1. INTRODUCTION

Wastewater from industries contain large amount of various organic and inorganic pollutants. Out of these pollutants, heavy metals are the cause of concern as they do not get degraded or destroyed naturally and are toxic in nature. These metals keep on cycling between abiotic and biotic components of the environment. Discharge of untreated effluent containing heavy metals pollutes the surface and ground water bodies. Intake of water from these polluted water bodies leads to serious health problems in human beings.

Copper (Cu), lead (Pb), and zinc (Zn) are among the most widespread contaminants discharged into the water bodies through industrial effluent. Lead is one of the most toxic heavy metals. It has wide applications in various industries like printing, pigments, photographic materials, battery, fuels, explosives manufacturing etc. (Paulino et al., 2007; Saifuddin and Raziah, 2007; Wan et al., 2010; Younis et al., 2015) and hence, discharged in huge amount to the water bodies through untreated effluent of these industries. Further, lead contamination of drinking water also occurs as a result of corrosion and leaching from lead pipes. The excessive intake of the same leads to lead poisoning in human beings which causes severe damage to the kidney, nervous system, reproductive system, liver and brain, and can lead to sickness or death. Severe exposure to lead is also associated with sterility, abortion, stillbirth and neonatal death (Goel et al., 2005).

Although, Cu(II) is one of the micronutrients involved in regulation of various body functions desired for growth of all living organisms, however, excessive intake of same leads to various health problems like nausea, headache, dizziness, hemolytic anemia, massive gastrointestinal bleeding, liver and kidney failure, and even death (Ahamed and Begum, 2012). The potential industrial sources of its discharge in effluent includes mining, metal cleaning, plating baths, pulp, paper and paper board mills, refineries, fertilizer manufacturing industries, etc. (Amarasinghe and Williams, 2007; Gündoğan et al., 2004).

Zinc when ingested in excess causes depression, increased thirst, lethargy, and neurologic signs such as seizures and ataxia (Kurniawan et al., 2006). The industrial sources of zinc discharge are chemical manufacturing, pulp and paper,
steel works with galvanizing lines, plating, viscose rayon yarn and fiber production, etc. (Mohan and Singh, 2002).

Among various polluting industries, electroplating industries are potential sources of discharge of heavy metals like Cr, Cu, Ni, Zn, Pb and Cd etc. in their wastewater streams. As per Comprehensive Industry Document on Electroplating Industries by Central Pollution Control Board (2007), these industries are spread across the entire country with significant numbers in the state of Punjab, Haryana, parts of U.P., Maharashtra, Karnataka, Andhra Pradesh, Tamil Nadu and West Bengal. Most of these electroplating industries are small scale units and release their heavy metals containing effluent without any treatment. The reasons cited for the release of untreated effluent include high capital cost for installation of effluent treatment plant, high operation and maintenance cost, requirement of skilled manpower and problem of sludge disposal. However, to meet the standards prescribed for discharge of trade effluent under The Water (Prevention & Control of Pollution) Act, 1974, adequate treatment of industrial effluent is mandatory before discharging it into water bodies. So, the need of the hour is a treatment method which has low capital requirements for initial set up, operation and maintenance.

1.1 METHODS FOR HEAVY METAL REMOVAL

Presently a number of physical and chemical methods like oxidation-reduction, precipitation, electrolysis, ion exchange, membrane processes and adsorption are employed for the removal of heavy metals from wastewater (Ahalya et al., 2007; Kumar, 2006; Malaviya and Singh, 2011). Among these wastewater treatment techniques, adsorption is preferred over the others due to simple design, easy operation and lesser initial cost for setting up (Fadali et al., 2004; Younis et al., 2015). All other methods have one or the other problem associated with them like high operation and maintenance cost, high reagent requirement, high energy requirement and moreover, generates highly toxic sludge or waste product (Das et al., 2008).

1.2 ADSORPTION

Adsorption is a mass transfer process in which a constituent from liquid phase get transferred to the surface of solid phase (Artioli, 2008; Metcalf and Eddy, 2004).
The constituent which get transferred to the surface of solid phase from the liquid phase is termed as adsorbate while the solid phase on the surface of which adsorbate get transferred is termed as adsorbent (Metcalf and Eddy, 2004). Unbalanced forces on the surface of adsorbent are responsible for accumulation of adsorbate on the surface of adsorbent (Eckenfelder et al., 2009). Depending upon the forces involved in adsorption process, it can be broadly classified into three types: physical, chemical and exchange adsorption.

- **Physical adsorption:**
  
  Physical adsorption results due to weak Van der Waals’ forces of attraction between the molecules of adsorbate and the adsorbent. Adsorbate molecules form several superimposed layers on the surface of adsorbent. It is usually reversible in nature.

- **Chemical adsorption:**
  
  It takes place due to bond formation as a result of stronger forces equivalent to those leading to the formation of chemical compounds. The adsorbate forms a monomolecular layer over the surface of adsorbent. It is irreversible in nature.

- **Exchange adsorption:**
  
  It occurs due to strong electrostatic forces of attraction between the adsorbate molecules and the sites of opposite charges on the surface of adsorbent (Sawyer et al., 2003).

Different parameters like physico-chemical characteristics of the adsorbent and adsorbate, experimental conditions like pH, temperature, time, absorbate concentration, adsorbent size and dose etc. affect the adsorption efficiency (Fahim et al., 2006).

