BIOSORPTION AND RECOVERY OF Cu(II), Cr(VI), Pb(II) AND Zn(II) IONS FROM INDUSTRIAL EFFLUENTS BY USING LEMON PEELS

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Abstract: The discharge of heavy metals from industrial effluents has been a major concern in the present era. Heavy metals not only cause pollution to the air, water and soil but also cause various health hazards. Various methods are available for the removal of heavy metals from industrial effluents but all these methods are costly and involve tedious techniques. The present work reports a cost effective, rapid and easy method to remove metal ions *viz.* Cu(II), Cr(VI), Pb(II) and Zn(II) from industrial effluents using powder lemon peels through biosorption process. The factors *viz.* pH, temperature, biosorbent dosage and contact time affecting biosorption process were investigated. Lemon peels were found to be efficient to remove Cu(II), Cr(VI), Pb(II) and Zn(II) ions from effluents of electroplating, textile, powder coating and chemical industries. The surface morphology of lemon peels showed distinct changes after biosorption process which was observed under Scanning Electron Microscope (SEM). Further, the desorption of adsorbed metal ions from powder lemon peels were studied by using various eluents *viz.* HNO_3, NaOH, EDTA and deionized water. EDTA was found to be best desorbing agent as compared to other eluents for the recovery of metal ions. The use of lemon peels (waste) as biosorbent can help in environmental sustainability as it combines two goals *i.e.* the removal of heavy metals from wastewaters and the reuse of waste materials thus resulting in green technology.

Keywords: Lemon peels, Biosorption, metal ions, desorbing agent, SEM analysis.

I. INTRODUCTION

In the 21st Century, industrialization, urbanization and associated environmental alterations pose a threat to environment as well as living organisms. Environmental pollution particularly from heavy metals and minerals in the industrial effluents is the most serious problem in India. Metals are ubiquitous in nature and with increasing industrialization, the potential of metallic poisoning is increasing day by day. During the last two centuries, heavy metals released by human activities have superimposed new pattern of metal distribution as compared to those which are naturally occurring (Hariprasad and Dayananda, 2013). Various point sources of heavy metal pollutants are industrial effluents from mining, tanneries, pharmaceuticals, pesticides, organic chemicals, metal processing, rubber and plastics, etc. (Srivastava et al, 2006). Majority of industries have treatment facilities for industrial effluents (Singhare and Dhabarde, 2014) but the problem of pollution is not completely resolved. The heavy metals are transported by surface runoff and contaminate water sources downstream from the industrial site.

Most of the heavy metals discharged into the wastewater are toxic, carcinogenic and cause a serious threat to the human health (Srivastava et al, 2006). Acute effects of heavy metals exposure include damage to central nervous function, the cardiovascular and gastrointestinal (GI) systems, lungs, kidneys, liver, endocrine glands, and bones while chronic effects include several degenerative diseases and may increase the risk of cancer. To avoid health hazards, it is essential to remove toxic heavy metals from effluents before its disposal (Lakherwal, 2014).

Different methods have been developed for heavy metals removal such as chemical precipitation, ion exchange, reverse osmosis, electrodialysis, ultrafiltration, nanofiltration, coagulation, flocculation, floatation, etc. However, chemical processes produce a large amount of metallic sludge which needs further disposal, making metal recovery difficult. Such processes are costly and require high level of expertise. In contrast to above processes, adsorption technology has gained a wider application due to its inherent low cost, simplicity, versatility and robustness. Earlier studies in environmental biotechnology have shown that many organic materials occurring in the environment have the capacity to remove heavy metals from solutions by biosorption process (Monisha et al, 2014).

Biosorption may be simply defined as the removal of substances from solution by using biological material. Such substances can be organic or inorganic and soluble or insoluble forms (Geoffrey, 2009). Biosorption can be attributed to number of metabolism independent processes such as complexation, chelation, coordination, ion-exchange, etc. that takes place in the cell wall (Sharma et al, 2016). Agricultural residues are usually composed of lignin and cellulose as the major constituents along with other polar functional groups such as alcohols, aldehydes, ketones, carboxylic acids and ethers that facilitate metal complexation resulting in biosorption of metal ions from wastewater (Hashem et al, 2005; Hashem et al, 2007).

