Synthesis of Chemically Modified Cellulose Bearing Schiff Base with Chelating Groups for Removal of Heavy Metals from Aqueous Solution

J. Senthilkumaran[1]* G. Annamalai[2]

[1] Assistant Professor, Dhanalakshmi Srinivasan College of Arts and Science for Women, Perambalur, Tamil Nadu, India

[2] Assistant Professor, Dhanalakshmi Srinivasan College of Arts and Science for Women, Perambalur, Tamil Nadu, India

ABSTRACT

Chemically modified cellulose bearing metal binding sites were synthesised and characterised by Fourier transform infrared and solid state 13C-nuclear magnetic resonance (NMR) analysis, such as Schiff base and carboxylic acid groups. Due to its metal ion absorption potential for Cu (II) and Pb(II) ions from aqueous solution, the chemically modified cellulose (Cell-PA) adsorbent was examined. Under optimal conditions, kinetic and isothermal studies were carried out. The experimental data matches well with pseudo-second-order kinetics and Langmuir isotherm. Thermodynamic tests along with efficiency studies of adsorption regeneration were also conducted. The adsorbent (Cell-PA) demonstrates a high propensity for the removal of metal ions Cu (II) and Pb(II) and demonstrates antibacterial activity against selected microorganisms. The most vital element of natural resources is water, which is essential for the survival of all living species, including human beings, food production, and agricultural, recreational and industrial activities. Economic development, patterns and the climate are all highly impacted by the quality and availability of water. Water quality is altered by anthropogenic activities and is decreasing as urbanisation, waste disposal, climate change, population growth, industrial development and other factors increase.

***Keywords** – Physical Sciences, Chemistry, Chemistry Analytical.*

INTRODUCTION

Water contamination has become a major problem in many countries in recent years, primarily due to the existence of untreated waste, sewage spills, heavy metals, oil spillage, industrial waste dumping, groundwater pollution by drilling operations, radioisotopes, combustion, hazardous waste disposal, mineral processing plants, eroded sediments, deforestation, mining, littering, animal waste disposal, A major danger to living organisms is the resulting contamination of water. Not only does dirty water impact the life of the present generation, it also affects the life of future generations as its adverse influence lasts for a long time. Pure and pollution-free water is indispensable for a healthy life. With the increase in population density and industrial growth, waste water originates from domestic applications and even from factories. Where pollution comes from a particular, individual source, such as industrial wastewater outlet, point source water pollution occurs.

Diffuse water contamination is caused by numerous causes, which are also difficult to classify. There may be comparatively small individual sources, but the cumulative impact of multiple sources can be detrimental. There is a greater effect on the water quality from diffuse emissions than any other form of pollution. The natural environment, particularly aquatic ecosystems, has always been disrupted by human activity. The use of insecticides and heavy metals in industries has contributed to significant pollution of the environment.

