

Development of Natural Cation Exchanger for the Treatment of Lead ions from Aqueous Solution

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Abstract

*Cellulose, hemicelluloses and lignin are the main constituents found in sugarcane (*Saccharum officinarum*) bagasse having many surface active sites containing hydroxyl and/or phenolic groups which are effective for chemical modification. The biowaste was first charred with concentrated sulphuric acid and then the charred aminated sugarcane bagasse (CASB) was prepared by reduction followed by oxidation. The developed bio-sorbent was characterized by SEM, TGA/DTA, FTIR and elemental analysis. Batch adsorption methods were carried out to determine Pb^{+2} sorption capacities at different pH ranges and sorbate concentrations. The maximum adsorption capacity for Pb^{+2} was found to be 323 mg g^{-1} with an efficiency of 98% at pH 4. The experimental data showed a good fit to Langmuir isotherm as compared to Freundlich isotherm models. The kinetics was best fitted with the pseudo-second order model. The adsorption equilibrium was attained within 20 min. The high adsorption capacity and fast kinetics results of the charred aminated sugarcane bagasse indicated that it might be potential adsorbent for the removal of lead from contaminated water.*

Keywords: *Charred aminated sugarcane bagasse, Lead, Isotherms, Adsorption.*

Introduction

Presence of heavy metals in the environment is a serious pollution problem that has been and still is a focus of attention all over the world. Contamination of soils, groundwater, surface water and air with hazardous and toxic chemicals poses significant problems for human health and the environment. Heavy metals are considered to be particularly dangerous pollutants for all living beings. Their presence in the wastewater of several industrial processes, such as electroplating, metal finishing, metallurgical work, tanning, chemical manufacturing, mining and battery manufacturing, has brought about more environmental concerns due to their toxicity even at low concentration. Since heavy metals are non-biodegradable and they can be accumulated in living tissues, causing various diseases and disorders; therefore they must be removed before discharge. Lead has been cited as one of the three most toxic metals that have latent long-term negative impacts on health, causing anemia, encephalopathy, hepatitis and nephritic syndrome. Different conventional techniques like ion-exchange, membrane separation, lime precipitation, reverse osmosis, solvent extraction, electro-dialysis and adsorption are often used for the separation of heavy metals. The application of low-cost adsorbents obtained from agricultural by-products¹⁻⁵ widely used in the recent research as a replacement for costly conventional methods of removing heavy metal ions from wastewater. The bio-sorbent obtained from plant wastes are environmentally friendly in comparison to synthetic adsorbent in the incineration process. It is well known that all plant materials are composed of cellulosic network which can be easily converted into required modification. Recently, much attention is given to prepare adsorbents from various wastes generated from forestry⁶ and fishery⁷⁻⁸. In Nepal, sugarcane industries produce a large amount of

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sugarcane bagasse (SB) as a byproduct which is found free of cost and that requires little chemical processing to increase its sorptive capacity, hence its cost is supposed to be low even after chemical modification. The main constituents of sugarcane bagasse are cellulose (46.0 %), hemicellulose (24.5 %) and lignin⁹ (19.95%) The polysaccharides found in sugarcane bagasse are biopolymers having many hydroxyl and/ or phenolic groups that can be chemically modified to form new compounds with changed properties¹⁰⁻¹¹. Although there are some reports of raw sugarcane bagasse as the adsorbent¹²⁻¹³, however, owing to its low adsorption capacity, we have explored a simple means of chemical modification to enhance its metal adsorption properties in the present study. The study of bagasse as an adsorbent to reduce the environmental pollutants has also received much attention recently^{5, 14}.