Many active principles of plants and animals can chelate with metal ions. Citrus peels contain pectin, limonene, flavonoids, phenolic compounds, etc. which makes them useful in nutraceuticals and medical fields (Rafiq et al, 2018). These components can also play an important role to chelate with metal ions (Sharma et al, 2016). The present work focuses on application of lemon peels for the detoxification of industrial effluents by using biosorption process. The factors *viz.* pH, temperature, biosorbent dosage and contact time influencing biosorption process were studied. The change in morphology of lemon peels after biosorption process was studied by using SEM. Further, the recovery of metal ions from lemon peels was studied by desorption process using certain eluents.

II. RESEARCH METHODOLOGY

2.1 Preparation of biosorbent

Lemon peels were collected from local fruit juice center. The peels were washed thoroughly with distilled water to remove the adhering dust particles, sun-dried followed by oven drying at 80°C for 24 hrs. The dried peels were ground into fine powder and stored in polythene bags till further use as biosorbent.

2.2 Preparation of solutions of metal ions

Stock solutions (1000 mg/L) of metal ions *viz.* Cu(II), Cr(VI), Pb(II) and Zn(II) were prepared by dissolving analytical grade of respective metal salts like $CuSO_4.5H_2O$, $K_2Cr_2O_7$, $Pb(NO_3)_2$ and ZnO in deionized water. The standard solutions were prepared by diluting respective stock solutions to appropriate volumes.

2.3 Biosorption of metal ions using powder lemon peels

The biosorption process was studied by using batch experiment. 100 mL of 50 mg/L solutions of metal ions containing 1 g of biosorbent in 250 mL conical flasks were agitated at 150 rpm in an orbital shaker at 30 ^oC. After an hour, the solutions were filtered using Whatmann filter paper no. 1. The aqueous solution of lemon peel powder was used as blank. The concentrations of the metal ions in the filtrate were determined by using ICP-AES.

2.4 Calculation of percent biosorption

The percent biosorption of metal ions was calculated as follows:

$$\text{Biosorption (\%)} = \frac{(Co - Ce)}{Co} * 100$$

where Co is the initial metal ion concentration (mg/L), Ce is the final metal ion concentration after biosorption process (mg/L) and v is the volume of solution (L) (Kariuki et al, 2017).

2.5 Factors affecting biosorption process

The effect of various factors *viz.* pH, temperature, biosorbent dosage and contact time on biosorption process by using lemon peels was studied by using batch experiment.

2.5.1 Effect of pH

To study the effect of pH on biosorption process, 1 g of biosorbent was added to 100 mL of aqueous solutions containing 50 mg/L Cr(VI), Cu(II), Pb(II) and Zn(II) ions in 250 mL conical flasks and the biosorption process was studied at different pH *viz.* 2, 4, 6, 8 and 10 for 60 mins at 30 ^{o}C. The pH of the solution was adjusted using 1N NaOH and 1N HCl.

2.5.2 Effect of temperature

The biosorption process of Cr(VI), Cu(II), Pb(II) and Zn(II) ions by lemon peels was studied by adding 1 g of biosorbent into aqueous solutions containing 50 mg/L of four metal ions under study having pH 8 and incubating the solutions at different temperatures *viz.* 10, 30 and 50 ^{o}C for 60 mins.

2.5.3 Effect of biosorbent dose

The effect of biosorbent dose was studied by adding different doses *viz.* 0.5, 1, 2 and 3 % of lemon peels to 250 mL conical flasks containing 100 mL solutions of 50 mg/L Cr(VI), Cu(II), Pb(II) and Zn(II) ions having pH 8 and the biosorption process was carried out for 60 mins at 30 ^{o}C.