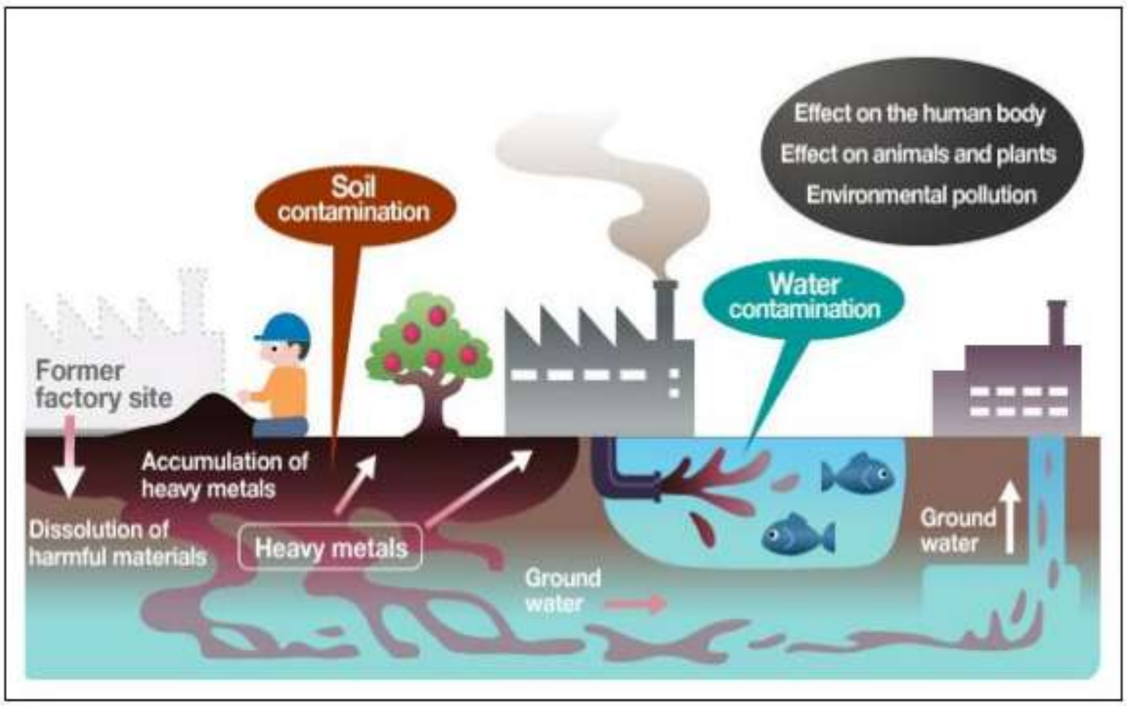

Fig.1.1

Another cause of water contamination is nuclear waste. In nuclear power plants, industrial, medical, and other research methods, radioactive substances are used. They can be used in watches, luminous clocks, x-ray machinery and television sets. There are also radioisotopes from animals and within the atmosphere that occur naturally. Radioactive waste can result in significant incidents of water contamination if not properly disposed of.

Heavy metal pollution has been a major environmental issue in recent years. Generally, heavy metal contamination in water is caused by human activities. Although plants need many of the heavy metals at the micronutrient stage, Fig.1.1. In contaminated water treatment, the issue of dealing with the presence of heavy metal ions has become a top priority. Some of the pollutants, due to their toxicity, are the target of the study and are also known to remain stable in the aquatic environment. By the strong implementation of the necessary steps, these pollutant triggers can be eliminated or at least restricted to the awareness among the people.

Chemical precipitation, ion exchange, coagulation-flocculation, membrane isolation, electrochemical treatment and adsorption are different treatment technologies for the removal of heavy metals from waste water. Adsorption using sorbents is one of the most common and successful processes for the removal of heavy metals from waste water, among all the treatment processes listed. The adsorption process provides design and operational flexibility and, in many instances, produces treated effluent suitable for reuse, free of colour and odour. In addition, because adsorption is often reversible, it may be possible to recycle the adsorbent with the resulting operating economy (Kelleher 2018).

Due to their high level of toxoids, the rising levels of mobile and soluble heavy metal species are a serious problem 1. Mining, electroplating, metal processing, battery production, pesticides, printing, photography, ceramics and glass industries are the most important sources of heavy metal contamination, such as Al, Cd, Co, Cu, Pb, Mn, Hg, Ni and Zn. U. Suggested amount of heavy metal pollution in water S. The Environmental Protection Agency (EPA) indicates that 1.3, 0.005, 5 and 0.04 were respectively 0.015 mg/L t of copper, cadmium, zinc, nickel and lead. The range of treatment methods available to eliminate metal contaminants from an aqueous medium are chemical precipitation, coagulation, ion exchange, solvent extraction, filtration, evaporation, electrolytic processes and photo catalytic degradation. The different adsorbents used for the heavy metal removal in aqueous solution are fly ash, blast furnace sludge, coffee husks red dirt, areca wastes, residual slurry, saw dust, microbial biomass, sugar beet pulp pine bark, metal oxides and polymeric resins.

Significant attention has been paid to the presence of hydroxyl groups found in cellulose-based derivatives. The aldehyde cellulose was prepared by periodate oxidation of cellulose, which was further oxidised using mild acidic sodium chlorite18. Great consideration has been given to the selective removal of heavy metals Pb^{2+}, Cu^{2+} and Ni^{2+} by chemically modified cellulose hybrid materials, 2,3-dicarboxy cellulose 20, Cellulose graft copolymer containing carboxylic group, Acrylamide grafted cellulose. This task is to synthesise the chemical alteration of the cellulose adsorbent and use Pb2+ ions to test its metal ion absorption. The adsorption of metal ions for the concomitant removal of metal ions was assessed by cellulose-based adsorbents (Cell-ABT). Various metal adsorption studies such as solution pH, contact time, dosage, adsorbent, metal ion concentration temperature, sorbent material desorption studies have been calculated.

