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Review Article

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Use of cellulose and its derivatives for metal ion sorption

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ABSTRACT

Due to industrial revolution and population explosion, environmental degradation has posed a great problem worldwide. Effluents of various industries are loaded with ions of Pb, Hg, As, Cd and many other toxic heavy metals. Unlike most of the organic pollutants, heavy metal ions are non-biodegradable and do not degrade into harmless end products. Due to their toxicity, heavy metal ions are a great threat to animals, plants and human beings. A large number of research groups have reported a variety of treatment processes for the removal of heavy metal ions from wastewater and industrial effluents. The most important of these include precipitation, membrane filtration, ion exchange, co-precipitation and adsorption. Most of these methods have one or the other limitations such as high cost, less efficiency, less selectivity and specificity, sensitive operating conditions and production of secondary pollutants. Out of these methods, adsorption is most widely used for removal of heavy and toxic metal ions as it is free from most of the limitations associated with conventional methods cited above. In recent years, the use of inexpensive, abundantly available and biodegradable cellulosics derived from forest and agro industry wastes as low cost, highly efficient and selective adsorbent has increased. In the present review, an attempt has been made to summarize some recent advances using cellulose and its derivatives for removal of heavy metal ions.

Keywords: adsorption; cellulose; heavy metal ions; sorption; toxic

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INTRODUCTION

In view of ever increasing industrialization, urbanization and above all population explosion, concentration of heavy toxic metal ions in air, water and soil has increased to an alarming level. This has drawn the attention of researchers and environmental agencies to look for the safe and economical methods for their removal. There is an urgent need that all possible inexpensive adsorbents originated from biological, domestic and industrial wastes should be explored and their feasibility for the removal of heavy metal ions should be investigated.

Many of the heavy metals are essential micronutrients, but their higher concentrations are known to produce a variety of toxic effects. High concentration of lead is known to cause behavioural disturbances, kidney damage, anaemia, encephalopathy, cognitive impairment, and damage to the reproductive system [1]. High concentrations of mercury has been reported to cause neuro-behavioural disorders, attention deficit hyperactivity disorder, developmental disabilities including dyslexia and intellectual retardation [2]. Chromium in its hexavalent form i.e. Cr(VI) is known to cause respiratory cancers [3]. Cadmium is known to cause nephrotoxic effects and bone damage[4]. High concentration of copper causes damage to the gastrointestinal tract, lethargy, anorexia and weakness [5]. In addition to these toxic effects, some other general threats associated with the accumulation of heavy metals are reduction in ecosystem biodiversity, plant and animal death, reduced rates of reproduction etc. [6–9].

Most of the organic pollutants are biodegradable and degrade into harmless end products. On the other hand, heavy metal ions are non-biodegradable and do not degrade into harmless end products [10]. Heavy metal ions are a great threat not only to the environment, but also to the very existence of animals, plants and human beings. Industrial effluents of many industries such as mining operations, metal plating, smelting, alloy industries, tanneries, chloralkali, storage batteries industries and radiator manufacturing consist of one or more heavy metal contaminants [11].

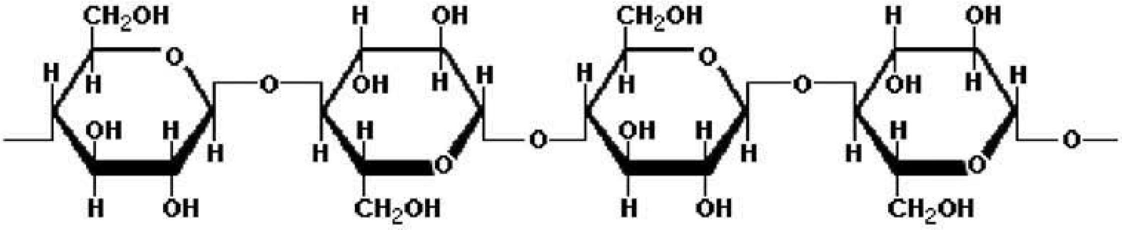
Conventional methods such as precipitation, membrane filtration, ion exchange and co-precipitation used for the removal of metals from wastewaters are unable to meet the new and more stringent requirements and/or are expensive [12].For last two to three decades, adsorption processes are being widely used for the removal of heavy metal ions from waste streams and industrial effluents. The adsorption is associated with many advantages such as: high efficiency, cost effectiveness, easy availability, eco-friendly, utilization of domestic, industrial and biological waste as adsorbents, high selectivity and specificity, less sensitive operating conditions, reusability of adsorbent, capacity of removing very low concentrations of heavy metal ions over wide range of pH and many others.