On the other hand, the application of raw plant wastes as adsorbents can bring a lot of problems due to release of soluble organic compounds contained in the plant materials⁶. The soluble organic compounds may increase COD, BOD and TOC which causes depletion of oxygen content in water and can threaten the life. Therefore, plant wastes need to be modified chemically before being applied for the removal of heavy metals. In general, the chemically modified plant wastes exhibit surface complex formation, ion exchange, and chelation that have been considered as the important adsorption mechanisms for heavy metal sequestration. It has been reported that adsorbents with carboxyl, sulphonic, and phosphoric groups on the surface favor metal ion adsorption through the ion exchange mechanism while those containing nitrogen on the surface with amino group facilitate metal ion adsorption through the chelation mechanism.

The main objective of this research work is to introduce an amine functional group onto the cellulosic backbone present in sugarcane bagasse. The nitrogen atom contained in charred aminated sugarcane bagasse has a greater tendency to form stable complexes with heavy metal ions to sequester them from aqueous solution. The adsorbent CASB is derived from natural polysaccharides which is easy to be incinerated in comparison to commercial ion exchange resin made up of plastic materials. Furthermore, the comparative adsorption capacity of Pb (II) ions onto different chemically modified adsorbent has been enlightened.

Experimental Methods

Preparation of adsorbent material

Locally collected sugarcane bagasse (SB) from Baneshwor juice centre, Kathmandu was cut into small pieces and dried under sunlight and then kept in air oven at 60°C for 24 h. The dried sample was grounded into fine particles with uniform size of 212 µm. The bagasse powder was treated with concentrated H₂SO₄ 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 opening¹⁵. In addition to dehydrating property of acid, such materials were found to be effective for further chemical modifications. In this regard, the charred material was aminated adding sodium dithionite, pyridine and ammonia at 20°C followed by nitration and left for overnight. It was washed till neutrality and dried at 70°C and finally kept in desiccator. This material is ready for the experiments and called as charred aminated sugarcane bagasse (CASB).

Chemicals

All reagents and chemicals (Wako Chem. Ltd. Japan) used in this study were analytical grade. Appropriate amount of lead nitrate salt was dissolved to prepare 1000 mg/L standard stock solutions. The working solutions of different concentrations were diluted using 0.1M HNO₃. The pH of experimental solution was adjusted using 0.1 M NaOH and 0.1M HNO₃ whereas 2-[4-(2- Hydroxymethyl) -1-piperazinyl] ethanesulfonic acid (HEPES) was used as a buffering reagent.

Adsorption experiments

The pH of the working solutions of lead (II) was adjusted by adding either small amount of nitric acid or sodium hydroxide after adding 0.1M of HEPES as a buffering agent. In the batch-wise experiments, 20 mg of dried adsorbent was taken into 50 ml Erlenmeyer flask with 15 ml test solution maintaining the concentration of 50 mg/L. The flasks were shaken vigorously in a thermostated shaker (Thermostatic Shaking Incubator AT 24R, Japan) at 303 K and 150 rpm for 24 h to attain the equilibrium. The initial and equilibrium concentrations of the metal ions were measured by using Shimadzu AA-6650 Atomic Absorption Spectrophotometer (AAS). The adsorption efficiency, A% of the metal ion was calculated from equation (1).

$$A \% = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

The sorption capacity of metal ions is the concentration of the metal ions on the adsorbent and can be calculated based on the mass balance principle using equation (2).

$$q = \frac{C_i - C_e}{W} \times \frac{L}{1000} \quad (2)$$

In the above equations, q represents the amount of metal uptake per unit mass of the adsorbent (mg g^{-1}), L is the volume of the test solution (mL), W is the dry mass of the adsorbent (g), C_i and C_e the initial and final concentrations (mg dm^{-3}), respectively.

Results and Discussion

SEM analysis

The surface morphologies of CSB and CXSB were observed by using a scanning electron microscopy (SEM) using an S-3000N Scanning Electron Microscope of HITACHI, Japan. 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 CSB and CASB was characterized by SEM images shown in Fig. 1(a) and 1(b). It can be seen that the external surface of CASB is full of cavities like a honeycomb structure containing isolated and irregular pores. Amination of charred sugarcane sufficiently enhanced the morphology of CSB and its physical, chemical and biodegradable characteristics which vary with respect to the nature of synthetic side chains incorporated.

