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In vitro Biosorption Metabolic Studies of Heavy Metals by Plant Based Biosorbent Materials

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Abstract

In vitro experiments on chromium, copper, fluoride, lead and zinc heavy metals biosorption using economically cheaper natural biosobents (Banana and Citron peels powder) were studied. Biosorption of heavy metals were confirmed with SEM-EDX analysis. Banana sorpedsamples have shown the accumulation of fluoride 13.29%, sodium 0.12%, calcium 1.98%, iron 0.18% and lead 0.02%, whereas Citron sorped samples have shown magnesium 0.16%, aluminum 0.20%, silica 0.75%, sulphur0.09% and calcium 0.09%. The probable metabolic pathway has been studied using GC-MS analysis and reported in this research article.

Keywords: *biosorption, banana peels, citron peels, heavy metals*

1. Introduction

Water is one of the basic natural resources for human life. It is an important resource in developing the economy and society in terms of agriculture, industry and many other sectors (Tabrez and Ahmed, 2009). Human body is 60% water and earth is 71% water, these two statistics are enough to illustrate the magnanimity of water.

Water as natural resource is absolutely essential to the human life and a precious resource for human civilization. The main source of water is from rain, lakes, streams, glacier, oceans and underground. The underground water is important because it is the most uniformly distributed and derived from sedimentary, igneous and metamorphic rocks of environment. The basic requirement for the availability of water is rock in the availability of porosity and permeability. The ground water makes up about 97% of the world's accessible fresh water reserve (Pacyna *et al*., 2001; Xu *et al*., 2008; Mas Rosemal*et al.*, 2010;Colonel *et al*., 2016). Urban areas are always associated with thick population and always depend on the groundwater for their day-to-day activities. Groundwater pollution and its consumption directly or indirectly act on the health problem of the population which depend on it (Mrinalini *et al*., 2015). It could cause eye irritation, nausea, vomiting, diarrhea, headache, respiratory diseases. Overconsumption and prolong consumption of pollutant groundwater will lead to kidney damage, liver damage, nervous system problems, bone problems, cancer and reproductive defects (Boulding, 1995; Wan Ngah*et al.*, 2002; Gode and Pehlivan, 2006). The aim of this research work is to use plant based biosorbent material to remediate groundwater contamination and the probable metabolic studies.

2. Materials and Methods

2.1 Sample collection

The ground water samples were collected from SemmankuppamCuddalore district. *Musa paradisiaca*L. Musaceae fresh banana peels (rasathali variety) were collected from various house and fruit juice centers from the surrounding areas. In a similar manner,*Citrus medica*L. Rutaceae(Citron peels) were also collected.

2.2 Preparation of adsorbents

Banana peels were washed thoroughly, allowed to dry in shade for 7-8 days until all the moisture content was lost from it and the colour change was observed from yellow to brownish black. Citron peels (Citron) were washed repeatedly with distilled water to remove dust and soluble impurities then dried under shade for 15-20days.Once, all these collected samples were completely shade dried, they were subjected to powdered using domestic mixer or electric mixer and then they were sieved to obtain uniform particle size. The samples were stored very carefully in air tight Ziploc bags to prevent it from moisture and contamination.

The biosorption metals from the ground water was conducted using banana and citron peels in the form of powder samples in *in vitro* condition for 60 minutes of contact time. The Scanning Electron microscopy equipped with Energy Dispersive X-ray (SEM-EDX) analysis consisting 3.5 nm and 2.5 nm resolution for tungsten filament (La B6) and EDX detector resolution 130 eV (TESCON, Czechoslovakia) (Jamari *et al*., 2014) was performed to determine the biosorption of heavy metals.

GC-MS was performed using Bruker-Scion SQ, Agilent J & W. Gas chromatography with DB WAX column, 30 m length, 0.25 mm diameter and 0.25 μm film was conducted in the temperature programming mode with a 20–250°C, Rate: 28/min, holding time: 10 min @ 250. The initial column temperature was held at 20 °C for 8 min, then increased linearly to 250 °C, 10°C and held for 4 min at 250 °C. The temperature of the injection port was 250 °C and the GC-MS interface was maintained at 250 °C. Helium gas was used as carrier gas with a flow rate of 1.0 ml/min. The injection was split less to increase sensitivity. Identification of remediation products was made by comparing the retention time and fragmentation pattern with reference compounds as well as with mass spectra in the National Institute for Standards and Technology (NIST) library search results stored in the computer software (Version 1.10 beta, Shimadzu) of the GC-MS (Gopi *et al*., 2012).

