American Journal of Environmental Sciences 1 (2): 102-105, 2005
ISSN 1553-345X

Removal of Mercury from chlor-alkali Industry Wastewater using *Acetobacter xylinum* Cellulose

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Abstract: In this study, the removal of mercury ions by cellulose of *Acetobacter xylinum* was investigated in the synthetic and chlor-alkali wastewater. Biofilms of *Acetobacter xylinum* were grown in laboratory column bioreactors. The biofilms were continuously treated with sterile synthetic model wastewater or nonsterile, neutralized chloralkali wastewater.The extent of adsorption was studied as function of pH, adsorbent dose and contact time. Efficiency of mercury ion removal from chlor-alkali industry wastewater by aluminum sulfate and ferric chloride was also determined. Under acidic condition the adsorption of mercury by cellulose was quite low and increasing processing time more than10_{min} has no remarkably effect on the adsorption rate. Adsorption capacity of cellulose under dynamic condition for chlor-alkali wastewater was 65μg/g which was less than the value (80μg/g) that obtained from batch adsorption experiments for synthetic wastewater.

Keywords: Biosorption, Mercury, Cellulose, *Acetobacter xylinum*,chlor-alkali.

INTRODUCTION

Environmental contamination due to mercury is caused by several industries, petrochemichals, minings, painting, and also by agricultural sources such as fertilizers and fungicidal sprays [1,2]. Mercury and it's compounds are cumulative toxins and in small quantities are hazardous to human health [3]. The major effects of mercury poisoning manifest as neurological and renal disturbances as it can easily pass the blood-brain barrier and affect on the brain. High concentration of Hg(II) cause impairment of pulmonary function and kidney. Consequently removal of mercury in water and wastewater assumes importance [1]. Various types of technology is available for removing of mercury in water and wastewater including chemical precipitation, conventional coagulation, lime softening, reverse osmosis, ion-exchange and activated carbon adsorption [2]. The search for alternate and innovative treatment techniques has focused attention on the use of biological materials for heavy metal removal and recovery technologics. It has gained important credibility during recent years because of the good performance and low cost of these complexing materials [4,5]. The strong, tough, highly pure cellulose synthesized by microorganisms is just emerging as a new industrial products with exciting new applications in industries. Cellulose is the commonest biopolymer in the world, with an estimated production of 10^{11} ton / year. Most of this is produced in cell walls of plants, where the cellulose forms semi – crystalline microfibrils (long, fine, mostly crystalline fibers) several nm in diameter [6]. Plant and bacterial cellulose are chemically the same,β-1,4-glucans,but the degree of polymerization differs from about 13000 to 14000 for plant and 2000-6000 for bacterial cellulose. Several bacteria are in condition to produce cellulose as reported from strains from the genera *Acetobacter*, *Agrobacterium*, *Pseudomonas*, *Rhizobium* and *Sarcina*[7]. *Acetobacter xylinum* is a gram-negative aerobic bacterium that secretes cellulose fibers as part of its normal metabic activity [8]. The cellulose synthesized by *Acetobacter xylinum* is identical to that made by plants in respect to molecular structure.The secreted polysaccharide is free of lignin, pectin and hemi cellulose, as well as biogenic products, which are associated with plant cellulose. This cellulose has high crystallinity, high water absorption capacity, and mechanical strength in the wet state, ultera – fine network structure, mouldability in situ, and availabity

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in an initial wet state [9]. Because of these features there is an increasing interst in the development of new fields of application. The typical properties of bacterial cellulose have also inspired investigation on the reactivity and availability of the hydroxyl groups for chemical reactions as well as the subsequent characterization of the products obtained [10]. In the present study cellulose of *Acetobacter xylinum* was used as a biosorbent for removing mercury from synthetic and chlor-alkali wastewater. In batch-type adsorption tests effects of some parameters such as pH, contact time and adsorbent dose were determined and in the down flow fixed-bed adsorption column breakthrough volume was evaluated.

