Preparation of low-cost adsorbent material from chicken bones and its removal of As(III) and Pb(II) toxic ions from wastewater

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Abstract: The low-cost adsorbent was prepared from chicken bone by pyrolysis at 700 ℃ for 1 hour in three different atmospheric conditions, such as Chicken Bone Adsorbent Materials in open air (CBAM-O), in nitrogen (CBAM-N) gas and in nitrogen gas and water steam (CBAM-NS). The specific surface areas of chicken bone adsorbent materials were determined by methylene blue adsorption method and found for CBAM-O, CBAM-N and CBAM-NS as 127, 130 and 206 m^2/g, respectively. Present study deals with the adsorption of As(III) and Pb(II) from aqueous solution on CBAM-NS adsorbent. The influence of various parameters like pH, contact time and concentration of adsorbate were studied. Studies showed that the maximum efficiency was achieved at pH 5 for As(III) and Pb(II). Kinetics and isotherm model studies demonstrated that the experimental data fitted with pseudo-second order and Langmuir isotherm model with the rate constants 0.0449 and 0.0354 g/(mg.min) and the maximum adsorption capacities 100 and 163.934 mg/g for As(III) and Pb(II) respectively.

The values of ΔG obtained from Langmuir equation was -21, -23 kJ/mole for As(III) and Pb(II) respectively. The negative values of free energy (ΔG) in adsorption process revealed the spontaneous nature and feasibility of the adsorption process for the adsorption of As(III) and Pb(II) onto CBAM-NS. The values of ΔG further confirmed that the adsorption process was favoured by physio-chemical-adsorption for As(III) and Pb(II) respectively. The values of the separation parameter K_L were found to be $0 \leq K_L \leq 1$ which revealed good adsorption of As(III) and Pb(II) onto CBAM-NS.

Keywords: Adsorbent; Arsenic; Bone char; Chicken bones; Lead.

Introduction

Waste is any substance which is discarded after primary use. According to the United Nation Statistics Division (UNSD) "wastes are materials that are not prime products for which the generator has no further use in term of own purposes of production, transformation or consumption''. Waste may be generated during the extraction and processing of raw materials into intermediate and final products, the consumption of final products and other human activities. Wastes can generally be categorized into two types: inorganic and organic wastes[1].

There are different types of solid wastes. Some of them are household waste, industrial waste, biomedical waste, agricultural waste *etc*[1]. Agricultural wastes are defined as the residues from the growing and first processing of raw agricultural products such as fruits, vegetables, meat, poultry, dairy products and crops[2]. Recently, by-products or waste from large scale agro-product production is attracting interest to researchers for using such wastes to remove heavy ions from water and wastewater[3].

A wide- variety of agricultural waste materials such as

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modified palm oil empty fruit bunch, tea waste, bagasse, fly ash, rubber, tree leaf powder, chicken bone, *etc*. used to remove heavy metal ions from water and wastewater by preparing low-cost adsorbent alternatives to expensive adsorbents[4-8].

The global average chicken meat consumption is 12 kg per person annually, according to the Food and Agriculture Organization of the United Nations in 2014-2015[9]. Commercial production of chicken meat in Nepal stands at 1,14,058 tons annually and Nepali eats chicken meat 4.1 kg per person annually, according to the Central Bureau of Statistics (CBS) in 2014-2015[9]. The waste obtained from chicken like feathers, bones, egg shell, *etc*. adversely affect the environment in numerous ways through poor management of manure, liter and odour[10].

Water is the most vital element among the natural resources and is critical for the survival of all living organisms. The water sources are getting polluted day by day due to sewage and other waste, agricultural discharges and industrial wastes from chemical industries, fossils fuel plants and nuclear power plants *etc*[11]. Contamination of water by toxic heavy metals through the discharge of industrial wastewater is a worldwide environmental problem. Rapid industrialization has seriously contributed to the release of toxic heavy metals to water streams. Mining, electroplating, metal processing, textile and battery manufacturing industry are the main sources of heavy metal ion contamination. Metals such as lead, cadmium, arsenic, nickel, chromium, zinc and mercury have been recognized as hazardous heavy metals[12].

Heavy metals are one of the most predominant hazardous pollutants in the environment. Heavy metal ions and dyes are often found in the environment as a result of their wide industrial applications. They are the common contaminants of wastewater and most of them are known to be toxic or carcinogenic. In addition, they are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders[13]. Among the heavy metals lead and arsenic are highly toxic and attention have been given by environmentalists due to its acute and chronic toxic effects on animals and human health[14].

There are several methods for removal of heavy metal ions from water such as precipitation, ion exchange, reverse osmosis, coagulation, electrolysis, solvent extraction, evaporation and adsorption. However, most of the methods are sophisticated and expensive and they cannot be practiced in the rural areas in developing and poor countries due to the disposal of residual metal sludge and inefficiency in avoiding secondary pollution[15].