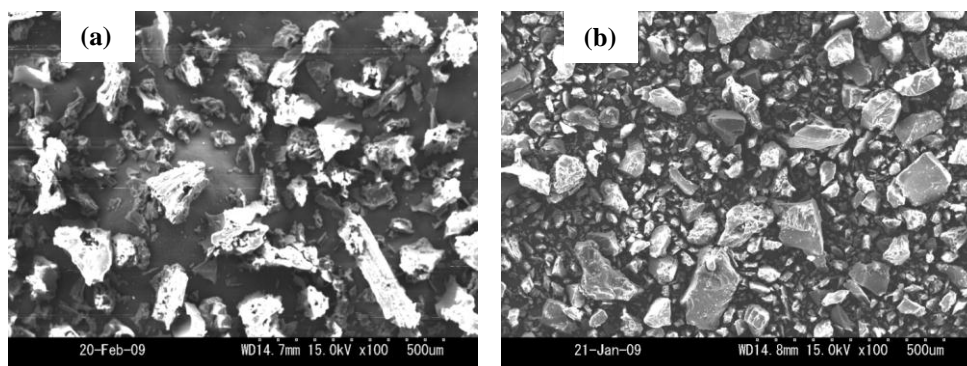


Figure 1: SEM images showing the surface morphologies of (a) CSB before modification and (b) CASB after modification.

FTIR Characterization

FTIR spectrophotometer (FT/IR-410 (JASCO, Japan) was used to identify the functional groups present in a bio-adsorbent. The spectra in the 3500- 400 cm^{-1} regions are shown in Fig. 2a and 2b for CSB and CASB. The modification of CSB with $\text{Na}_2\text{S}_2\text{O}_4$ and 25 % NH_3 transforms CSB to CASB. In this transformation many characteristics bands are shifted at the maximum peak, and absorbance is changed. The peak observed at 3484 cm^{-1} is due to the stretching vibration of the O-H groups. Although there is possibility of overlapping between the N-H and the O-H stretching vibrations, the strong broad band at the wave number region of $3300\text{-}3500 \text{ cm}^{-1}$ is characteristic of the N-H stretching vibration. The significant decrease of transmittance in this band region after lead adsorption indicates that the N-H

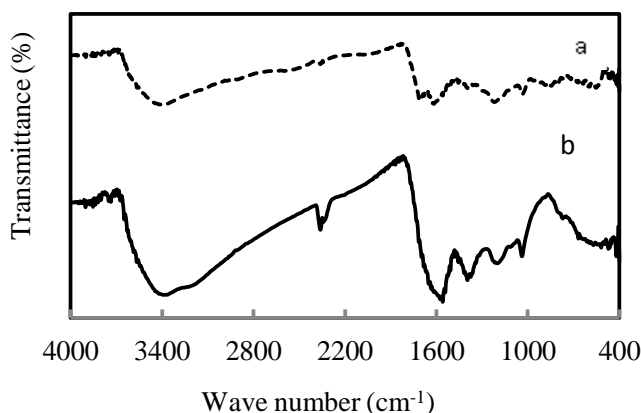


Figure 2: FTIR of (a) CSB an (b) CASB

vibration was affected due to lead adsorption. Other changes in the transmittance can be observed at the wave number of 1720, 1644, 1457, 1251, 1049 and 902 cm^{-1} , respectively. These wave numbers are closely related to the N-H bending, C-N stretching, and N-H rocking bands. The board and strong band ranging from $3300\text{-}3500 \text{ cm}^{-1}$ may be due to overlapping of O-H and N-H stretching, which is consistent with the peaks at 1644 and 1047 cm^{-1} assigned to alcoholic C-O and C-N stretching vibration¹⁶. Prior to modification of CSB the band at 1720 cm^{-1} is due to the $-\text{CHO}$ group formed during the charring process. This peak disappears after modification of CSB into CASB and an intense broad band depicted in Fig. 2(b) is observed at 1592 cm^{-1} revealing that amino group has been introduced onto CSB. The amount of carbon, hydrogen and nitrogen in CSB and CASB were found to be different from the raw sugarcane bagasse (RAW) is depicted in the Table1. After amination, the increased percentage of nitrogen confirmed that there was proper modification of charred sugarcane bagasse by the introduction of amine group.