MATERIALS AND METHODS

To produce the bacterial cellulose, *Acetobacter xylinum* ATCC 23768 was cultured in the SH medium containing glucose, 2%(w/v) ; Peptone, 0.5% (w/v); yeast extract,0.5%(w/v); disodium phosphate,0.27% (w/v);citric acid,0.115 (w/v); at pH 6.0 and under static culture condition [11]. The cellulose sheets after cultivation were removed and rinsed with distilled water and devoided from bacterial and medium residues by 2% SDS (Sodium Dodecyl Sulfate) and %4 NaOH solutions in a bath of water at boiled temperature[12]. The cellulose sheets were grinded and rinsed with distilled water. To set up the batch adsorption tests the dewatered cellulose was dried at 104 ^{oC} for five hours. To study effects of pH, contact time and adsorbent dose, synthetic wastewater was prepared by using mercury chloride and sodium chloride. Original wastewater was supplied from one of the chlor-alkali plant. For carrying out the batch adsorption tests exact amounts of 0.2g of dried cellulose were transferred into 100 ml Erlenmeyer flasks containing 50 ml synthetic wastewater of 500_{ppb} mercury concentration. The effect of pH, contact time and adsorbent dose were studied in batch system. In order to study, the effect of pH, samples were adjusted at different pH (2 – 12) and shake at 100 $_{rpm}$. Content of flasks were filtered, and filtrate analyzed for residual mercury concentration. For decreasing mercury concentration in original wastewater and using in adsorbent column, coagulation/co-precipitation process was used, proper coagulant, pH optimum and coagulant dose were determined in consecutive Jar tests. Chlor-alkali wastewater was pumped into laboratory column in the downflow mode. Adsorbent column was run with flow rate of $5_{ml/min}$ and empty bed contact time (EBCT) of 30. Mercury contents were determined by flameless cold vapor adsorption spectroscopy by using a flow injection system which linked to an atomic adsorbtion spectrophotometer (Model 929 Unicam, UK). To determine soluble mercury contents, sample (5ml) were routinely oxidized by adding 0.01 volume of 65% HNO_3. Ionic mercury was then reduced with $NaBH_4$ (4g/Liter) to metallic mercury, which was volatilized by the carrier gas argon and detected at 253 $_{nm}$ by the atomic adsorption spectrophotometer. If necessary, samples were diluted so that they contained less than 100 $_{\mu g}$ of Hg per liter.

RESULTS AND DISCUTION

Effect of pH: Under acidic condition the adsorption of mercury by cellulose was quite low (Fig. 1).

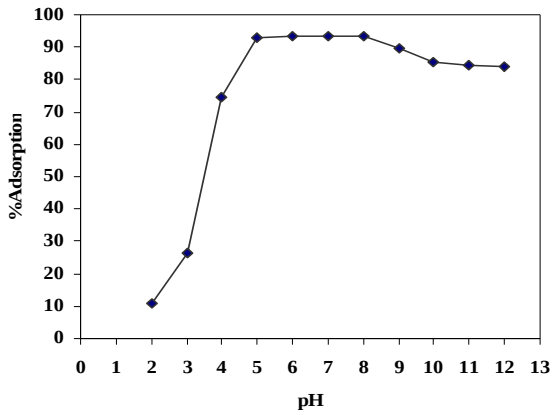

Fig. 1: Effect of pH on Adsorption of Mercury by Cellulose of Acetobacter *xylinum*

There was an increase in mercury adsorption with an increase in the pH from 3 to 5 and beyond which no real changes in mercury adsorption was observed. The results obtained indicate that the optimum pH range for adsorption of mercury in solution by cellulose of *Acetobaeter xylinum* was between 5-8. Normally metal adsorbents exhibit a drastic decrease in metal affinity at low pH condition. pH of medium affects the solubility of metal ions and ionization state of the functional groups [13].The increase in biosorption levels observed with increasing pH can be explained by strong relation of biosorption to the number of surface negative charges, which depends on the dissociation of functional groups. It can also partly explain the low amounts of metal ions retained by the biosorbent at pH values below 4, because most functional groups are expected to dissociate only at neutral pH values [4,]. The occurrence of competition between protons and metal ions for the same sites should also be considered particularly at low pH values [14].

Effect of Contact Time: Increasing processing time more than 10 $_{min}$ has no effect on the adsorption extent of the mercury removal by cellulose of *Acetobacter xylinum* and saturation level were obtained after 60_{min}, after this period the adsorbed mercury ion did not significantly change further with time (Fig. 2). Adsorption of mercury by cellulose of *Acetobacter xylinum* is reasonably fast. Several parameters such as:

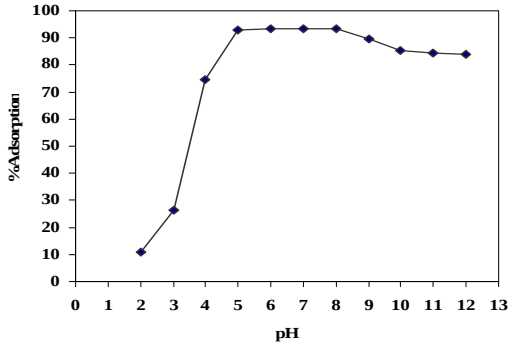

Fig. 2: Effect of Time on Adsorption of Mercury by Cellulose of *Acetobacter xylinum*

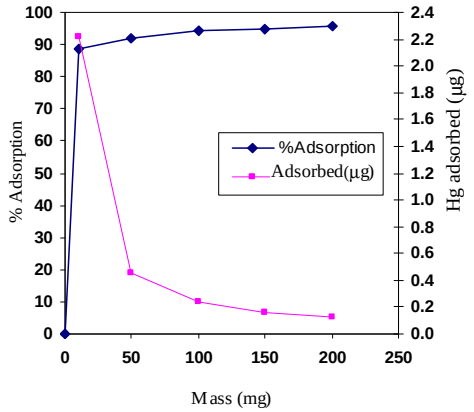

Fig 3: Effect of **Adsorbent** Dose of Microbial Cellulose Mass on Mercury Removal