2.5.4 Effect of contact time

The effect of contact time on biosorption process was studied by adding 1 g of biosorbent to 100 mL of aqueous solution containing 50 mg/L of Cr(VI), Cu(II), Pb(II) and Zn(II) ions at pH 8 and the biosorption process was carried out for different time period *viz.* 60, 120 and 180 minutes at 30 ^{o}C.

2.6 Collection and treatment of industrial effluents with lemon peels

The effluent samples were collected from different industries *viz.* electroplating and powder coating industries situated at Taloja MIDC area in Navi Mumbai (M. S.), paper and pulp, textile and chemical industries from Dombivali MIDC area in Thane (M. S.). The effluent samples were collected in polythene bottles from outlet of these industries by using standard procedures and stored at 4 ^{o}C till further use.

2.7 Treatment of effluent samples by biosorption process to remove heavy metals

The pH of the effluents was adjusted to 8 by using 0.1 N HCl or NaOH and biosorption process was carried out for 120 min at 30 ^{o}C using 1% biosorbent. After the biosorption process, the effluent samples were filtered by using Whatmann filter paper no 1. The concentrations of heavy metals in the filtrates were estimated by using ICP-AES (ARCOS, Simultaneous ICP Spectrometer, IIT-Bombay). The procedure was repeated till the concentration of heavy metals under study were reduced within standard values.

2.8 Regeneration studies

The metal ions loaded lemon peels were air dried to completely remove moisture from them. 2 g of air dried biosorbent loaded with metals ions *viz.* Cu(II), Cr(VI), Pb(II) and Zn(II) were transferred to conical flasks containing 100 mL of desorbing agent (eluant) *viz.* 0.1 M HNO_3, 0.1 M EDTA, 0.1 M NaOH and deionized water separately. The solutions were agitated at 100 rpm in a rotary shaking incubator (Remi Orbital Shaking Incubator, CIS 24 BL) at 30 ^oC for 2 hrs followed by filtration by using Whatmann filter paper no. 1. The concentrations of metal ions released in the desorbing agents were determined by using ICP-AES.

III. RESULTS AND DISCUSSION

Lemon peels were found to be efficient as biosorbent for the removal of Cu(II), Cr(VI), Pb(II) and Zn(II) ions from the spiked solutions of metal ions. The bar graph showing percent biosorption is presented in Figure 1. It was observed that the biosorption process was influenced by change in pH, temperature, biosorbent dosage and contact time. As the pH of the aqueous solutions increased from 2 to 8, the biosorption process by lemon peels was found to increase but further increase in pH to 10 led to decrease in the biosorption process of all four metal ions *viz.* Cu(II), Cr(VI), Pb(II) and Zn(II). This may be due to the precipitation of metal ions at higher pH (Figure 2). Patel and Chandel (2015) obtained similar result by using *Bacillus licheniformis* in which of maximum biosorption of Cu(II) and Fe(III) ions was achieved at pH 8.

The biosorption process was found to increase with the rise in temperature from 10 to 30 ^oC but further increase in temperature to 50 ^oC showed marginal changes in biosorption process (Figure 3). Sanusi et al, (2018) reported that the biosorption process of Cd(II) and Ni(II) ions by using *Glycine max* pod decreased with increase in temperature from 35 to 50 ^oC. The dose of biosorbent (0.5 to 3 %) was found to be a factor influencing biosorption process. It was observed that as the dose of the biosorbent was increased from 0.5 to 1 %, the biosorption process increased (Figure 4). This may be due to the fact that increasing dose of biosorbent increases the number of active sites on biosorbent to bind to metal ions but further increase of biosorbent might lead to their crowding and making them unavailable to bind to metal ions (shell effect). The decrease in biosorption with increase in biosorbent dosage to 3 % might have been due to shell effect. The biosorption process by lemon peels for metal ions *viz.* Cu(II), Cr(VI), Pb(II) and Zn(II) was found to increase with rise in contact time from 60 to 180 minutes (Figure 5). This may be because of the increase in time duration for the metal ions to bind to the active sites on the biosorbent. The biosorption process was found to increase with increase in contact time in the experiment carried by Kumar et al, (2012).