A promising method that can be considered efficient and low cost for wide-scale application is adsorption using appropriate readily available cheap adsorbent[13]. The activated carbon is widely used as adsorbent for removal of heavy metals. Activated carbon with their large specific surface area, micro porous character and activated carbon has shown good metal ion adsorption capacities. However, the high cost of activation process limits the use in wastewater treatment[16].

Thus, the researchers are interested to search for low cost and locally available materials as adsorbent for metal ion removal from the wastewater. However, efforts have been contributed to develop new adsorbent and improve the existing adsorbent to have an alternative to activated carbon. The adsorbent used for removal of Pb(II) has been studied using chicken bone, eggshell, sawdust, tea waste, chicken feather *etc*[12,17&18].

Bone charcoal is a granular material produced by burning animal bones. Bone char is cheap, effective and simple alternative for removing excess trace elements from wastewater. Animal bone waste is quite high due to the high consumption of chicken, beef, pork etc. all over the world. Bone charcoal is mostly composed of calcium phosphate and small amount of carbon. Chicken bone charcoal consists of O_2, Ca, P, C, Na, Mg and Al. Chicken bone charcoal can be applied to the process of water defluoridation and removal of heavy metals from ground water[19].

Activated carbon was obtained from chicken bone ash by heating at temperature higher than 500 °C. In this study, the effect of adsorbent dose, solution pH and contact time has been investigated. The result demonstrated that Pb(II)

adsorption onto activated carbon was pH dependent and the optimum removal was observed at pH 5.6. Adsorption isotherm followed both Langmuir and Freundlich isotherm and maximum adsorption capacity was 1,842 mg/g[15].

The adsorbent prepared from chicken egg shells was used for removal of Pb(II) ions from synthetic water. The result demonstrated that adsorption isotherm followed by Langmuir isotherm with the adsorption capacity of egg shell for Pb (II) ion was 154 mg/g at optimum pH 5 and pseudo-first order model with the rate constant 0.218/min[20].

The adsorption of lead (Pb^{2+}) onto activated carbon (AC) originating from cow bone, chemically modified with HNO_3, was investigated. Physico-chemical carbon characterization assays and the determination of the optimum pH conditions, contact time, initial concentration and adsorbent reuse, were carried out. The pH was 4.0 and the minimum contact time required for the assays to be performed was 6 h. It was observed that the time required reaching kinetic equilibrium decreased with increasing initial metal concentration in solution and the values found for q_{exp} were 32.1, 50.1 and 42.3 mg/g for concentrations of 100, 150 and 200 mg/L, respectively[16].

The equilibrium adsorption capacity of As^{3+} was found 101.01 mg/g with Fe loaded bentonite and the adsorption process was favored to Langmuir model and the adsorption process was controlled by pseudo-second –order kinetics with the rate constant value 0.03723 g/(mg.min)[21].

Activated alumina was used for removal of As(III) ion. In this studies effect of adsorbent dose, solution pH and contact time has been investigated. The results demonstrated that As(III) adsorption onto activated alumina was pH dependent and the optimum removal was observed at pH 7.6. Adsorption isotherm followed both Langmuir and Freundlich isotherm and maximum adsorption capacity was 7.6 mg/g[22].

Adsorbent was prepared from maize leaves powder for the removal of As(III) from wastewater. The result showed that the adsorption of As(III) had good with Frendliuch model with the maximum adsorption capacity of As(III) at pH 8, contact time 4 hours, temperature of 440 °C and the kinetics was suited to pseudo-second order model with rate constant 0.321g/(mg.min)[23].

The As(III) was removed by using iron oxide impregnated activated alumina. The result of this paper showed that As(III) removal was pH dependent and adsorption isotherm followed both Freundlich and Langmuir model. The adsorption kinetics followed a pseudo first order kinetics and the maximum adsorption capacity was 12 mg/g[24].

The main aim of this present work was to prepare low-cost adsorbent from chicken bone and to investigate its adsorption capacity for the adsorption of Pb(II) and As(III) from aqueous solution.

Materials and Methods

Preparation of adsorbent from chicken bone

Chicken bone was collected from meat shop Kirtipur, Kathmandu and was washed thoroughly first with tap water, then distilled water. It was left at room temperature for 3 days. Then it was placed in air dry oven at 110 ℃ for one night. The dried chicken bone was ground to make powder. The bone powder was subjected to pyrolysis in furnace (21100 Tube Furnace, USA) in three different conditions. It was heated at 700 ℃ for 1 hour in open air (CBAM-O), in nitrogen gas (CBAM-N) and in the mixture of nitrogen gas and water steam (CBAM-NS), separately. The schematic diagram of the pyrolysis of chicken bone is shown in Figure 1.