Thermal analysis

The thermal stability and degradation behavior of CSB and CASB samples were evaluated by thermo gravimetric analysis (TGA) and differential thermogravimetric analysis (DTA) in a N_2 atmosphere using a thermal analyzer (Model TG/ DTA 6300, Seiko Instrument Inc. Extar 6000). Charred sugarcane bagasse degraded mainly two stages such as devolatilization and solid decomposition, the first at $230 \text{ }^\circ\text{C}$ and last one at $430 \text{ }^\circ\text{C}$. The first step can be assigned to decomposition of fibers and second corresponds to the complete decomposition. Same way CASB also showed two decomposition steps at $250 \text{ }^\circ\text{C}$ and $520 \text{ }^\circ\text{C}$, respectively. These results are depicted in the TGA and DTA curves shown in Fig. 3(a) & (b) for CSB and CASB, respectively. The first stage started at about 100°C for all the materials with weight loss of 10-

20% due to loss of physically adsorbed water on membrane surfaces. The second stage exhibited a rapid weight loss at 230-430 °C and 250- 520 °C for CSB and CASB, respectively. The maximum oxidation reached at 430 °C for CSB and 520 °C for CASB. The second degradation stage of CASB took place at higher temperatures than the corresponding stage of CSB indicating that CSB is less stable than CASB. The weight loss for CSB (230-430 °C) and CASB (250- 520 °C) were found to be about 85% and 82%, respectively. The DTA curves revealed interesting and more accurate differences of the thermal behavior of the CSB and CASB than the TGA curves. The DTA peak of CASB had shown its maximum value at about 520°C, while it is 430°C for CSB indicating a strong evident in the increase in thermal stability of the CASB over CSB. From the aforementioned analysis it is concluded that chemical modification has taken place within the CSB.

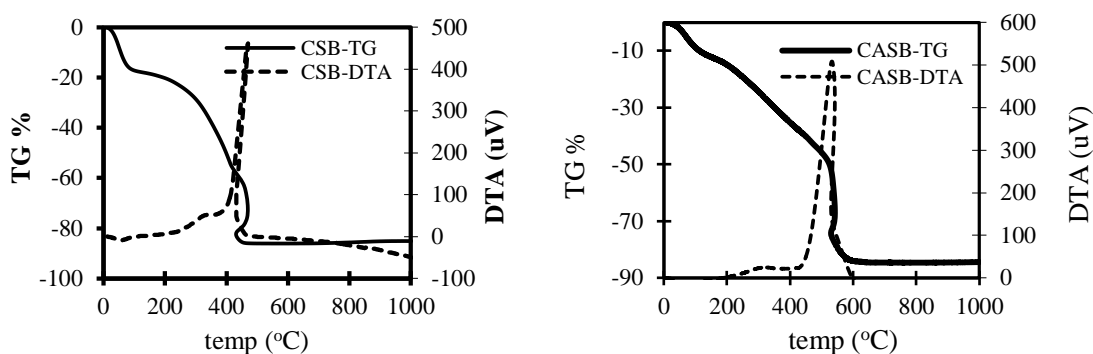


Figure 3: TG-DTA curves of (a) CSB (before modification)and (b) CASB(after modification)

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

Adsorbents/Elements	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulphur (%)
RSB	46.58	5.95	0.23	0.32
CSB	50.24	3.65	0.51	2.46
CASB	49.41	2.99	6.29	3.01

