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Effective Separation of Manganese (II) from Aqueous Solution using Modified Sugarcane Bagasse

***Puspa Lal Homagai**, Namita Bhandari*[1] *and Sahira Joshi*[2]**

[1]*Amrit Campus, Tribhuvan University, Thamel, Kathmandu, Nepal*
[2]*Pulchok Campus, IOE, Tribhuvan University, Lalitpur, Nepal*
E-mail: homagaipl@gmail.com

Abstract

The potential to remove the risk of Mn(II) from aqueous solutions through adsorption using Charred Xanthated Sugarcane Bagasse (CXSB) as a low cost natural wastes was investigated. CXSB were characterized using Fourier transform infrared spectra (FTIR) and Far-Emission Scanning Electron Microscope (FE-SEM). The batch experiments under different parameters such as effects of pH, effect of concentration and effect of time was carried out. The concentration of metal ions before and after the adsorption was determined by using AAS. Initial concentration and adsorbent dosage in the adsorption of Mn(II) was done onto CXSB as an adsorbent. Optimum condition for each metal ions were found to be at a pH of 5 at a dose of 0.025 g and agitation speed of 180 rpm for initial metal ions concentration fixed at 50 mg/L. The removal efficiency of Mn(II) ions was found to be 74.93% at pH5.Similarly, the kinetic data best fitted for pseudo-second order. It follows the Langmuir adsorption isotherm. Hence, CXSB can be used as bio-adsorbent for the removal of Mn(II) ions from aqueous solution.

Key words: *Adsorption capacity, Adsorption isotherm, Charred xanthated sugarcane bagasse, Removal.*

Introduction

It is a matter of global concern these days regarding the heavy metal pollution into the environment due to various human activities and rapid industrialization[1]. Manganese is one of the chemical risks in water although trace levels of manganese are essential for growth and development of humans, animals and plants. However, for health and aesthetic considerations the amount of manganese in drinking water should be limited to very low values[2]. In nature, manganese occurs as a compound, found in many types of rocks. It is usually found together with iron and silica and is the 10th most abundant element in the earth's crust. It is a constituent of more than 30 manganese oxide/hydroxide based minerals, playing an active role in the environmental geochemistry. Manganese oxides are ubiquitous in soils and sediments, and because they are highly chemically reactive and strong scavengers of heavy metals, they exert considerable influences on the chemical behavior of sediments, soils and associated aqueous systems.

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* *Corresponding author*

Manganese can exist in multiple oxidation states. The environmentally and biologically most important minerals are those containing Mn^{2+} or Mn^{4+} [3].

When dissolved in water, manganese reaches the surface of ground water and exposes to air, it becomes insoluble and makes water brown or red[4]. Manganese with low level concentration causes some problems such formation of oxide deposits in pipelines, discoloration of water and laundry as well as impart an unpleasant metallic taste[5]. In addition, the problems of manganese with high level concentration include health concerns, aesthetic and economic problems[6]. It is dangerous for brain tissue and affects the central nervous system. Also, the presence of high levels of manganese creates neurological disorders such as Parkinson's disease. Because of that problems occur due to presence of manganese in water, as well as of their toxicity, non-biodegradability and persistent nature, their removal becomes an absolute necessary. Adsorption technology is the most widely used treatment method of organic and inorganic toxic wastes[7].

Heavy metals are hazardous, and toxic even at low level bioaccumulation in water according to world health organization[8]. For this reason, the removal of heavy metal ions from wastewater have become major source of concern to water quality managers and is given extensive research attention. Conventional methods were used for removing manganese ions include chemical precipitation, chemical oxidation and reduction, ion exchange, electrochemical treatment. These methods are expensive and generation of toxic sludge[9].