Abundantly available biopolymers have extensively been investigated as adsorbents for the removal of heavy metal ions because of their strong interactions with these metal ions. Most of the bioadsorbents such as rice husk [13-16], sugarcane bagasse [17-21], sawdust [22-24], pine needles [25], neem bark [26] etc., in native state and chemically modified forms are inexpensive, low cost biodegradable agricultural waste by-products and are effectively being used for removal of heavy metal ions from industrial effluents. An adsorbent that is abundant in nature, or is a by-product or waste material from another industry and requires little processing, can be termed as a low cost adsorbent [27].

Ever growing problems of waste disposal, increasing need for new and low-cost adsorbents, the high cost of synthetic resins and high ability and selectivity of cellulosics for metal sorption, make them one of the most suitable materials for industrial effluent treatment. This review is an attempt to highlight the current status of research on the use of the naturally occurring cellulose, its modified forms and their use as adsorbents for the removal of heavy metals from industrial effluents and waste water.

STRUCTURE OF CELLULOSE

Cellulose is a well-known carbohydrate polymer. It is the most abundant and renewable polymer resource available worldwide. Photosynthesis produces approximately 10^{11}–10^{12} tons of cellulose annually in a relatively pure form in the seed hairs of the cotton plants and combined with lignin and other polysaccharides (so-called hemicelluloses) in the cell wall of woody plants [28].



Cellulose

Cellulose is a large, linear-chain polymer consisting of repeating β-D-glucopyranose units which are covalently linked through acetal functions between the -OH group of the C_4 and C_1 carbon atoms (β-1,4-glucan). There are three hydroxyl groups per anhydroglucose(AGU) unit which are present in the preferred $^4C_1$conformation. Every second AGU unit is rotated through 180° in the plane in order to accommodate the preferred bond angles. The length of the polymeric cellulose chain varies with the origin and treatment of the cellulose raw material and also depends on the number of constituent AGU units[28]. Cellulose is moderately flexible polysaccharide and has property of twisting and bending in the direction out of the plane owing to its ribbon like shape. The neighbouring cellulose molecules show a strong interaction due to the presence of the hydroxyl (–OH) groups. This peculiar molecular structure of cellulose accounts for its characteristic properties like hydrophilicity, chirality and degradability. Chemical reactivity is largely a function of the high donor reactivity of the OH groups [29].

USE OF CELLULOSE AND ITS DERIVATIVES FOR METAL ION SORPTION

With annual production of approximately 3.0×10^8 kg, cellulose based agricultural by-products are one of the most abundant renewable resources in the world [30].Considerable work has been carried out on the use of cellulose and its derivatives as metal ion sorbent. Cellulose is not only relatively cheap and abundant in supply, but also has significant potential for modification and ultimately enhancement of its adsorption capabilities. In order to enhance heavy metal ion sorption potential of cellulose from aqueous solutions, two main approaches have been tried. These are: (i) Direct modification of the cellulose backbone involving incorporation of chelating or metal binding functionalities. (ii)Grafting of suitable monomers to the cellulose backbone either directly or with subsequent functionalization of these grafted polymer chains with polymer analogous reactions.

There are numerous reports regarding use of cellulose and its derivatives in the sorption of heavy metals [31–36]. Although reports of membrane forming property of cellulose are scanty. This is due to low stability of cellulose and its poor interactions with water. However, these limitations can be improved by cross-linking, surfactant adsorption and grafting of suitable monomers with hydrophobic and hydrophilic moieties. Grafting and crosslinking not only induce high degree of selective permeability and permeability but also impart greater stability and enhances complexation power of cellulose [37-39]. In order to achieve selective separation of metal, use of a metal specific ligand is an ideal approach. Many researchers have made numerous attempts in this direction but till date it has proved almost impossible to find metal specific ligands.

Bicaket al.[40] reported a sorbent prepared by grafting polyacrylamide onto cellulose using Ce(IV) sulphate. This sorbent was found to be highly selective for removal of mercuric ions from aqueous solutions. The sorption was fairly fast and mercury-uptake capacity of the sorbent was found to be 3.55 mmol/g. The Hg(II) sorption was highly selective without formation of any interface in the presence of Ni(II),Co(II), Cd(II), Fe(III), Zn(II) ions in 0.1 M concentrations at pH 6. The polymer was regenerated without losing its original activity by using hot acetic acid. The graft copolymer has great potential for removal of large amounts of mercury in hydrometallurgical applications and other water treatments. Navarro et al. [41] carried out grafpolymerisation of glycidyl methacrylate on porous cellulose material(aquacel) using ceric ammonium nitrate as the initiator. This was followed by the functionalization of the reactive epoxy groups present in poly(glycidyl methacrylate) with polyethyleneimine to introduce nitrogenous ligands. The resulting adsorbent was employed for effective adsorption of Cu(II), Co(II) and Zn(II) from aqueous wastewater.