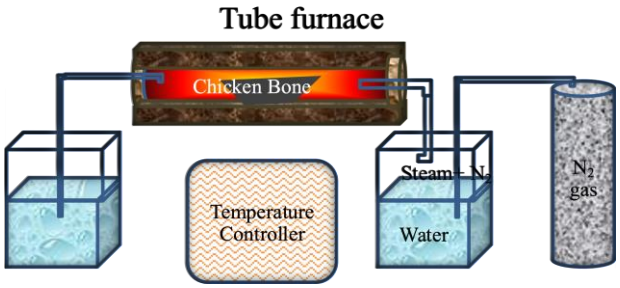

Figure 1: Schematic representation of the pyrolysis of chicken bone in tube furnace.

The technique is environment friendly since the gas is passed from one site of the tube and other side contains the outlet of black smoke dipped into water trough. The tube containing chicken bone powder was placed inside the

furnace heated according to the requirement using temperature controller.

Preparation of stock and standard solutions

Preparation of As(III) solutions

1.32 g of arsenic trioxide (As_2O_3, LR Grade, dried at 110 °C for an hour) was dissolved in 5 mL of 10 M sodium hydroxide and transferred in a 1000 mL volumetric flask. The volume was made 1000 mL with distilled water. Working solutions of 1 to 500 ppm were prepared by dilution method.

Preparation of Pb(II) solutions

0.8073 g of $Pb(NO_3)_2$ was dissolved 5 mL of concentrated HNO_3 and transferred in 1000 mL volumetric flask. It was then diluted with distilled water up to the mark. The obtained stock solution was used for working solutions preparation required for each experiment.

Preparation of methylene blue (MB) solutions

The 1.00 g methylene blue (AR Grade, Qualigens Fine Chemicals, India) was weighed and transferred to 1000 mL volumetric flask. It was then dissolved with distilled water and diluted up to the mark. The appropriate volume of stock solution was taken to get the working methylene blue solutions of required concentration by dilution method.

Ammonium molybdate reagent (I)

Ammonium heptamolybdate [$\{(NH_4)_6Mo_7O_{24}.4H_2O\}$, LR Grade] 12.5 g was dissolved in 87.5 mL of distilled water. The 140 mL concentrated sulphuric acid was added to 200 mL of distilled water cautiously. It was cooled and added to the ammonium molybdate solution and diluted to 500 mL.

Ammonium molybdate reagent (II)

20.05 g of ammonium molybdate was transferred into 500 mL volumetric flask and dissolved in 250 mL of distilled water. Ammonium molybdate reagent(I) 198 mL was added to the reagent(II), cooled and diluted up to 500 mL with distilled water. The concentration of reagent (II) was 5%. Working solution of ammonium molybdate of the concentration 0.5 M was prepared from dilution method.

Similarly, Potassium permanganate (0.1 N), Sulphuric acid (1.5 N), Hydrazine Hydrate (0.5 M), NaOH (0.1 M), HCl (0.1 M) solutions 250 mL each, 100 mL each of buffer solutions of pH 4.0, 7.0 and 9.2 were prepared.

Calibration curve for MB solution

For the preparation of calibration curve, at first the maximum absorbance was obtained by finding λ_{max} (665 nm) using spectrophotometer (2306, Electronics, India). After that the methylene blue solutions of 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 mg/L were prepared. The absorbance of all these solutions was taken at 665 nm wavelength. A plot of absorbance versus concentration thus gave a calibration curve for methylene blue solution.

Preparation of calibration curves for metal ions

1, 2, 3, 4, 5, 6, 8, 9 mg/L arsenic solution and blank solution were prepared in 25 mL volumetric flasks by the method shown in Figure 2.

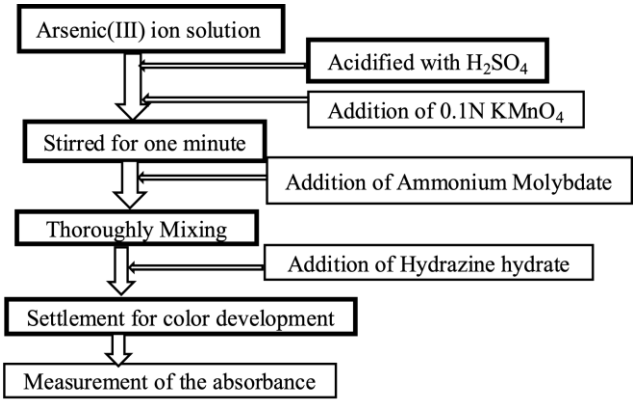

Figure 2: Schematic diagram for quantitative measurement of As(III) ion.

The required amounts of diluted solutions were pipetted out and transferred into 25 mL volumetric flask. To each solution 4.5 mL of sulphuric acid (0.5 N) was added then one drop of potassium permanganate (0.1 N) was added, stirred for one minute. 3 mL of ammonium molybdate (0.5%) and 3 mL of hydrazine hydrate (0.5 M) were added. Then the volume was made up to mark by adding distilled water. The above solutions were left for 20 minutes at room temperature for full colour development. The absorbance of each solution was measured at 840 nm against blank solution with the help of spectrophotometer (2306,

Electronics, India). A plot of absorbance versus concentration of arsenic was made.