Recently, numerous higher plants biomass materials utilized as solid phase extractors and they have good adsorption properties such as sugarcane bagasse[4], maize husk[10] and rice husk ash[11]. The study of adsorption for the treatment of wastewater has been proven to be less expensive, effective for wastewater treatment depending on the type of adsorbent used. Sugarcane bagasse is the kind of byproducts obtained from juice shop. They contain cellulose, hemi-cellulose and lignin. This variety of chemical composition and consequently functional groups make Sugarcane Bagasse (SCB) showed different efficiencies for removal of heavy metal ions such as for SCB Fe(III), Cd(II), Cr(IV) and Ni(II)[12, 13,14]. In this regards, locally available sugarcane bagasse will be considered for the chemical modification with the introduction of xanthate group onto its polymer analog. The selectivity of xanthate group is more due to sulphur has more affinity towards manganese in the adsorption process. Further, the effectiveness of adsorbent thus prepared will be applied for the removal of manganese from contaminated water. Since, the presence of manganese in drinking water is of particular risk. The WHO health based guideline value for manganese in drinking water is 400 μg/L[15].

The general objective of the research is to develop efficient and selective adsorbent by simple chemical modification from locally available agricultural waste product, which can replace expensive synthetic chelating resin.

Experimental Methods

Preparation of adsorbent material

Locally collected sugarcane bagasse (SCB) from juice center, Kathmandu was cut into small pieces and dried under sunlight, kept in air oven at $60^{\circ}C$ for 24 hrs and dried sample was grounded into fine particles with uniform size of 250 μm. The bagasse powder was treated with concentrated H_2SO_4 and left for overnight. It was washed with deionized water until neutrality and drying it is referred as charred sugarcane bagasse (CSB). It is known to us that acid treatment with such biopolymer creates a suitable environment for its ring opening. In addition to dehydrating property of acid, such materials were found to be effective for further chemical modifications. In this regard, the 20 g of charred material was xanthated by adding 100 mL of 15% sodium hydroxide and then mixture was left for 3 hrs. After that 20 mL carbon-disulphide was added to mixture and was stirred and kept for 48 hrs. It was washed till neutrality and dried at 70-80 °C and finally kept in desiccator. This material is ready for the experiments and called as charred xanthated sugarcane bagasse (CXSB).

Chemicals

All reagents and chemicals used in this study were LR/AR grade. Appropriate amount of monohydrated manganeous sulphate salt was dissolved to prepare 1000 mg/L standard stock solutions. The working solutions of different concentrations were diluted using 1M HNO_3.The pH of experimental solution was adjusted using 1 M NaOH and 1M HCl.

Adsorption experiment

In the batch adsorption method, a definite mass of adsorbent is agitated with the series of required volume of solution containing different amount of heavy metals and supernatant liquid is analyzed to determine the extent of adsorption. In this study to understand the mechanism and effectiveness of adsorption, any parameter is changed by keeping other constant. Adsorption of Mn(II) on different adsorbent is influenced by various parameters like pH of the solution, amount of adsorbent used, initial concentration of Manganese(II) solution, contact time etc. So these parameters are studied by batch adsorption method in which a series of solutions are prepared by varying any one parameter keeping other parameter constant [16].

The amount of metal ion adsorbed in mg/g at time 't' is computed by the formula

$$q_t = (c_o - c_e) \times \frac{v}{m_s} \quad \text{..............................(1)}$$

Where, C_o and C_e are the metal ion concentrations in mg/L initially and at time 't' respectively. V= volume of the metal ion solution in L and m_s = weight of adsorbent in gram.

The percentage of metal ion adsorbed (A %) is calculated by;

$$A\% = \frac{C_o - C_e}{C_0} \times 100 \quad \text{.................... (2)}$$

$$\text{And, } D = \frac{C_o - C_e}{C_0} = \frac{q_e}{C_e} \quad \text{.................... (3)}$$

Where, D= distribution factor for the adsorption in (L/g).

Results and Discussion

Element Analysis

In order to detect the element present in the prepared sample, it was analyzed using the element detector (Nepal Bureau of Standard and Metrology).

Table 1: Elemental analysis of sugarcane bagasse before and after modification

SN	Samples	% C	% S
1	RSB	41.17	0.04
2	CSB	45.77	0.80
3	CXSB	42.10	1.27

From the above table, it is clear that the percentage of carbon and Sulphur varies in the RSB, CSB and CXSB respectively which indicates the good modification of the sample. The percentage of Sulphur in CXSB is more in comparison to other because carbon-disulphide was used during xanthation process. The percentage of Sulphur needs to be more because the adsorption of Mn is more in the CXSB than in the RSB and CSB.

