initial metal concentrations is important to get better metal uptake.

5- Pretreated biomass is mostly more efficient than untreated

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