Effect of pH

The removal of metal ion from aqueous solution by adsorption is dependent on solution's pH and, since it affects adsorbent surface charge, on the degree of ionization, and on the adsorbates species. The solution pH was measured before and after adsorption of metal ions from aqueous solution by using a pH meter (HM- 30R, TOA-DKK). At low pH, there is high concentration of H⁺ that has high mobility as compared to metal ions and competition between H⁺ with metal ions decreases their adsorption. On the other hand, as the pH value of the solution increases, adsorption also increases due to lesser number of H⁺ and greater number of surface ligands with negative charges. The low adsorption of metal ions at low pH may be due to sorbate lyophobic behavior¹⁷. In the same way, the solubility of metal in solution decreases with increasing pH and the sorption increases with increasing of pH. The optimum pH for Pb (II) was found to be 4 for all adsorbents where adsorption efficiency of CASB was evaluated 98% .The adsorption capacities onto raw sugarcane bagasse (RSB), CSB and CASB were compared to find out

maximum sequestration of lead (II) ion from the aqueous solution at different pH ranges which is shown in Fig.4.

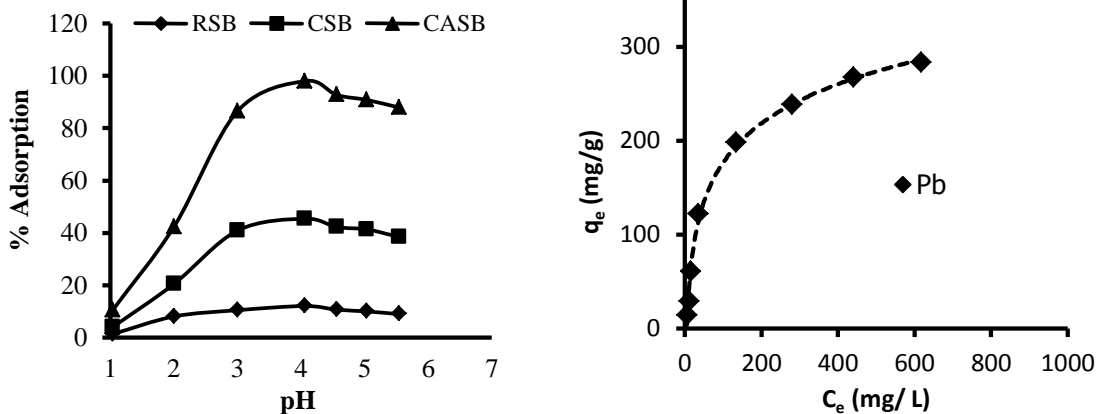


Figure 4 (left): Adsorption Pb(II) ion as a function of pH onto RSB, CSB and CASB. **Figure 5 (right):** Adsorption isotherm plot for the adsorption of Pb²⁺ ions onto CASB.

Adsorption isotherms

Adsorption isotherms describe how adsorbates interact with adsorbents and are important in optimizing the use of the bio-sorbent. The functionalized adsorbent CASB has been allowed to react with aqueous solution of Pb(II) for the attainment of equilibrium state. Here isotherm studies were performed using various concentrations of the metal ion ranging from 25 to 1000 mg/L. For batch adsorption experiment, 20 mg of adsorbent was equilibrated with 15 ml of synthetic lead (II) solution in 50 ml Erlenmeyer flask for 24 h to attain equilibrium. All the adsorption data were tested with the Langmuir isotherm and Freundlich isotherm model using the linear form as represented by Eqs. (3) and (4).

$$\frac{C_e}{q_e} = \frac{C_e}{q_m b} + \frac{C_e}{q_m} \quad (3)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

Where C_e (mg/L) is the equilibrium concentration of metal ion in aqueous solution and q_e is the amount lead adsorbed at equilibrium (mg/g). The Langmuir constant q_m (mg/g) represent the monolayer adsorption capacity, b (L/mg) the binding constant, n (dimensionless) a constant of adsorption intensity and K_F (L/mg) is Freundlich constant characterizing the adsorption capacity. To examine the relationship between the metal sorption capacity (q_e) and the metal ions at equilibrium (C_e), the sorption equilibrium data for lead was compared to Langmuir and Freundlich isotherms models, where the Langmuir and Freundlich constants and its correlation coefficients evaluated from the isotherm for Pb²⁺ are given in Table 2. The sorption characteristics of the metal ions on the CASB followed more closely the Langmuir isotherm model than the Freundlich isotherm model. The high value of Langmuir correlation coefficient confirmed that the Langmuir isotherm is best fitted than the Freundlich isotherm onto CASB. The maximum adsorption capacity based on experimental results as shown in Figure 5 found to be 267mg/g.