3. Results and Discussion

3.1 SEM-EDX elemental analysis

Studies on *in vitro*biosorption metabolic studies of heavy metals by biosorbent materials like banana and citron peel powder was conducted for 60 minutes contact time and the SEM-EDX analysis of metal sorption was given in Fig. 1 and 2 and Tables-1 and 2. Banana peel before biosorption have shown the presence of magnesium, aluminium, silica, phosphorus, sulphur, chlorine and potassium, whereas after biosorption banana peel powder absorbed as much as 13.29% of Fluoride, 0.12% of sodium, 1.98% of calcium, 0.18% of iron and 0.02% of lead. The citron peel powder before biosorption showed sodium, phosphorus, chlorine, potassium and calcium, whereas the biosorbed citron peel have shown magnesium 0.16%, aluminium0.20%, silica 0.74%, sulphur0.09% and copper 0.09%. The biosorption studies of Qin Lu *et al.* (2011), Saman Khan *et al.* (2013), Rupa Chakraborty *et al*. (2014), AdamnYunusUgya*et al*. (2015), Sudha *et al.* (2015), and Abubacker and Sathya (2017a, 2017b) indicated the biosorption of metals like Ag, Cd, Cr, Cu, Hg, Ni, Pb, Co, F and Zn from contaminated water bodies using plant based biosorbent material, the present study is yet another example of biosorption of metals using different biosorbent materials from ground water polluted source.

3.2 GC-MS metabolic pathway analysis

The GC-MS metabolic pathway has revealed sequence of biochemicals which are listed in Fig. 3 and 4 and Tables-3 and 4. According to the Tables, the peak one have shown 5-methyl-alpha-L-Galactopyranose and 6-hydroxy-4-methyl-dimethyl acetal, acetate for before biosorption of banana peel powder. The biosorbed material revealed the formation of phenol, pentanoic acid, 5-hydroxy-2,4-di-t-butylphenyl esters. About 12 peaks were obtained by the GC-MS studies, the last peak have shown the formation of methyl tetradecanote and heptadecanoic acid for before biosorbed banana peel powder, the biosorbed material revealed the formation of cyclopentaneundecenoic acidand 11-bromoundecanoic acid in their metabolic pathway. The citron peel powder before biosorption according to peak one 5-trimethy cis-linaloloxide, lilac alcohol, and Trans-linalool oxide, after biosorption the metabolic product have shown 2,6-dimethyl octane, oxalic acid and hydroxylamine. The peak 12 have revealed the presence of 2-ethyl-2-propyl benzene, 15-hexadecenoic acid for before biosorption and after biosorption phthalic acid and octadecyl-2-propyl pentyl ester as the metabolic product.

Brunori*et al*. (2005) and Santona*et al*. (2006) have found that metal trapping ability of biosorbantmaterial is due to negative change density it result in the equilibrium of pH in the ground water which led to the biosorption of metals. Aadil Abbas *et al*. (2010) used different agricultural byproducts like cereal crops as biosorbent material and the metabolic pathway have been worked and for the removal of chromium. Balaji *et al*. (2014) also used agricultural waste as natural adsorbents and removed iron from drinking ground water. Jamil Anwar *et al*. (2010) used banana peels and removed lead and cadmium from water by adsorption method. Copper ions were removed by *Tectonagrandis* leaf by King *et al.*(2006), *Carica papaya* seed as low-cost sorbent for zinc removal by Siew-Teng Ong *et al*. (2012), many such biosorbent materials have been used in treating ground water pollution, the present study of using banana and citron peels and its biosorption metabolic studies is yet another contribution for this studies.

Higher levels of heavy metals disturb the normal physiology and biochemistry of living systems (Akpor*et al*., 2014). The most hazardous heavy

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metals are Cr, Cu, Zn, Pb, Hg, As, Cd and Sn (Gosh, 2010; Abubacker and Sathya, 2017c, 2017d). The concentrations of heavy metals increase in the environment from year to year. Therefore, decontamination of heavy metal from contaminated water and soils is very important for maintenance of environmental health and ecological restoration (Govindasamy*et al*., 2011).