FE-SEM Analysis

The surface morphology of RSB, CSB before modification whereas for CXSB and CXSB (ads) after chemical modification, was analyzed using far-emission scanning electron microscopy (FE-SEM). The surface of RSB was found to be smooth whereas the fiber surface of CSB was found to be relatively rough and non-uniform due to hydrolysis reaction on the surface of SB by the action of concentrated sulphuric acid. The surface morphology of RSB, CSB, CXSB and CXSB (ads) was characterized by SEM images shown in Fig. 1(a), 1(b), 1(c) and 1(d) respectively. Xanthation process had considerably enhanced the morphology of charred sugarcane bagasse and its physical, chemical and biodegradable characteristics, which varies with respect to the nature of synthetic side chains incorporated. SEM observations of CSB revealed its non-uniform and rough surface that changed into irregular honeycomb structure of CXSB. The CXSB showed apparently isolated and irregularly distributed pores, which are supposed to be formed due to the increase in effective diffusion surface area that helps to expose more surface-active binding sites and finally enhance adsorption capacity of the modified sugarcane bagasse. Similarly, the CXSB (ads) showed that after the adsorption of metal, the honeycomb surface like structure is completely filled which indicates that the adsorption takes place properly.

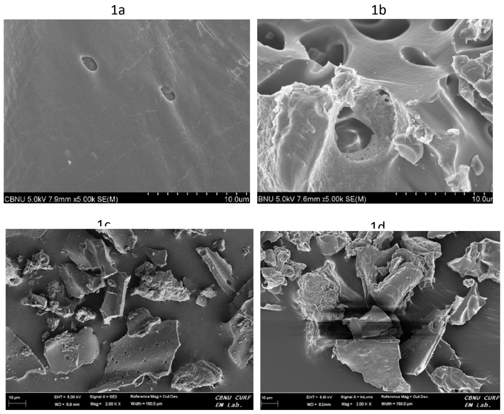

Figure 1: *SEM image of (1a=RSB), (1b=CSB), (1c=CXSB) and (1d=CXSBads)*

FTIR Analysis

FTIR is a useful tool to identify the presence of certain functional groups in a molecule as each specific chemical bond often has a unique energy absorption band. The spectral analysis was employed to confirm changing of functional groups for pretreated and xanthated sugarcane bagasse. The FTIR spectrum of different sugarcane bagasse was recorded with KBr dispersion method where SB and KBr ratio was taken 1:100 to make tablet. The broad, intense absorption peaks observed at 3396.33 cm^{-1} are due to the existence of bounded hydroxyl groups in CSB than RSB. Similarly, hydroxyl groups were observed at 3381.02 cm^{-1} and 3379.15 cm^{-1} in CXSB and CXSB (ads). The peaks observed at 1034 cm^{-1} are characteristics of C-O group of primary hydroxyl stretching that may be attributed to cellulose structure of the sugarcane bagasse. The band at 1708 cm^{-1} was observed is due to the –CHO group formed during the charring process before modification of CSB. This peak disappears after modification of CSB into CXSB and an intense broad band depicted in Figure: 2 is observed at 1576 cm^{-1} revealing that xanthate group has been introduced onto the CSB. Absorption peaks appeared at 1576 cm^{-1} corresponding to the C=S stretching vibration of the xanthate unit and it may be attributed to the –CS_2H deformation suggesting that CXSB has been successfully xanthated. The stretching vibration of C=S, S=O and S-S found at 1206, 1038 and 438 cm^{-1}, respectively in the spectrum of CXSB were strong indicative of the presence of xanthate group bonded to the charred materials. The major absorption bands characteristic of the C=S groups lay in the region 1563 -700 cm$^{-1.}$ This region is much more intense for CXSB in comparison to CSB. The peak corresponding to C-S-S and C-O-C symmetric stretching seemed to have merged into a broad band at 1576 cm^{-1}. The asymmetric stretching vibration of C-O-C is observed at 1206 cm$^{-1,}$ [17].