Lead solution containing 1.0, 5.0 and 10.0 mg/L and blank solution were prepared in 25 mL volumetric flask. The absorbance of each solution was measured at 282.3 nm against blank solution with the help of AAS (AA-7000, Shimadzu, Japan). A plot of absorbance versus concentration of lead was made.

Specific surface area determination

Langmuir adsorption isotherm model was used for the specific surface area determination of chicken bone adsorbent materials. For this, 0.05 g of chicken bone adsorbent material was transferred to each reagent bottle containing methylene blue (MB) solutions of varying concentrations in between 50 to 300 mg/L.

The solutions were shaken for 24 hours in a mechanical shaker and then allowed to rest for half an hour. The supernatant solution was pipetted out after it settled down. The absorbance of the resultant solution was noted at 665 nm wavelength. From the Langmuir adsorption isotherm, Q_{max} value was calculated. The specific surface area is calculated by following equation[25]:

$$S_{MB} = \frac{N_g \times a_{MB} \times N \times 10^{-20}}{M} \quad \ldots\ldots\ldots \quad (1)$$

Where, S_{MB} is the specific surface area in 10^{-3} $km^2\,kg^{-1}$, N_g is the number of molecules of MB adsorbed at monolayer of adsorbent in kg, a_{MB} is the occupied surface area of one molecule of MB = 197.2 $Å^2$, N is Avogadro's Number (6.023×10^{23}), M is the molecular weight of the MB (319.85 $gmol^{-1}$) and N gives mmol/g which is equivalent to Q_m of the Langmuir equation.

Effect of pH

For the pH of As(III) and Pb(II) adsorption, the initial concentration and volume of solution were taken 20 mg/L and 50 mL respectively. The solutions were taken in 100 mL Erlenmeyer flask and pH of the solutions was adjusted from 2 to 8 using appropriate strength of NaOH and HCl solutions by the help of pH meter. To each flask, 0.05 g CBAM-NS adsorbent was added and then shaken in mechanical shaker for 24 hours at speed 220 rpm. After shaking, each solution was filtered immediately using Whatman No. 41 filter paper and the equilibrium pH of the filtrate was noted. The filtrates were analyzed separately to determine the equilibrium concentration of As(III) with the help of UV-Visible spectrometer while for Pb(II) Atomic Absorption Spectrophotometer was used.

Kinetic studies

The adsorption kinetics experiments were performed at corresponding optimum pH for As(III) and Pb(II) ions by equilibrating. For this, 50 mL of 20 mg/L arsenic and lead solutions in 100 mL Erlenmeyer flask containing 0.05 g CBAM-NS adsorbent were used separately. These flasks were shaken for different length of time 2 to 90 minutes, in a mechanical shaker at speed of 220 rpm. The kinetics were investigated by taking out flask at desired period of contact time and filtrated through Whatman No. 41 filter paper and concentrations were determined spectrophotometrically. The data obtained was tested with pseudo-first order and pseudo-second order kinetic models.

Adsorption isotherm studies

For the study of isotherm studies of As(III) and Pb(II), the effect of arsenic and lead concentrations on the adsorption was studied under optimum pH. The adsorption isotherm studies were done with different initial concentrations of As(III) and Pb(II) ions ranging from 10 to 100 mg/L with 0.05 g of CBAM-NS adsorbent. The solutions were shaken in a mechanical shaker for 60 minutes at speed of 220 rpm. The equilibrium concentrations of arsenic after adsorption were determined by molybdenum blue method using spectrophotometer while that of lead concentration was determined by Atomic Absorption Spectroscopy (AA-7000, Shimadzu, Japan). Two models Langmuir model and Freundlich model have been tested to study the adsorption isotherm study.

X-ray diffraction (XRD) measurement

The raw chicken bone and its adsorbents without any adsorption were analyzed for the phase detection using X-ray Diffractometer with monochromatic CuKα radiation (D2 Phaser Diffractometer, Bruker, Germany) at Nepal Academy of Science and Technology (NAST). The samples

were scanned at 2θ from 10 to 80º. The XRD analysis was done to determine the chemical structure of the adsorbent material obtained from spinach.

Fourier transform infrared (FTIR) analysis

All the four samples prepared in different environment, without any adsorption were analyzed by using FTIR Spectroscopy (IRTracer 100, Shimadzu, Japan) at Central Department of Chemistry, Tribhuvan University for the chemical identification of organic and inorganic material in adsorbent materials prepared from chicken bone.

Results and Discussion

Characterization of adsorbent materials

The λ_{max} determination and calibration curve of MB solution

The maximum absorbance i.e., λ_{max} was obtained at 665 nm which is in trend with the previous reports[26-29]. The linear relationship of the absorbance with the concentration up to 10 mg/L of MB solution indicates to follow the Beer Lambert's law.