The concentrations of metal ions *viz.* Cu(II), Cr(VI), Pb(II) and Zn(II) in the effluents of textile, powder coating, electroplating and chemical industries (T0) and after treatment with biosorbent (T1) are presented in bar graphs in figures 6 to 9. The lemon peels were found to be efficient in the removal of metal ions under study and showed more than 90% removal of metal ions in some cases. But the concentration of Pb(II) ions from effluents of textile and powder coating industries was above the standard value. Hence, the biosorption process was repeated (T2) to reduce Pb(II) concentration below the standard value. The biosorption process was repeated thrice (T3) for effluents of electroplating and chemical industries to reduce the concentrations of metal ions under study within standard values (SV) for the discharge of environmental pollutants through effluents to the inland surface water (Schedule-VI, MOEF, GSR 422E, 1993) (Maiti, 2004).

Recovery of metal ions is very important step for the treatment of heavy metals. Figure 10 represents desorption of metal ions from eluents viz. 0.1 M HNO3, 0.1 M NaOH, 0.1 M EDTA and deionized water. The desorption of metal ions from lemon peels was negligible by using deionized water. Hence, deionized water was considered as noneffective desorbing agent (eluant). The chelating agent (EDTA) showed maximum desorption of metal ions *viz.* Cu(II), Cr(VI), Pb(II) and Zn(II) from lemon peels. Further, 0.1 M NaOH was found to desorb all four metal ions from lemon peels more effectively as compared to 0.1 M HNO_3. Desorption process studied by Deng et al, (2007) observed that EDTA was effective as a desorbent for the recovery of Pb(II) ions from green algae *Cladophora fascicularis*.

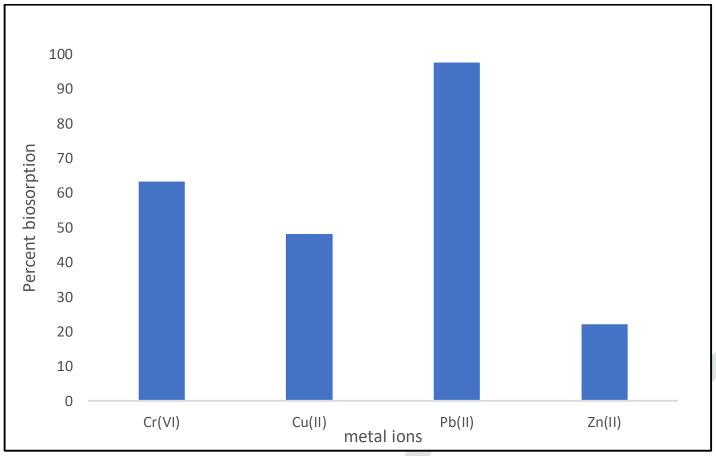

Figure 1 Biosorption of metal ions Cu(II), Cr(VI), Pb(II) and Zn(II) by using Lemon peels