Table-1: SEM-EDX analysis of metal biosorption observed in bananapeel powder

Elements	**Before sorption (%)**	**After sorption (%)**
C	54.23	53.45
O	28.08	28.63
F	-	13.29
Na	-	0.12
Mg	0.16	0.2
Al	0.12	0.15
Si	1.3	0.97
P	0.16	0.16
S	0.12	0.27
Cl	6.39	0.07
K	9.45	0.5
Ca	-	1.98
Fe	-	0.18
Pb	-	0.02

Table-2: SEM-EDX analysis of metal biosorption observed in citron peel powder

Elements	Before sorption (%)	After sorption (%)
C	51.42	48.11
O	46.47	47.43
Na	0.14	0.22
Mg	-	0.16
Al	-	0.2
Si	-	0.74
P	0.15	0.17
S	-	0.09
Cl	0.36	0.08
K	0.99	1.74
Ca	0.47	0.97
Cu	-	0.09

Different physical and chemical methods are used for this purpose with each method having its merits and demerits and generally considered expensive and causing secondary problems (Wu *et al*., 2010). In comparison, plant based biosorbent material is a novel, less-expensive, efficient, environmental and eco-friendly remediation strategy with good public acceptance (Revathi *et al*., 2011). The GC-MS metabolic studies conducted in this study have shown the formation of different compounds during biosorption by metal-chelating proteins related to metallothioneins as stated by Robinson *et al*. (1993) or by phytochelatins (Reeves, 2003; Gaikward Rupali and Khan Shahana, 2014) or by acidifying process as stated by Crowley *et al*. (1991) Alkorta and Garbisn (2001). From these reports, it is to ascertain that these process might have occurred and resulted in the biosorption of metals by banana and citron peel powder.

Table-3: GC-MS metabolic studies of biochemicals predicted in *M. paradisiaca*L. (banana)peel powder before and after biosorption

Peak	**Before Sorption**	**After Sorption**
1	Cytidine	Phenol
	5-Methyl alpha-L-Galactopyranose	Pentanoic acid
	6-Hydroxy-4-methyl-dimethyl acetal, acetate	5-hydroxy-2,4-di-t-butylphenyl esters
2	Azulene	Dodecane, 2-methyl
	Naphtalene	1-Iodo-2-methylundecaneoctane
	1,2-dihydro-acetate-acetic acid	2,6,8-trimethyl sulfurous acid
3	Pentadecane	Hydroxylamine
	2,4,6-Trimethyl heptadecane	2,3-Dimethyldecaneunecane
4	Tridecane, 6-methyl-dodecane	Pyrrolidine, 1-(1,6-dioxooctadecyl)- Nonadecane
	Pentadecane	1,1-bis (dodecyloxy)-cyclooetane
5	3-Furanacetic acid, Isopropyl ester Benzenamine	Hydroxylamine
	3-methyl-4-propyl-2,3-dimethylfumaric acid	2,3-dimethyldecane undecane
6	2-methyl-2-bromododecane Heptadecane	Pyrrolidine
	2,6-dimethyl-sulfurous acid	1,1-bis(dodecyloxy)-cyclooctane
7	Methyl ester Hexadecanoic acid	n-Hexadecanoic acid
	Methyl Actradecnoate	2-(2-hydroxyethoxy) ethyl ester
8	1-(+)-Ascorbic acid 2,6-dihexadecanoate	Octadecanoic acid,Eicosanoic acid
	Nonedocanoic acid	L-ascorbic acid
9	Methyl ester 6-octadecenoic acid	9,15-octadecadieonic acid
	Methyl ester 7-hexadeceonic acid	2,4-octadecen-1-ol-acetate
10	9,12-Octdecadienoic acid	Pentadecanoic acid
	9,12-Hexadedienoic acid	Hexadecanoic acid
11	17-Octadecyonic acid	11-Octadecenoic acid
	Oleic acid	Cis-13-Octadecenoic acid
12	Methyl tetradecanote	Cyclopentaneurdecanoic acid
	Heptadecanoic acid	11-Bromoundecanoic acid