OBJECTIVE OF THE STUDY

1. Selective periodate oxidation at C2-C3 cleavage followed by aromatic amine polycondensation techniques is used to synthesise chemically modified cellulose.

2. Antibacterial activity against selective microorganisms should be examined.

METHODS AND ANALYSIS

Materials

As administered, cellulose (Loba), p-aminopyridine (Alfa Aesar), p-toluidine (Alfa Aesar), p-aminophenol (Loba), p-aminobenzoic acid (Loba), sodium metaperiodate (Sigma-Aldrich), 2-aminobenzothiazole (Sigma-Aldrich) were used. From Sigma-Aldrich chemicals, copper and lead salts were procured. Either analytical grades or purified according to standard protocols were used for all other chemicals and solvents. The solvents used, such as N, Ndimethyl formamide (DMF) and ethanol, were distilled in accordance with standard methods. Throughout the work, deionized water was used.

Metal solutions

For preparing stock solutions, metal salts $CuSO_4.5H_2O$, $Pb(NO_3)_2$ were used. By dissolving the exact sum of the salts in 1000 ml of double distilled water to make a concentration of 1000 mg/L of Cu(II) and Pb(II) ions, the different concentrations of metal solutions were prepared. For the batch adsorption tests, the stock solutions were diluted to the appropriate experimental concentration. By using 0.1 M HCl or 0.1 M NaOH solutions, the pH of the test solution was modified.

Analytical Method

Fourier Transform Infrared Spectroscopy (FT-IR) analysis using the Shimadzu Spectrophotometer with KBr pellets in the range 4000-400 cm-1 was performed to characterise CMC and metal-chelated CMC. Using a Perkin-Elmer analyzer in static air at a heating rate of 10 C/min, thermo gravimetric analysis (TGA) was reported. Using a Leo Gemini1530 scanning electron microscopy, the SEM images of the CMC and metal loaded-CMC were analysed.

The solid state 13C-MAS NMR spectrum was conducted on a Bruker AMX-200 spectrometer at 100.52 MHz. To confirm the adsorption of Cu(II) and Pb(II) ions into the CMC adsorbent, the Energy Dispersive Study of X-Ray (EDAX) was employed.

The Malvern Zetasizer analyzer (range 0.3nm to 10μm) analysed the particle size of CMC. Atomic Absorption Spectrometer AA6300 (Shimadzu-AA6300, Japan, detection limit 0.006 mg/L) was used to determine the heavy metal ion concentration of the solutions before and after equilibrium. Antibacterial experiments were performed in the laboratory of Bioline, Coimbatore, Tamilnadu. Using a Hanna pH metre using glass electrodes, the pH of the solution was measured.

HEAVY METALS IN THE ENVIRONMENT

Heavy metals are classified on the basis of three parameters, including their atomic number, density or chemical characteristics. Radojevic et al. reported that the density of such metals (5 g/cm-3), which is five times denser than water, can be characterised by heavy metals. With the exception of alkaline metals, alkaline earths, lanthanides and actinides, Yu classified metals as any element with an atomic number greater than 20.

While elements such as Cu (copper), Pb (lead), Ni (nickel), Cr (chromium), Cd (cadmium), Hg (mercury) and Zn (zinc) are widely recognised and applied, they are commonly associated with problems with contamination and toxicity. Heavy metals are a natural part of the earth's crust, occurring in rocks and dispersed through many pathways into the components of the environment (water, air and soil), biodegradation, natural weathering, volcanic eruptions, water-rock interaction, mining and galvanization, etc. Since important anthropogenic sources of heavy metals in the environment include metal mining, agricultural mining, etc.

Heavy Metal Poisoning and Biotoxicity

In developing countries, existing heavy metals in the atmosphere and industrial waste water are rapidly polluting habitats and harming human health. In all environments, varying amounts of heavy metals generally occur. Although basic indicators of their toxicity are given by individual metals such as copper, lead, zinc, arsenic, cadmium, aluminium and mercury. Stomatitis, diarrhoea, hemoglobinuria, depression, gastrointestinal disorders, tremor, vomiting, paralysis and pneumonia when toxic vapours and fumes are inhaled have been identified as general signs associated with metals.