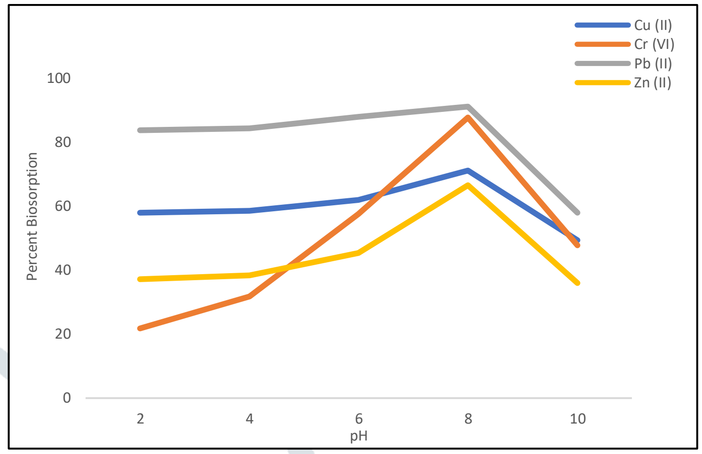

Figure 2 Effect of pH on biosorption process of metal ions by using Lemon peels

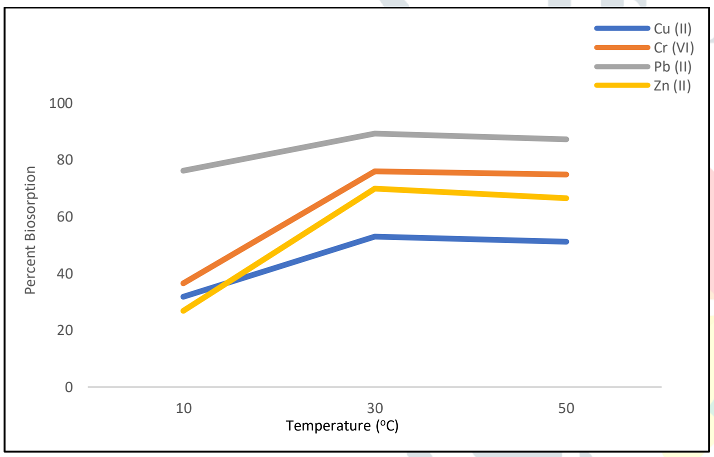

Figure 3 Effect of temperature on biosorption process of metal ions by using Lemon peels

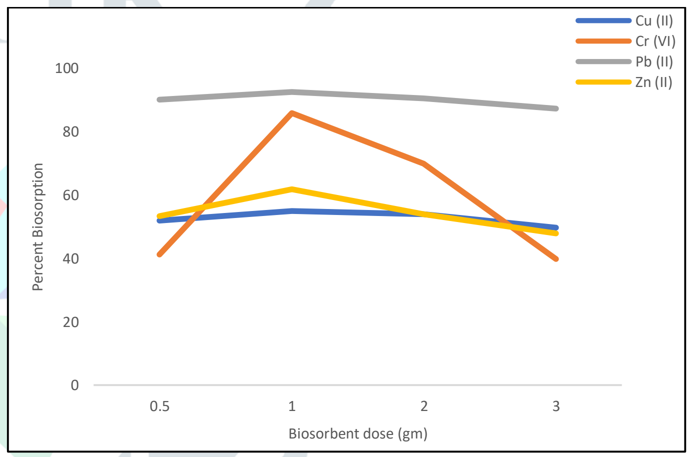

Figure 4 Effect of biosorbent dose on biosorption process of metal ions by using Lemon peels

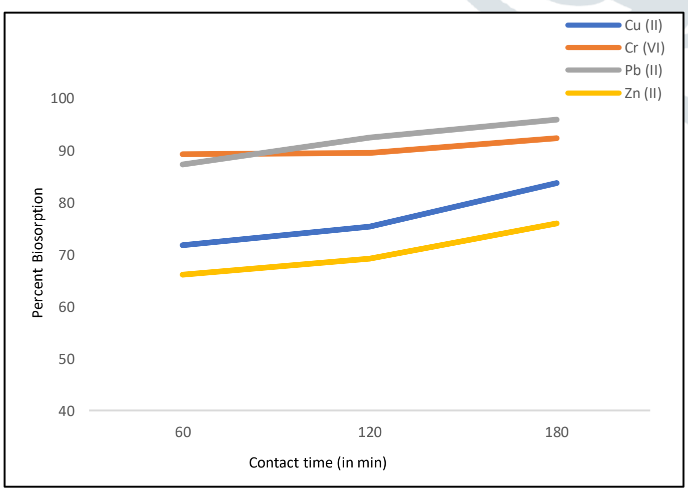

Figure 5 Effect of contact time on biosorption process of metal ions by using Lemon peels