Generally, the binding of metal ions to adsorbents may be proceed via complexation with functional groups, ionic exchange, surface precipitations and chemical reaction with surface sites. Regarding FTIR for CXSB after Mn(II) adsorption, it was found that carbonates, -C-OH and phenyl group are affected after uptake process. This is judging from shifts in their position, shape or band intensity from 1390.22, 1206.88 and 646.97 cm^{-1} to 1380.44, 1203.65 and 622.93 cm^{-1} for CXSB and CXSB (ads) respectively.

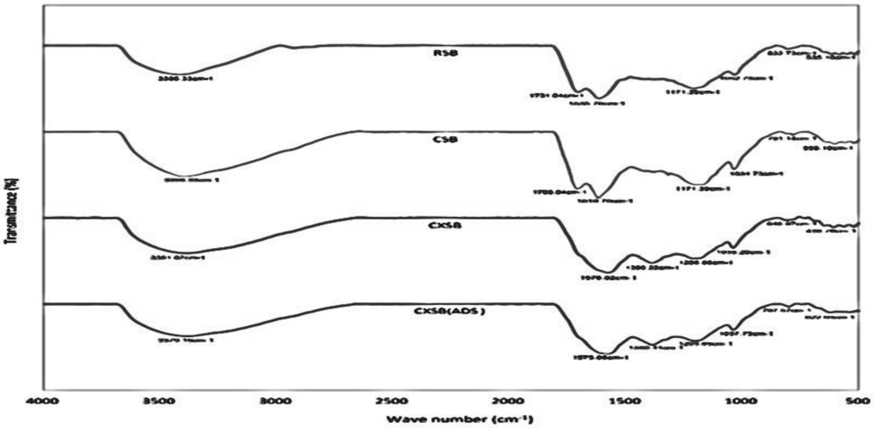

Figure 2: *FTIR peaks showing the functional groups of RSB, CSB, CXSB and CXSB (ads).*

pH_{PZC} (Point of Zero Charge)

Depending on solution pH, the adsorbent surfaces can bear net negative, or positive, or no charge. The pH where the net total particle charge is zero is called the point of zero charge (pH_{PZC}), which is one of the most important parameters used to describe variable-charge surfaces. If the pH of adsorbent surface is above its $pH_{PZC,}$ the adsorbent surface will have a net negative charge and predominantly exhibit an ability to exchange cations, while the modified adsorbent will mainly retain anions (electrostatically) if its pH is below its PZC. The point of zero charge for RSB and CXSB was found to be 5 and 6 as shown in Figure: 3.