HEAVY METAL IONS AND THEIR HARMFUL EFFECTS ON HUMAN HEALTH

Copper:

Copper (Cu) is known as heavy metal and is often present in a reddish brown colour deep within the earth. According to Davies and Bennett, copper in the periodic table is known as a transition element and has an atomic number of 29 and an atomic weight of 63.5. It is a rare element that is present both in the uncombined state and in ores such as chalcopyrite in nature.

For the existence of living beings, copper is an important element. Copper is currently used in power generation and transmission, building construction, industrial machinery manufacturing, wiring and plumbing, heating and cooling systems, manufacture of electronic devices, and connections to telecommunications. In generators, wiring, radiators, connectors, brakes, bearings used in automobiles and trucks, etc., copper is also an integral part.

Exposure and dose

Copper metal pollution can be harmful for human health. It can affect humans either through its toxicity or through chronic illnesses. With the decrease of the zinc element and sulphate ion, the accumulation of Cu in organs and toxicity within human bodies is increased. It also endangers the stock of fish. If the presence of heavy metal is strongly detected in the body of the fish, the functioning organ system can be adversely altered. While copper plays an important role in haemoglobin development of many enzymes, it has detrimental effects on some of the organisms' truth. Cu is necessary for living organisms in living things as it serves as an antioxidant, participating in the transport chain of electrons, as well as in collagen and elastin. This micronutrient is required only in certain amounts, most of which have accumulated within human tissues. Under the Environmental Quality Act 1974, the acceptable level for copper in drinking water is 0.20 mg/L.

METHODS FOR HEAVY METAL REMOVAL

Maximum Polluted Level (MCL) criteria set by the Environmental Protection Agency of the United States (USEPA) and the World Health Organization (WHO)[28] for heavy metals[28]. To achieve successful environmental management, Minimize, Recycle, Reuse (3R) and Recovery were agreed. Therefore, prior to its release into the atmosphere, metal-contaminated waste water must be treated.

In order to remove environmental pollutants and also to uphold environmental quality, many companies have partnered with researchers to establish efficient wastewater management technology. By traditional treatment methods, heavy metal removal from inorganic effluent can be accomplished. Different treatment methods, including chemical precipitation, coagulation, complexation, ion exchange, solvent extraction, flotation, electrodeposition, cementation, membrane operations and adsorption, can be used to remove heavy metals from industrial waste water. These different treatment methods and methodologies used for heavy metal removal are listed in this work.

Electrochemical Treatments

One advanced oxidation technology used to extract metals from waste water sources is electrolytic recovery. This method uses electricity to pass between a cathode plate and an insoluble anode containing an aqueous metal bearing solution. The electrochemical approach for treating heavy metal waste water is to precipitate the heavy metals as hydroxides in a weak acidic or neutralised catholyte. Electro-deposition, electro-coagulation, electro-flotation and electro-oxidation are electrochemical treatments of waste water. Several technologies are based on the hydroxide-like precipitation of metal ions. The hydroxide ion benefits from the water's cathodic reduction:

$$2\,H_2O(l) + 2e^- \rightarrow 2\,H_2(g) + O_2(g)$$

Coagulation and precipitation by the deposition of hydroxide to appropriate levels is called electro destabilisation of colloids. It is the most common method of heavy metal precipitation, forming coagulants by electrolytic oxidation and destabilising folk-forming pollutants. By electrolytic oxidation of a suitable anode material, the coagulant is produced in situ. In this process, charged species of ionic metal are removed from waste water by allowing them to react in the effluent with anion. For the elimination of ions such as Cu(II), Cd(II), Fe(II), Ni(II), Al(III) and Cr, the method was used (III).

ANTIMICROBIAL ACTIVITY TEST

Using the agar well diffusion assay process, the antimicrobial activities of modified cellulose were tested against both gramme positive (Staphylococcus aureus) and gramme negative (Escherichia coli and Enterococcus faecalis) bacteria. On sterile Mueller-Hinton agar plates, diluted bacterial cultures were seeded, and then CMC was mounted on the agar disc surface with a diameter of 6 mm for examination. At 37 0C over 24 h, the plates were inserted into an incubator. By calculating the diameter of the inhibition zones antimicrobial potential can be measured.