Polyacrylonitrile and poly(acrylic acid) grafted on cellulosic materials were used for removal of Cd(II) and Cu(II) ions from aqueous solution. Graft polymerization was carried out at fixed cellulosic substrate/monomer ratio and ceric ion concentration at various temperatures between 35 and 60 °C. The cellulose-graft-polyacrylonitrile copolymer was treated with dilute NaOH solution for 1 h in order to hydrolyse the nitrile groups to amide and carboxyl groups. It was observed that grafting enhanced the metal ion binding capacity of the cellulosic material to a great extent. A number of factors were found to affect the extent of ion binding capacity including the metal ion type and the level and nature of the incorporated graft polymer. The equilibrium sorption was in accordance with Langmuir adsorption isotherm and metal ion binding capacity and binding constant for the grafted cellulosic materials were much higher than for the cellulosic material. The grafted polymer was regenerated without losing its original activity by using 2% (v/v) HNO_3[42].Mishra et al.[43] have reported the graft copolymer of N-vinylformamide onto sodium carboxymethylcellulose (sodium carboxymethylcellulose-g-N-vinylformamide). The copolymer was prepared by free radical polymerization using potassium peroxymonosulphate/thiourea redox system in an inert atmosphere. The reaction conditions for maximum grafting were optimized by varying reaction time, temperature and the concentration of N-vinylformamide, potassium peroxymonosulphate, thiourea, sulphuric acid and sodium carboxymethylcellulose. The graft copolymer was used for sorption of five metal ions i.e. Cu^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+} and Hg^{2+}.It was observed that the synthesized graft copolymer showed better metal ion sorption as compared to sodium carboxymethylellulose.

Two carboxyl groups are required to form a chelate with a divalent metal. Liu et al.[44]synthesised a spheroidal adsorbent by grafting acrylonitrile onto cellulose and subsequent saponification using sodium hydroxide. The resulting adsorbent was effectively used for the removal of Cu(II) ions from aqueous solutions by forming a bidentate arrangement between the Cu(II) and the carboxyl groups on the adsorbent. O’Connell et al. [45-47]reported the adsorption of Cu(II), Ni(II) and Pb(II) using grafted glycidyl methacrylate grafted on cellulose backbone and subsequent functionalization of the grafted product with the imidazole ligand. Aoki et al. [48] grafted bead cellulose with acrylonitrile using ceric ammonium nitrate as the initiator. The cyano groups on the poly(acrylonitrile) chains were amidoximated by reacting with hydroxylamine in methanol. Amidoxime groups can chelate a range of heavy metal ions. In this study, alkali treatment of amidoxime functionalised cellulose accelerated the sorption of metal ions. Guclu et al. [49]has reported the adsorption of Pb(II), Cu(II) and Cd(II) under competitive conditions by using a series of polymers obtained by grafting acrylic acid, N,N-methylene bisacrylamide, 2-acrylamido-2-methylpropane sulphonic acid and a mixture of acrylic acid and 2-acrylamido-2-methylpropane sulphonic acid separately. It was observed that cellulose-g-poly acrylic acid with its carboxyl groups responsible for chelating the divalent metal ions exhibited maximum uptake. High uptake of Pb(II), Cd(II) and Cu(II) have been reported by Zhou et al. [50]by using cellulose/chitin beads from aqueous solution. Ninety-eight percent of the adsorbed metals were recovered within 15 minutes using 1 mol/L HCl and the beads werere-used a number of times without any appreciable loss of activity .Sawdust modified with polyacrylic acid was found to possess 15 – 40 times higher adsorption capacity for Cu(II), Ni(II) and Cd(II) than the unmodified sawdusts [51].

CONCLUSION

Increasing environmental degradation has motivated many researchers to develop new low cost adsorbents derived from renewable resources. Major advantages of using cellulose for this purpose lies in the fact that it is not only cost effective and abundantly available adsorbent, but also has great potential for chemical modification. The efficiency of cellulose and its derivatives can be enhanced mainly by two approaches; direct chemical modification and grafting of suitable polymeric chains onto the cellulose backbone followed by functionalisation in some cases. The grafting of amine, amide, amidoxime, carboxyl, hydroxyl and imidazole to cellulose backbone enhances the adsorption capacity of the cellulose. In order to reduce the cost, regeneration and reuse of the polymeric adsorbents is one of the most desirable properties. All these aspects have been demonstrated in a number of papers reviewed in this work.

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