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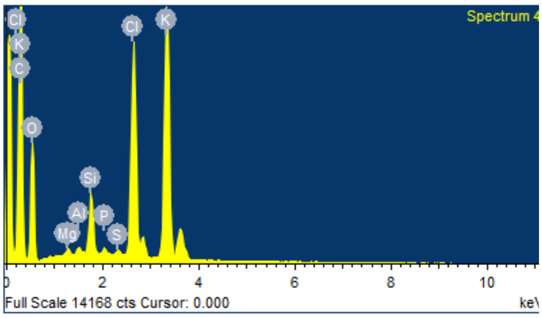

Fig.1a: Musa paradisiacaL. Musaceae (banana) before metal biosorption (Control)

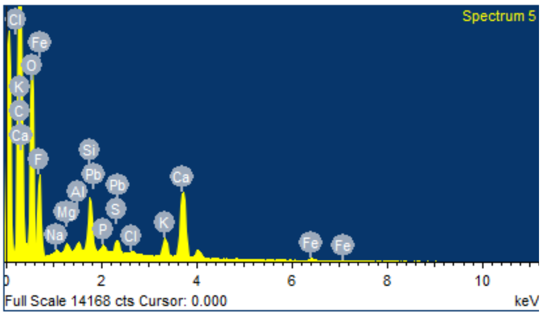

Fig.1b: Musa paradisiacaL. Musaceae (banana) after metal biosorption

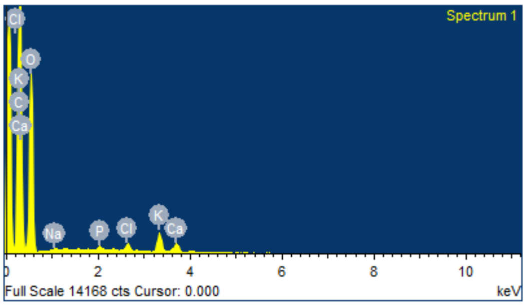

Fig.2a: Citrus medicaL. Rutaceae (citron) before metal biosorption (Control)

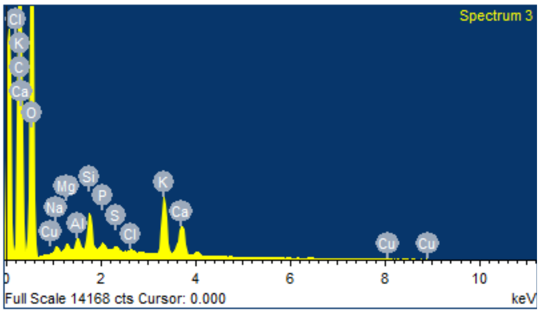

Fig.2b: Citrus medicaL. Rutaceae (citron) after metal biosorption

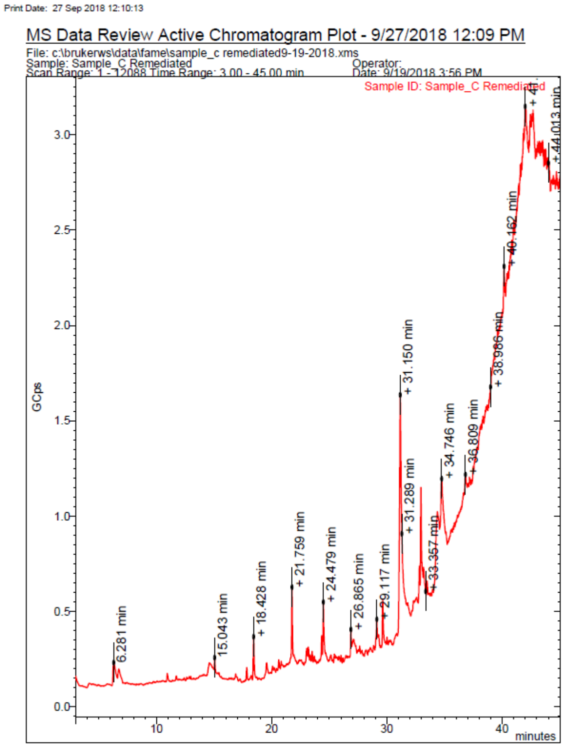

Fig. 3a: Musa paradisiacaL. Musaceae (banana) before metal biosorbiton (control)