### 1.3 TYPES OF ADSORBENTS

#### 1.3.1 Commercial adsorbents

Commercial adsorbents include activated carbon, synthetic polymers and silica based adsorbents. However, synthetic polymeric and silica based adsorbents are rarely used for industrial wastewater treatment due to their higher cost. Activated charcoal is the most widely used adsorbent in industrial effluent treatment plants,
commercial and domestic water purifiers (Metcalf and Eddy, 2004). It is efficient in the removal of organic compounds, heavy metals and colouring materials from wastewater by adsorption (Fadali et al., 2004). But, the critical disadvantage associated with the use of activated charcoal is the requirement of chelating agents for increasing its efficiency (Oliveira et al., 2005). Further, the activated charcoal is non-biodegradable and its use produces a huge quantity of metal loaded charcoal, disposal of which is again a problem. Therefore, efforts have been made to develop an alternative low-cost adsorbent which should be easily available, biodegradable, reusable, generate a minimum amount of sludge and exhibit high efficiency.

1.3.2 Low-cost adsorbents

A number of materials such as aquatic weeds (Elangovan et al., 2008), non-living biomass of fresh water macrophytes (Saraswat and Rai, 2010; Schneider and Rubio, 1999), agricultural waste materials (Demirbas, 2008; Ertugay and Bayhan, 2010; Mohan and Singh, 2002; Mohan et al., 2008; Oliveira et al., 2008; Sud et al., 2008; Vinodhini et al., 2010; Zheng et al., 2010), industrial by-products (Fadali et al., 2004; Gupta et al., 2010; Khan et al., 2009; Lin and Yang, 2002; Malkoc et al., 2006; Mishra and Tripathi, 2008), clay minerals (Etci et al., 2010; Jiang et al., 2010) and zeolites (Erdem et al., 2004; Motsi et al., 2009) have been explored for the adsorptive removal of heavy metals. Although, these materials have different affinity and efficiency but are limited by availability, heterogeneous and variable composition and leaching of the adsorbent itself. Thus, there is a need for cost effective and sustainable adsorbents, having uniform reproducibility, wide spectrum, higher efficiency, produce minimum sludge and leachate.

Such attempts have led to the exploration of natural polymers/biopolymers like alginic acid (Abdel-Halam and Al-Deyab, 2011), chitin (Shao et al., 2003; Yang and Shao, 2000), chitosan (Ngah and Fatinathan, 2010; Tang et al., 2007; Tran et al., 2010), starch (Hashem et al., 2007; Renault et al., 2008) and cyclodextrin (Ozmen and Yilmaz, 2007). Biopolymers have been reported to have fair tendency to adsorb heavy metals, however, these are not quiet competitive with the alternates which have found commercial utilization. However, functionalization of biopolymers with suitable functional groups would lead to synthesis of a better,
efficient and economically viable adsorbent (Shao et al., 2003; Tabakci et al., 2007; Vinodh et al., 2011).

Among the polysaccharide biopolymers, alginates have good complexing ability with various heavy metals (Abdel-Halim and Al-Deyab, 2011) due to the presence of a number of free hydroxyl and carboxyl groups distributed along polymer backbone (Yang et al., 2011). Hence, it can be used as an efficient adsorbent for the removal of these metals from wastewater. Although, sodium alginate is soluble in water, but its acidic form i.e. alginic acid is practically insoluble in water under acidic pH.

Further, alginic acid can easily be functionalized on the carboxylic arm of the polymer, whereby a cooperative/allosteric binding of heavy metals on the surface of modified alginic acid can be studied. This research work aimed at the incorporation of heavy metal binding functional moieties on alginic acid and evaluation of adsorptive efficiency of these derivatives for the removal of heavy metals (Cu, Pb and Zn) from wastewater. The effect of various parameters like sorbent dose, contact time, pH and initial metal ion concentration on copper, lead and zinc adsorption from the simulated sample was investigated.

1.4 Objectives of the Study

The objectives of the present study are

- To synthesize alginic acid derivatives
- To explore the use of these derivatives for the removal of heavy metals (copper, lead and zinc) from their aqueous solution
- To evaluate the efficiency of the adsorbents with the real wastewater

In order to achieve the above objectives following work was planned:

- Synthesis of alginic acid derivatives
- Characterization of these alginic acid derivatives
- Batch sorption experiments to study the effect of following parameters on the heavy metal cations (copper, lead and zinc) adsorptive behaviour of alginic acid and its derivatives from aqueous solution:
  - sorbent dose
- contact time
- pH
- initial metal ion concentration

- Calculation of sorption efficiency by mass balance equation
- Development of sorption isotherms
- Study of reaction kinetics
- Study on competitive sorption of copper, lead and zinc by alginic acid derivatives
- Preliminary continuous column studies

1.5 HYPOTHESIS

The derivatization of biopolymers provides tailor-made materials for efficient sorption of heavy metals. The increase in the sorption behaviour of the derivatized natural polymers is governed by Hard and Soft Acid Base (HSAB) principle which govern the complexing ability of organic functional moieties. Based on HSAB principle, nitrogen and sulphur containing compounds have affinity for soft acids like heavy metal ions. Thus, suitable derivatization of natural polymers with functional groups containing nitrogen and sulphur moieties, in conjunction with proper pre-organization of these groups, is the driving force for the affinity of a sorbent for heavy metal adsorption.

Thus, it is hypothesized that the presence of heavy metal binding complementary hetero atom substituents and its pre-organization on alginic acid will furnish suitable sorbent for heavy metals present in electroplating wastewater.

The present work will add substantial contribution in understanding the performance of alginic acid and its two derivatives as adsorbent for removing heavy metals from aqueous solution.