Specific surface area determination

In order to obtain the specific surface area of the adsorbents prepared from chicken bone, the linearize Langmuir plots for the adsorption of MB were made and the Langmuir parameters were obtained. Finally, the specific surface areas of chicken bone adsorbents were calculated using above mentioned equation (1) and were 127, 130 and 206 m^2/g for CBAM-O, CBAM-N and CBAM-NS, respectively.

The specific surface area of CBAM-NS was the highest among these three samples which may be due to the fact that more adsorbents were formed with a greater number of pores in the CBAM-NS in comparison to others. This also implies that the ash content and other impurities were lower in the CBAM-NS.

X-ray diffraction (XRD) analysis

The XRD pattern of raw chicken bone and the adsorbents obtained from it are shown in Figure 3. Broad and comparatively weak diffraction bands at about 2θ = 26.3 and 42 are presented in each activated sample, corresponding to the (002) and (001) crystal planes of carbon. The broad diffraction bands at about 2θ = 32, 33, 40, 47 and 50° may be of hydroxyapatite (based on ICDD 9–432 and JCPDS 84-1998). Thus, from XRD patterns, the present low-cost adsorbent material seemed to contain activated carbon along with hydroxyapatite and hence it

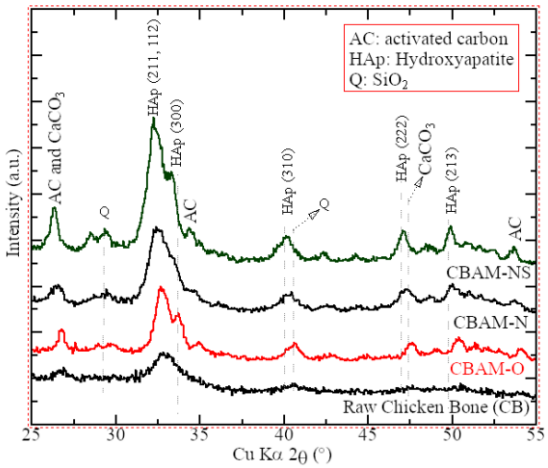

Figure 3: X-ray diffraction patterns of raw chicken bone and adsorbent materials obtained from it.

was the composite material.

Fourier transform infra-red spectra analysis

The FTIR spectra of raw chicken bone and the adsorbents obtained from it are shown in Figure 4. The FTIR spectrum of above figure showed that spectrum of raw chicken bone was not well observed. The spectrum of CBAM-NS was showed clear bands than CBAM-O and CBAM-N.

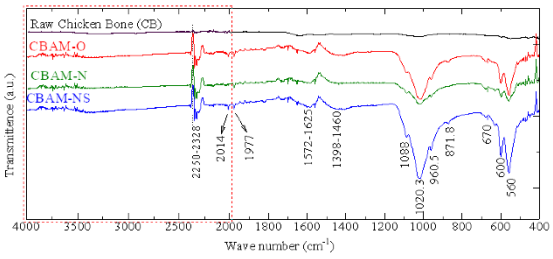

Figure 4: FTIR spectra of raw chicken bone and the adsorbents obtained from it.

The functional groups and the mode of vibrations of the IR peaks appeared in FTIR spectra of activated carbon prepared from chicken bone are tabulated in Table 1.

The effect of initial pH on the adsorption of As(III) and Pb(II) was studied in the rage from 2 to 8. The adsorptions of As(III) and Pb(II) were found increasing with increasing

initial pH value from 2 up to 5 and then decreased with further increase the initial pH. The maximum adsorptions of As(III) and Pb(II) were found at initial pH 5 with the values 16.83 and 18.98 mg/g respectively.

In a study, the value of the pH of the point of zero charge (pH_{pzc}) for activated carbon was found in the range between 3 to 4[30]. The pH_{pzc} of an adsorbent gives essential information about the surface charge of an adsorbent. The surface of an adsorbent is positively charged below its pH_{pzc} and it is negative above pH_{pzc}.

Table 1: Functional groups and the modes of vibrations of various peaks.

Absorption band (cm^{-1})	Functional group with mode of vibration
3630 & 3745	Hydrogen-bonded OH group of alcohols and phenols
2250-2328	symmetric or asymmetric stretching of aliphatic band in -CH, $-CH_2$ or $-CH_3$
2014	Residual water
1977	Symmetrical stretching of C=O of carboxylic groups
1572-1625	Due to asymmetric stretching of the carboxylic C=O double bond
1398-1460	Aromatic carbon–carbon (C=C) stretching vibration
1020-1088	Either Si-O-Si or C-O stretching in alcohol, ether or hydroxyl groups or C-O-C stretching mode
960.5	symmetrical non- degenerate P-O stretching (ν_1, PO_4^{3-}) of phosphate
871.8	C–H stretching vibrations
670	Out-of-plane C-H bending mode
600 and 560	corresponding to PO_4^{3-} group

Effect of pH

The effect of pH for the adsorption of As(III) and Pb(II) onto the CBAM-NS is shown in Figure 5.