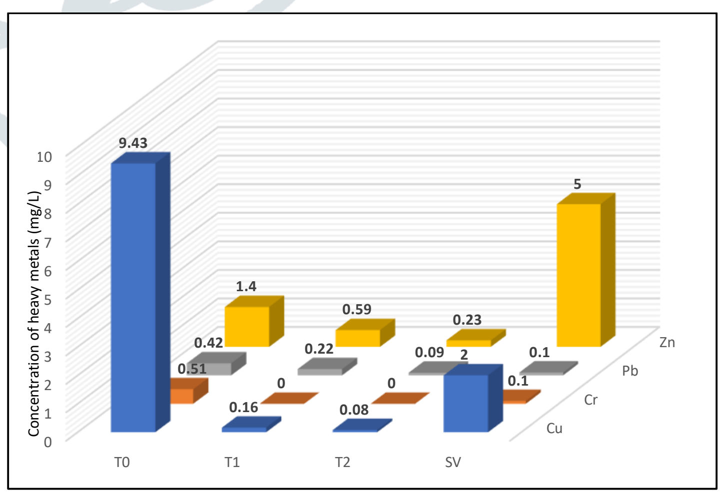

Figure 6 Biosorption of metal ions Cu(II), Cr(VI), Pb(II) and Zn(II) from effluent of textile industry

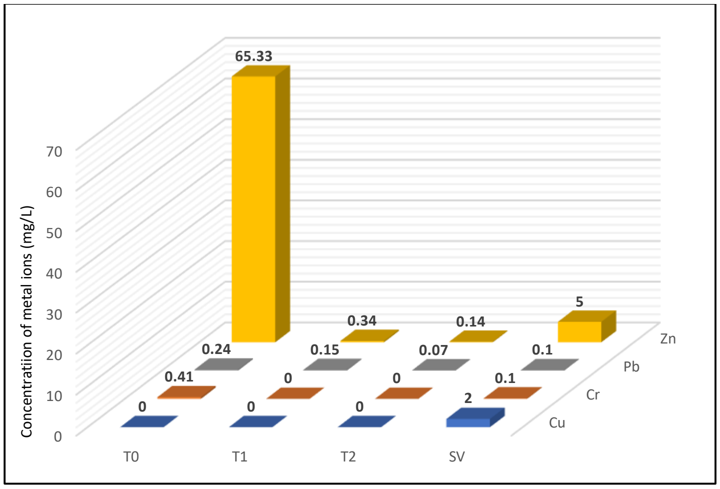

Figure 7 Biosorption of metal ions Cr(VI), Pb(II) and Zn(II) from effluent of powder coating industry

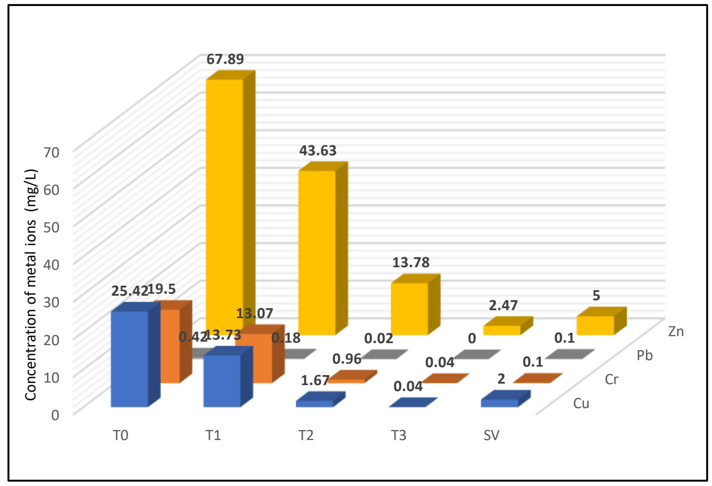

Figure 8 Biosorption of metal ions Cu(II). Cr(VI), Pb(II) and Zn(II) from effluent of electroplating industry.