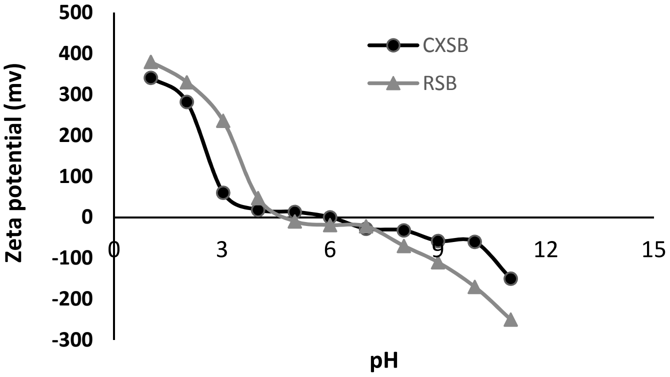

Figure 3: *A typical plot of Zeta potential Versus pH*

Effect of pH

Figure: 4 shows that effect of pH on adsorption of Mn (II) onto Charred Xanthated Sugarcane Bagasse at initial concentration of 50 ppm at room temperature. The pH value of the heavy metals plays an important role in the adsorption process on not only the site dissociation of the adsorbent surface but also on the solution chemistry of the metals, which include; hydrolysis, complexation by organic and inorganic ligands, redox reactions, precipitation, the speciation and the adsorption availability of the heavy metals. This is clearly indicated as shown in figure: 4 for the uptake of Mn(II) ions as a function of pH (1.0-6.5). Therefore, at low pH values showed very low tendency for uptake of Mn(II) due to protonation of its functional groups or competition of H^+ with metal ion for binding sites[18]. The binding capacities reached their maximum percentage removal around pH 5.0. At pH<5.0 Mn(II) was precipitated due to presence of OH^- forming manganese hydroxide precipitate. Thus, the maximum adsorption was obtained at pH 5.0 for Charred Xanthated Sugarcane Bagasse[19].

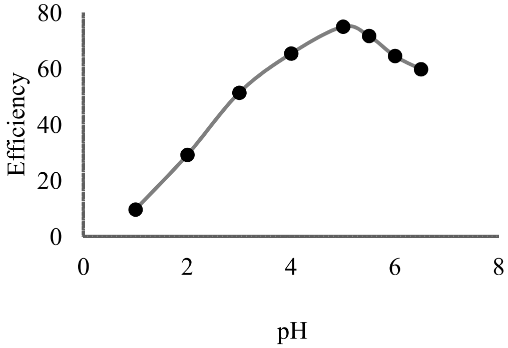

Figure 4: Effect of pH for adsorption of Mn(II) onto CXSB

Effect of Initial Concentration

The adsorption isotherms for the adsorption of Mn(II) onto CXSB are shown in figure : 5. The adsorption of Mn(II) onto CXSB, adsorbents increases with increase in initial concentration of the ions solution and then reaches a plateau where it attains equilibrium. Experimentally, it was observed that the amount of adsorption increased from 5 mg/g to 40 mg/g in a rapid manner and after the initial concentration of 70 mg/L, there was not any significant changes at its optimum pH 5. Hence, the maximum adsorption was 250 mg/g.

The chemical modification on CXSB results in enhancing the sorption capacity. This may be attributed to an increase in the driving force of the concentration gradient with increase in order to overcome all mass transfer resistance of metal ions between the aqueous and solid phase. Therefore, higher initial concentration of metal ions may increase the adsorption capacity. It can also be explained that the adsorbent has a limited number of active sites, which becomes saturated at a certain concentration. This indicates that the sorption capacity will increase with the increase in initial concentration gradient.

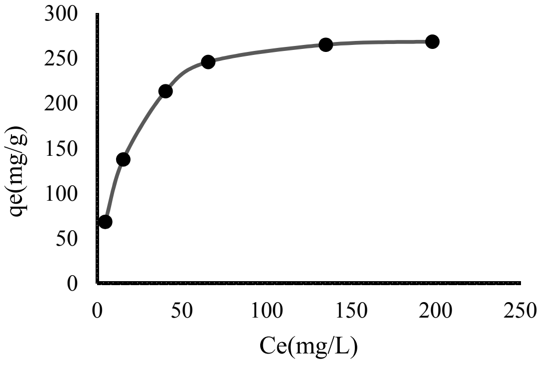

Figure 5: *Adsorption Isotherms for Adsorption of Mn(II) onto CXSB*

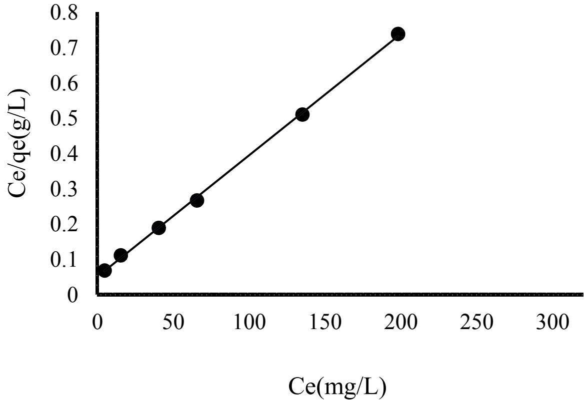

Figure 6: *Langmuir Adsorption Isotherms for Adsorption of Mn(II) onto CXSB*

At lower initial concentration sufficient sorption sites are available for the sorption of the metal ions therefore the fractional sorption is independent of initial metal ion concentration. Therefore, at higher initial concentration, the numbers of metal ions are relatively higher than adsorption sites; hence the removal percentage depends on the initial concentration. At higher metal ion concentration adsorption tends to be constant which indicates Langmuir type of adsorption as shown by figure: 6.