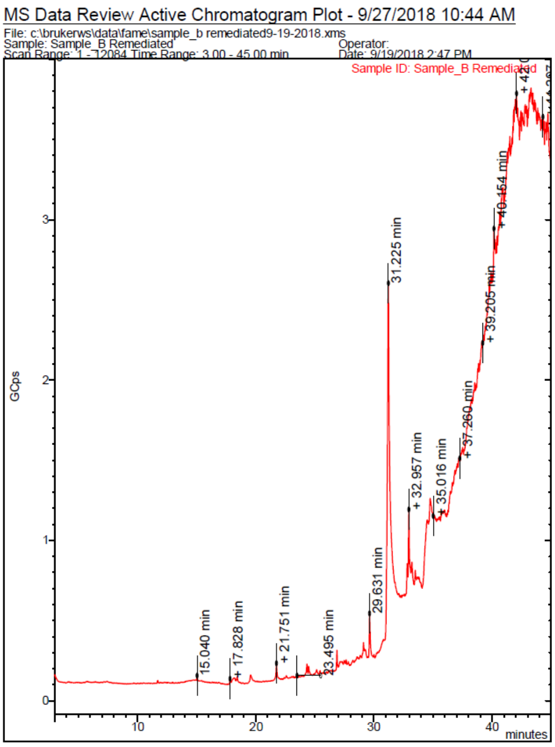

Fig. 3b: Musa paradisiacaL. Musaceae (banana) after metal biosorbiton

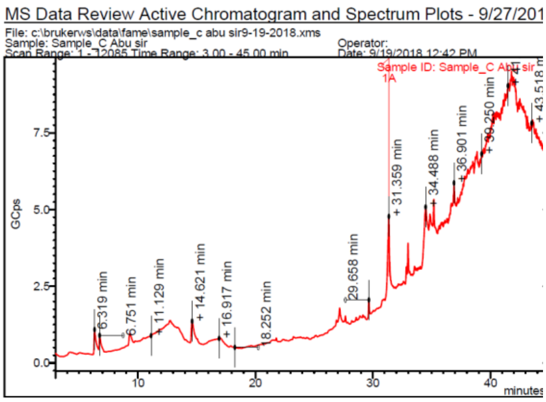

Fig. 4a: Citrus medica L. Rutaceae (citron) before metal biosorbiton (control)

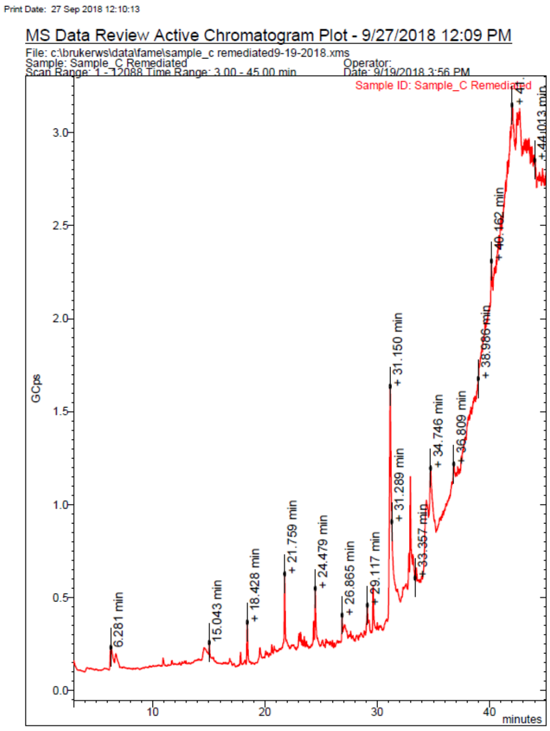

Fig. 4b: Citrus medica L. Rutaceae (citron) after metal biosorbiton

4. Conclusion

Ground water is the largest and most important source of potable water for human consumption. It is also available everywhere can be drawn and made useful to day to day human activities. However, the ground water gets contaminated by the development of industries and their discharge, percolate and reach the ground water. The use of biosorbent material of plant origin is a solution to remediate ground water contamination and it an ecofriendly approach. It is also necessary to know the metabolic status of biosorption for the safer use of ground water.

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