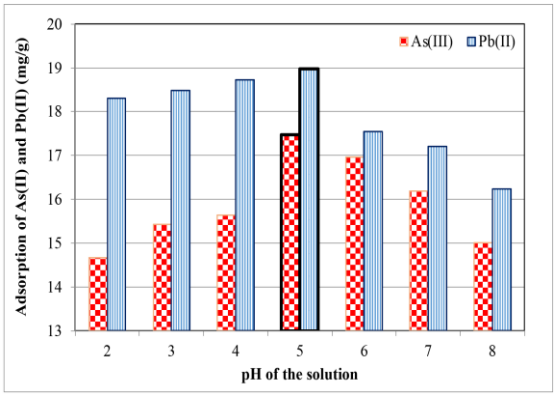

Figure 5: Effect of pH for the adsorption of As(III) and Pb(II) onto the CBAM-NS.

Arsenite species exist as neutral H_3AsO_3 at pH range between 1 to 9 and AsO_2^- at pH higher than 9[31]. Thus the maximum adsorption of As(III) was expected to occur at pH 9 if the adsorbent material were purely activated carbon. Similarly, the adsorption of Pb(II) at pH in between 3 to 4 is not favorable for activated carbon due to positively charged surface of the adsorbents where Pb(II) has to compete with H^+ ions and the adsorption of Pb(II) should occur at pH > pH_{pzc} where the surface of the adsorbents become negative[32].

The maximum adsorption of As(III) at pH 5 actually did not support the theoretical background mentioned above while the maximum adsorption of Pb(II) at pH 5 is in trend with previous reports[15, 33]. The theoretical background mentioned above is for pure activated carbon while the present low-cost adsorbent material contains activated carbon along with hydroxyapatite where there is the presence of exchangeable cation as Ca^{2+}. Thus, the adsorption of As(III) and Pb(II) onto the present low-cost adsorbent material (CNAM-NS) may be due to partially ion-exchange process.

For further experimental works, the adsorption of As(III) and Pb(II) onto the present low-cost adsorbent material, the optimum pH value was set to pH 5.

Batch kinetic studies

The study of adsorption kinetics describes the solute uptake and the time required for the adsorbate uptake at the solid-solution interface. For kinetic studies two models namely pseudo-first order and pseudo-second order were employed to the experimental kinetics data.

The differential form of pseudo-fist order rate equation, applicable for the reversible reaction, is mentioned as[34]:

$$\frac{dQ_t}{dt} = K_1(Q_e - Q_t) \quad \cdots \quad (2)$$

Where, Q_e (mg/g) is the amount of adsorbate adsorbed at equilibrium and Q_t (mg/g) is the amount of adsorbate adsorbed at time 't'. The term K_1 (min^{-1}) is the rate constant of pseudo-first order adsorption.

After integration and applying boundary condition, t = 0 to t and Q_t = 0 to Q_t the linearized from of equation (2)

becomes:

$$\log(Q_e - Q_t) = \log Q_e - \frac{K_1}{2.303}t \quad \cdots \quad (3)$$

The plot of log (Q_e - Q_t) versus 't' will give a straight line from which K_1 and Q_e can be determined from slopes and intercepts of the plot (Figure 6) respectively.

The pseudo-second order kinetic model states that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites[35]. It is expressed as:

$$\frac{dQ_t}{dt} = K_2(Q_e - Q_t)^2 \quad \cdots \quad (4)$$

Where K_2 (g/mg·min) is the pseudo-second order rate constant and Q_e and Q_t are the amount of adsorbate adsorbed at equilibrium and any time 't' respectively.

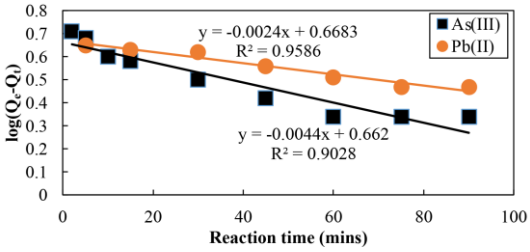

Figure 6: Pseudo-first order kinetic model for adsorption of As(III) and Pb(II) ion onto CBAM-NS.

With integration and applying boundary conditions, t=0 to t and Q_t = 0 to Q_t the equation becomes:

$$\frac{1}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{1}{Q_e}t \quad \cdots\cdots\cdots \quad (5)$$

If the initial adsorption rate is V_0 (mg/g min), then

$$V_0 = K_2 Q_e^2 \quad \cdots \quad (6)$$

The equation can also be written as:

$$\frac{1}{Q_t} = \frac{1}{V_0} + \frac{1}{Q_e}t \quad \cdots \quad (7)$$

The values of Q_e and K_2 can be determined from the linear plot of t/Q_t versus 't' with the slope and intercept of the plot (Figure 7) respectively.