Kinetic Studies of Adsorption of Mn(II)

The bio sorption of mercury was fast in the early stages, and the equilibrium attained in 60 min of contact time as shown in figure: 7. The removal of Mn(II) increased from 12 mg/g to 25 mg/g sharply with time in the initial stage of 0-60 min range and then steady augmentation to attain equilibrium to just about 60 min time. Therefore, the optimum time and initial concentration for attaining the adsorption equilibrium is 60 min and 50 mg/L, respectively. It is perceived from the outcome that additional increase in the contact time has negligible effect on the sorption of metal ion. Kinetics studies for the adsorption of Mn(II) on CXSB were studied by using different kinetics models and pseudo second order.

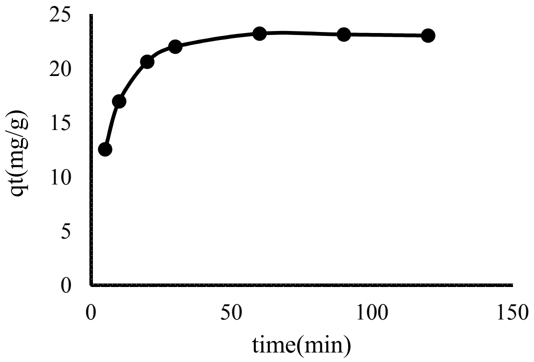

Figure 7: *Effect of contact time in the adsorption of Mn(II) onto CXSB*

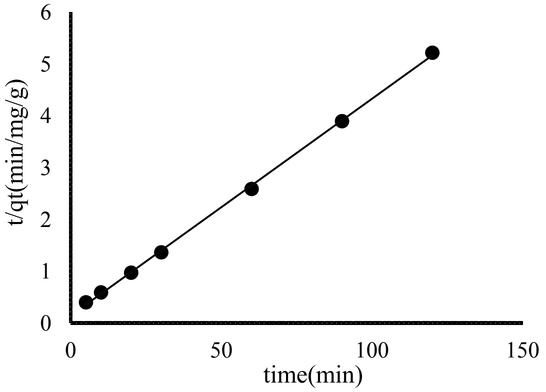

***Figure 8:** Pseudo-second order kinetics for Mn(II) onto CXSB*

Pseudo second order kinetic plot of (t/q_t) vs t gave the perfect straight line for the adsorption of Mn(II) onto CXSB indicating that the adsorption reaction can be followed through the pseudo second order kinetic model as shown by figure: 8. High value of correlation coefficient in pseudo second order plot than pseudo first order are the additional evidence to conform that the adsorption reaction proceeded by the pseudo second order kinetic model.

Conclusion

An effective adsorbent for the removal of the Mn(II) has been investigated by making simple chemical modification of Sugarcane Bagasse Waste. The Charred Xanthated Sugarcane Bagasse (CXSB) prepared at our laboratory was found to be good adsorbent for its removal than those which were previously found in different literature. The optimal conditions for Mn(II) removal onto CXSB occured at pH 5.0 with adsorbent dose 0.025 g, agitation speed 180 rpm at room temperature. The equilibrium was found to be 60 minutes to sufficiently remove Mn(II). The obtained data were used for mathematical description of the biosorption process for Langmuir and Freundlich isotherms. The data were fitted to Langmuir isotherm with higher correlation coefficient values is 0.999. The adsorption process followed Pseudo-second order kinetics with a correlation coefficient value is 0.999. The results obtained from the batch experiments concluded that CXSB has the potential to be used in real practice for manganese removal from the aqueous solution. Thus, it can be concluded that CXSB is highly effective in the separation / purification of Mn(II) from waste water.

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