On the other hand, the theoretical maximum monolayer capacity (q_m) of the metal ions based on Langmuir adsorption equation was determined to be 323mg/g from Figure 6. This result is in close agreement against each other suggesting that lead like heavy metal can be quantitatively sequestered onto CASB. The adsorption sites for the mentioned metals are at nitrogen atoms of attached to amine groups. The complexation mechanism of the metal ions with the amino group is taken place through ion exchange process. According to HSAB theory, aminated biosorbent acts as soft bases tends to form stable complexes with heavy metals such as Pb (II), thus CASB will have a much higher affinity and sorption capacity as compared to that of raw biomass. The essential characteristics and the feasibility of the Langmuir isotherm in terms of a dimensionless constant, separation factor or equilibrium parameter R_L , which is defined as by Eq. (5)

$$R_L = 1 / (1 + bC_i) \quad (5)$$

The R_L value indicates the shape of the isotherm as $R_L > 1$: unfavourable, $R_L = 1$: linear, $0 < R_L < 1$: favourable, $R_L = 0$: irreversible adsorption. The value of R_L found to be 0.8711 by calculating the data of b, taking initial that concentration of sorbate and concluded that Langmuir adsorption isotherm is favourable.

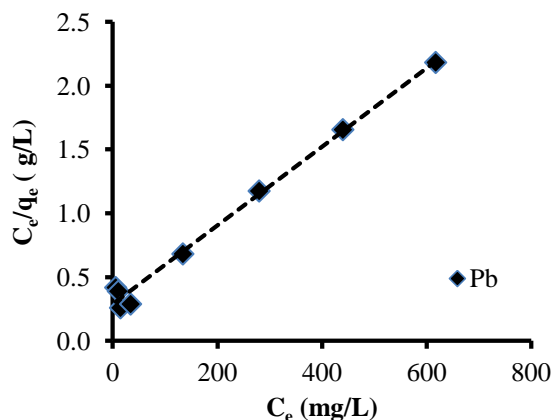


Figure 6: Langmuir isotherm plot for adsorption of Pb^{2+} ion onto CASB

Table 2: Pb(II) adsorption onto CASB for different constants of Langmuir and Freundlich isotherms

Langmuir model				Freundlich model		
q_m (mg/g)	R^2	b (L/g)	R_L	K_f	n	R^2
323	0.990	0.0059	0.8711	1.063	1.154	0.807

Sorption kinetics

The rate of metal sorption is an important factor and a prerequisite for the determination of a successful practical adsorption application. The kinetic results of the adsorption of metal ions onto CASB are shown in Fig7. The sorption kinetics of the metal ions onto CASB was analyzed as the function of

time at an initial concentration of 100 mg/L solutions. The concentrations of the metal ions were analyzed keeping their optimum pH 4 in a regular and certain interval of time by AAS. From the experimental data, it is observed that the percentage of adsorption increased with the increase in time from 5 to 20 min and then it became constant in the range from 20 min to 240 min. The pseudo-second order kinetics model has often been used to fit the experimental kinetic adsorption data. The linearized pseudo-second order kinetic equation¹⁸ is used as the following form:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

Where q_t (mg/g) is the amount of adsorption at time t (min), K_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant of the pseudo-second order kinetic adsorption. The values of K_2 and q_e can be obtained from the intercept and slope of the plot of the experimental t/q_t versus t . The experimental data which can be explained by the pseudo-second order kinetic model, with the correlation coefficient R^2 being almost unity (0.99) for the lead ions. The experimental value of K_2 was found to be $2.21 \times 10^{-2} \text{ g mg}^{-1} \text{ min}^{-1}$, computing the intercept values from the plot that is based on kinetic model as shown in Figure 8.