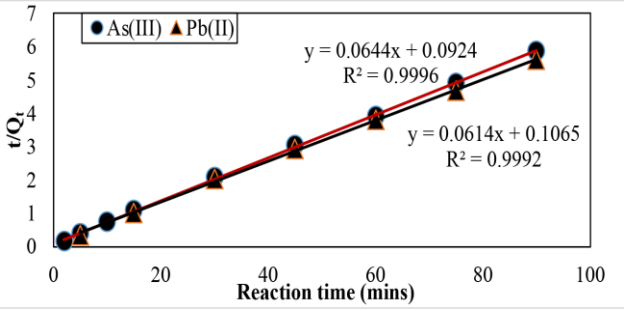

Figure 7: Pseudo-second order kinetic model for the adsorption of As(III) and Pb(II) ion onto CBAM-NS.

The rate of reactions as well as the maximum adsorption capacities obtained from the slopes and intercepts of the Figures 6 and 7 are tabulated in Table 2.

The correlation coefficient values of pseudo- first order and pseudo-second order models of As(III), Pb(II) found to be 0.9028,0.9586 and 0.9996, 0.9992 respectively showed that the kinetics of As(III) and Pb (II) ion onto CBAM-NS followed pseudo-second order kinetics. The solid line curves of Figure 8 are calculated curves using maximum adsorption capacity and the rate of reaction of pseudo-second order kinetics obtained from Table 2.

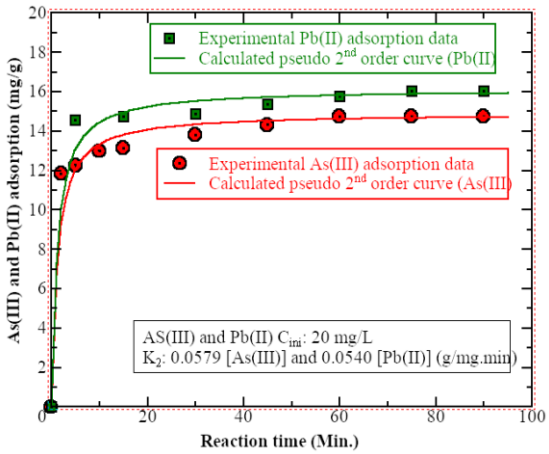

Figure 8: Kinetic plots for the adsorption of As(III) and Pb(II) on adsorbent CBAM-NS.

The rate constant values of pseudo-first and pseudo-second orders for As(III) and Pb(II) were found to be 0.0106, 0.0083 min^{-1} and 0.0579 and 0.0540 g/mg·min respectively. It is very clear from the graphs that initially the process of adsorption was rapid and the equilibrium reached in 40 minutes for As(III) and Pb(II). After reaching the saturation point there was no significant change in the rate of adsorption. The initial rapid increase in the rate was due to the availability of more number of active sites so that large number of As(III) and Pb(II) ion got attached to adsorbent sites. As the time passed the number of active sites becomes less and finally the equilibrium state was reached.

Batch adsorption isotherms of As(III) and Pb(II)

As Langmuir and Freundlich adsorption isotherms are the well-known most popular models used to analyze adsorption behavior, these two models were applied for isotherm study.

Langmuir model is normally applied for the adsorption of solute from a liquid solution on homogeneous adsorbent with the formation of monolayer coverage while adsorption is independent of the occupation of neighboring sites[36]. The linearized form of Langmuir adsorption isotherm is given as:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \quad \cdots \quad (8)$$

Where Q_e (mg/g) is the weight of adsorbate adsorbed per unit weight of adsorbent at equilibrium, C_e (mg/L) is the equilibrium concentration of the adsorbate, Q_m (mg/g) is the maximum adsorption capacity and 'b' (L/mg) is the Langmuir adsorption equilibrium constant.

Table 2: Kinetic parameters for adsorption of As(III) and Pb(II) onto adsorbent CBAM-NS.

	1st order		2nd order	
Ion	As(III)	Pb(II)	As(III)	Pb(II)
K_1	0.0101	0.0055		
K_2			0.0449	0.0354
Q_t	4.5920	4.6591	15.53	16.29
R^2	0.9028	0.9586	0.9996	0.9992

A plot of C_e/Q_e against C_e gives a straight line with slope $1/Q_m$ and intercepts $1/Q_m b$ from which Q_m and 'b' can be determined.