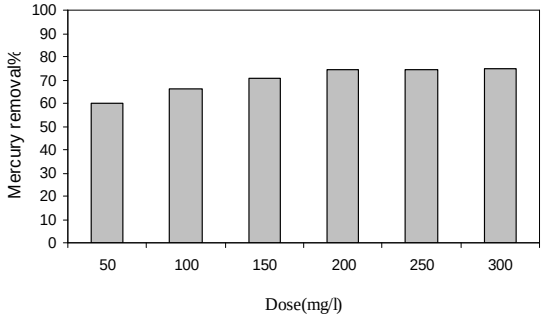

Fig 4: Effect of FeCl3 Dose on the Mercury Removal from chlor-alkali Wastewater

stirring rate, structural properties of biosorbent (e.g carbohydrate composition, surface charge density, topography and surface area), amount of sorbent, properties of the ions under study, initial concentration of ionic species and the presence of other metal ions affect the biosorption rate [14].

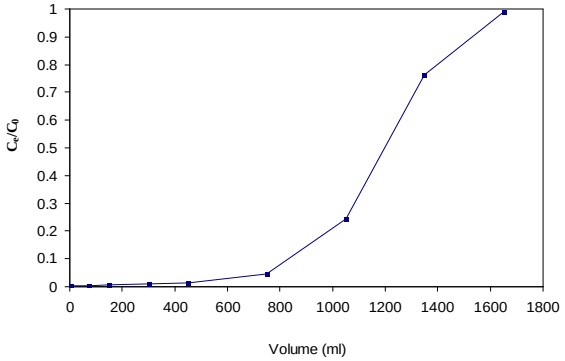

Fig 5: Breakthrough Curve for Mercury Removal From Chlor-alkali Wastewater by *Acetobacter xylinium* Cellulose

Effect of Adsorbent Dose: The difference in mercury removal with 10 mg of cellulose (88.76 %) and 200 mg of cellulose (95.64 %) was very little. With increasing adsorbent dose from 10 to 200 mg at the fixed initial concentration of 500 ppb the amount of mercury ion adsorbed per unit weight of cellulose decrease from 2.219 to 0.1195µg/mg (Fig.3). The most important factor, which can contribute to these amounts of Hg^{+2}, is that adsorption sites remain unsaturated during the adsorption reaction due to low level of the initial concentration of Hg^{+2}.

Jar Tests Evaluation: Two coagulants were employed include alum and ferric chloride. The result of Jar tests showed that size of flocs and sedimentation condition at pH 9 are of better quality and mercury removal efficiency was considerably higher when ferric chloride was used as a coagulant agent. More study proved that increasing the coagulant dose of ferric chloride up to 250mg/l results in higher mercury removal efficiency and beyond which no remarkably changes in mercury removal was observed (fig.4). In pilot plant tests of alum and iron treatment of inorganic and methylmercury, was removed effectively only by iron. Similar results have been reported in another study, which also found that increasing coagulant dosage did not improve mercury removal [2].

Mercury Mitigation: For decreasing initial concentration of mercury (9.635mg/l) in chlor-alkali wastewater the coagulation/co-precipitation process using 250mg/l (Fe) of ferric chloride as proper coagulant at pH 9 was carried out. The removal efficiency (78%) and final concentration (2.12 mg/l) was obtained. The dominant mercury removal mechanism is most likely by adsorptive co-precipitation. The adsorption process is isothermal, and treatment performance can be enhanced by optimal bulk solids formation and by pH manipulation to optimize bulk solid surface change and soluble mercury speciation [15].

Continuous Adsorption: Laboratory scale column study using cellulose of *Acetobacter xylinum* as biosorbent with flow rate of 5 ml/min and EBCT of 30 min, showed that 15 ml of chlor-alkali wastewater could be treated per gr of cellulose before breakthrough occurred (fig. 5). Adsorption capacity of cellulose under dynamic condition was 65g/g which is less than the value (80 g/g) that obtained from batch adsorption experiments for synthetic wastewater.

CONCLUSION

The cellulose of *Acetobacter xylinum* can be employed as an environmentally friendly adsorbent for the removal of mercury from industrial wastewater. The biosorption depends on pH of solution and optimum pH range was between 5-8. Adsorption of mercury by cellulose of Acetobacter *xylinum* is reasonably fast, and processing time more than 10 min. has no remarkably effect on adsorption rate. Coagulation process using ferric chloride as a coagulant was effective to remove mercury (78%) from chlor-alkali wastewater. The laboratory scale column study using cellulose of *Acetobacter xylinum* as adsorbent with flow rate of 5 ml/min and EBCT of 30 min. showed that 15 ml of wastewater could be treated per gr of cellulose before breakthrough occurred.

Acknowledgement: This work was supported by grant from national petrochemical company of Iran.

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