MODIFIED CELLULOSE WITH ANTIMICROBIAL PROPERTIES

The use of antibacterial textile fibres in medicinal applications has been increased as public health illnesses and cross-infection caused by microbes have increased. To meet the challenges, antibacterial wrapping materials have been established as new ecological functional materials that can boost the consistency of the product and keep it free of microbial adhesion. Antibacterial textile fibres have gained more and more popularity in recent years because they deliver some

Article submitted at :
National Conference on Advances in Multidisciplinary Research (NCAMR-2019)
Organized by : Kurukshetra Institute of Professional Studies, Kurukshetra, Haryana

fascinating properties. It may be either bactericidal (to destroy bacteria) or bacteriostatic (to prevent the proliferation of bacteria) and it will protect the human body in both cases.

Many researches on antibacterial plastics, antibacterial fabrics and antibacterial ceramics have been performed. The ongoing search for possible antimicrobial agents has led to the discovery of polymer-based or composite-based antimicrobial biomaterials. Due to their stability and efficiency in inactivating harmful bacteria, the antimicrobial activities of the resulting cellulose derivatives have been studied extensively. In the literature, however, there are only a few illustrations where practical materials for the reduction of metal ions and antibacterial action have been transmitted.

By the introduction or grafting of quaternary ammonium salts, phosphonium salts, molecularly engineered peptides, N-halamine compounds releasing bacterial moieties such as metal ions, antibacterial surfaces of fabrics and polymers have been developed.

CONCLUSION

A fascinating field is the production of new low-cost adsorbents derived from renewable resources, historically and commercially. In this sense, the benefits of using cellulose as a fresh adsorbent are due to its high availability, low cost and ease of chemical modification. Because of its strong thermal stability, chelation, environmental stability and adsorption capacity for heavy metal removal, chemically modified celluose with chelating groups have been extensively studied. The study highlights the synthesis, characterization and application of Schiff's new chemically modified cellulose based biopolymer with methyl benzalaniline, pyridine, carboxylic acid, hydroxyl and benzothiazole classes. This is a crucial field for chemistry researchers to investigate Schiff's chemically modified cellulose bearing base, but there has been no detailed study of their surface chemistry and biological activities. The latest work in the thesis includes the synthesis, spectral and biological studies of the new CMC-TD, CMC-Py, CMC-PA, CMC-Hy and CMC-Bz chemically modified cellulose sequence. FT-IR and Solid-state 13C-NMR spectra have been used to describe the chemical structure. As a possible adsorbent for the removal of Cu(II) and Pb(II) metal ions from aqueous solutions, modified cellulose (CMC) is used. In addition, antimicrobial tests against selected microorganisms were performed on the CMC.

REFERENCES

[1]. A. Aklil, M. Mouflih, S. Sebti, J. Hazard (2018). Mat., 112(3), pp. 183-190.

[2]. D. McCluggage (2018). Heavy metal poisoning. Available at: ww.cockatiels.org/articles/ Diseases/metals.htm.

[3]. D. William O’Connell, C. Birkinshaw, T. (2018). Francis O’Dwyer, Biores. Technol., 99, pp. 6709–6724.

[4]. G. Vazquez, M. Calvo, M.S Freire, J.Gonzalez-Alvarez, G. Antorrena (2017). J. Hazard. Mat., 172, pp. 1402-1414.

[5]. K.L. Rule, S.D.W. Comber, D. Ross, A. Thornton, C.K. Makropoulos, R. Rautiu (2016). Chemosphere 63, pp. 64–72.

[6]. K. M. S. Sumathi, S. Mahimairaja, R. Naidu (2015). Biores. Technol., 96(3), pp. 309-316.

[7]. M. Radojevic, M.H Abdullah, A. Z. Aris (2017). Analisis Air. Scholar Press, Selangor.

[8]. M. Ajmal, R.A.K. Rao, R. Ahmad (2019). J. Ahmad, J. Hazard. Mat., 69, pp. 263-268.

[9]. R. Wahi, Z. Ngaini, V.U. Jok (2019). World App., Sci. J., 5 (Special Issue for Environment) pp. 84-91.

[10]. Ravi Kumar L. (2017). http://hdl.handle.net/10603/301916, Department of Chemistry, Bharathiar University.

[11]. T. Batey, C. Berryman, C. Line (2017). J. Br. Grassland Social, 27, pp. 139-143.

[12]. Y. Fernandez, E. Maranon, L. Castrillon, I. Vazquez (2015). J. Hazard. Mat., 126, pp. 169–175.