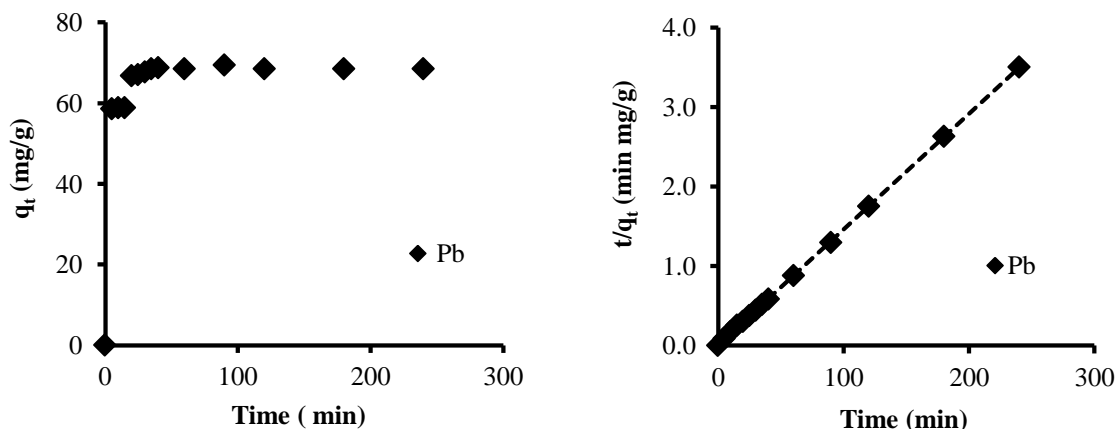


Figure 7 (left): Kinetic study for the adsorption of Pb^{2+} ion onto CASB **Figure 8 (right):** Pseudo-second order sorption kinetic for adsorption of Pb^{2+} ion onto CASB

Desorption Studies

The regeneration of the sorbent may be crucially important for keeping the process costs down and to recover the pollutant extracted from the solution. In this studies, desorption was carried out by batch method for the evaluation of the adsorbed metals as well as the regeneration of the adsorbent. Pb (II) desorbed from CASB was found to be 96% using 0.1 M HNO_3 as an eluting agent. After three cycles of operation the adsorption capacity decreased from 96% to 76%. Regeneration of the CASB with 0.1 M CaCl_2 was efficient for further use. Here 76% desorption was achieved for Pb^{+2} with 0.1M HNO_3 solution. Thus the study reveals that the adsorbent can be reused which makes the process more economical and eco-friendly due to minimal solid waste generation.

Table 3: Comparative adsorption capacity of Pb(II) onto different adsorbents at optimum pH

Adsorbent materials	Adsorption capacity (mg/g)	pH	References
Modified Cassia grandish (CG-g-PMMA)	126	2	4
Saw dust carbon(SDC)	199	5	2
Palm shell activated carbon	95	3	19
<i>Control Undaria pinnatifida</i>	302	4	20
Charred xanthated sugarcane bagasse(CXSB)	327	4	5
CASB	323	4	This study

Conclusions

A novel charred aminated sugarcane bagasse (CASB) was prepared by two step reactions of CSB in which reduction with ammonia was followed by nitration. It was characterized and evaluated for its adsorption capacity of lead ion from its aqueous solution. The maximum adsorption capacity of Pb(II) onto the CASB was found to be higher than the reported value mentioned in the literature (Table 3). This indicates that the introduction of amine group onto charred sugarcane bagasse is of importance in enhancing the adsorption properties of raw sugarcane bagasse. Finally, it can be concluded that chemically modified aminated sugarcane bagasse might be low cost potential adsorbent in industrial wastewater as well as drinking water treatment.

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