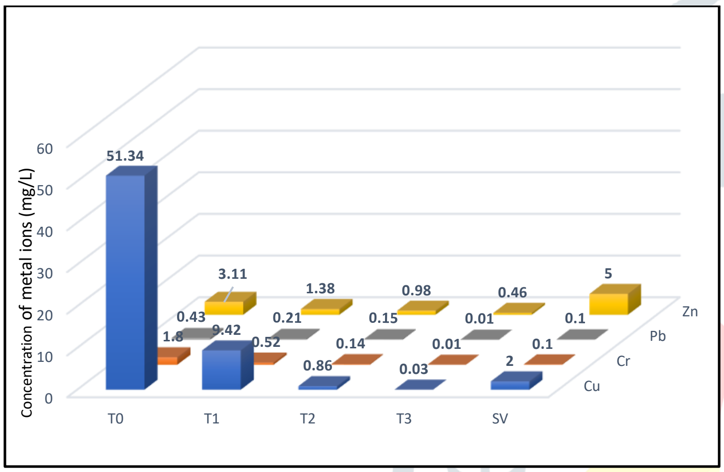

Figure 9 Biosorption of metal ions Cu(II). Cr(VI), Pb(II) and Zn(II) from effluent of chemical industry

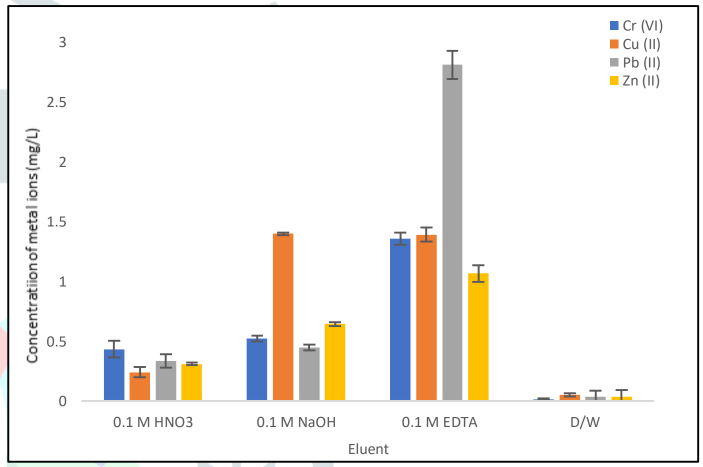

Figure 10 Desorption of metal ions Cu(II). Cr(VI), Pb(II) and Zn(II) from lemon peels by using eluents

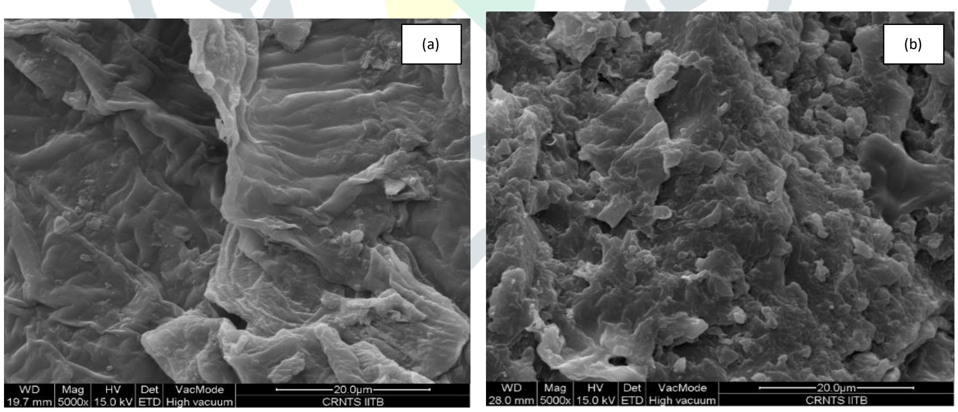

Figure 11 SEM images of lemon peels (a) before and (b)after biosorption process

IV. CONCLUSION

The problem of growing ecosystem degradation due to rapid industrialization is a matter of concern which needs to be minimized in a sustainable manner. Green technology is one such approach to minimize the problem of pollution caused due to treatment process in an ecofriendly manner. The present work shows that lemon peels are capable of adsorbing metal ions viz. Cu(II), Cr(VI), Pb(II) and Zn(II) from various industrial effluents in a cost effective manner. Hence, heavy metals biosorption and possibility of recovery of metal ions from industrial effluents can be considered a promising technique in the treatment of industrial effluents.

V. ACKNOWLEDGEMENT

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