Thermodynamic study of adsorption isotherm

Thermodynamic consideration of the adsorption process is necessary to know whether the process is spontaneous or not. The Gibbs free energy change (ΔG^o) is a critical factor for determining the spontaneity of a process. The Langmuir parameter b is related to free energy change of adsorption ΔG (kJ/mole) by the relation[37]:

$$\Delta G = -RT\ln(b) \quad \cdots\cdots \quad (9)$$

Where, R = Universal gas constant (8.314 $Jmol^{-1}K^{-1}$), T = Temperature in Kelvin and b is Langmuir constant in (L/mol). Gibbs free energy indicates the degree of spontaneity of adsorption process. More negative value reflects greater energetically favorable process.

The Langmuir isotherm can be expressed in terms of dimensionless constant separation factor or equilibrium parameter (K_L), which is given by the relationship[38].

$$K_L = \frac{1}{1 + bC_i} \quad \cdots\cdots \quad (10)$$

Where, C_i is the initial concentration of the adsorbate (mg/L) and K_L is the Langmuir equilibrium parameter. Langmuir equilibrium parameter (K_L) indicates the shape of isotherm and nature of adsorption process, [$K_L > 1$, unfavorable, $K_L = 1$, linear, $0 < K_L < 1$, favorable, $K_L = 0$, irreversible]. The value of K_L between 0 and 1 indicates that adsorption is favorable.

Another adsorption isotherm model applied in this study is Freundlich model which was established in 1939[39]. The linear from of the Freundich isotherm is:

$$\log Q_e = \log K_F + \frac{1}{n}\log C_e \quad \cdots \quad (11)$$

Where Q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent, C_e (mg/L) is the equilibrium concentration of the adsorbate, K_F [(mg/g) $(L/mg)^{1/n}$] and n (g/L) are Freundlich equilibrium coefficients, which are considered to be the relative indicators of adsorption capacity and adsorption intensity.

The $\log Q_e$ is plotted against $\log C_e$ a straight line is obtained with slope 1/n and intercept $\log K_F$. From this plot, the value of 1/n and K_F can be determined. The value of 1/n between 0 and 1.0 indicates the favorable adsorption of adsorbate.

Error analysis for isotherm studies

For single element isotherm studies, it is necessary of error function to optimize the procedure in order to evaluate the fit of the isotherm to the experimental equilibrium data. There are several error functions[40]. The error functions are the sum of the squares of the errors, the hybrid fractional error function, Marquardt's percent standard deviation, the sum of the absolute errors and chi square test. The best fit among the isotherm models is given by the linear coefficient of determination (R^2) and non-linear Chi square (χ^2)[41]. In this study, the Chi-square test was performed by using the mathematical expression:

$$\chi^2 = \sum \frac{(Q_{e,cal} - Q_{e,exp})^2}{Q_{e,cal}} \quad \cdots\cdots \quad (12)$$

Where, $Q_{e,calc}$ is the equilibrium capacity obtained by calculated from model (mg/g) and $Q_{e,exp}$ is the equilibrium capacity (mg/g) from the experimental data. The lower value of χ^2 suggests the best fit model.

Adsorption of As(III) and Pb(II) onto CBAM-NS was done by optimizing the pH at 5 and varying the concentrations of Pb(II) and As(III) from 10 to 100 mg/L that gave the linear relationship with Langmuir and Freundlich isotherms. The parameters of both isotherm models obtained from the slope and intercept of the linearized curves, the coefficient of determinations, values of χ^2 for both isotherms of As(III) and Pb(II) adsorption and change in free energy during adsorption process are mentioned in Table 3.

The correlation coefficient of Langmuir and Freundlich isotherms of As(III) and Pb(II) were 0.9950, 0.9950 and 0.6558, 0.9928 respectively.

Table 3: Parameters of Langmuir and Freundlich constants.

Ions	Langmuir model				
	Q_{max} (mg/g)	b (L/mg)	R^2	ΔG (kJ/mol)	χ^2
As(III)	100.0	0.063	0.9950	-21	0.25
Pb(II)	163.934	0.054	0.9950	-23	0.34
Ions	Freundlich Model				
	K_F [(mg/g)(L/mg)$^{1/n}$]		n	R^2	χ^2
As(III)	3.26		1.08	0.6558	30.09
Pb(II)	9.38		1.30	0.9928	0.67

Since the R^2 of Langmuir is greater than that of Freundlich, so the adsorption of As(III) and Pb(II) ions onto CBAM-NS is monolayer and involved the adsorption on homogeneous active surfaces. This implies that the experimental data fitted with the Langmuir model. The Q_{max} values obtained from Langmuir model for As(III) and Pb(II) were found to be 100.0, 163.934 mg/g respectively, which are significantly higher and the values of χ^2 for the Langmuir model were smaller than those of the Freundlich model which further concludes that adsorptions of As(III) and Pb(II) on activated carbon followed the Langmuir adsorption isotherm.

The values of ΔG were calculated and found to be -21 and -23 kJ/mol for As(III) and Pb(II) respectively. These values reveals the spontaneous nature, feasibility of the adsorption process and the adsorption process is favoured by physio-chemical-adsorption for As(III) and Pb(II). The experimental K_L values for As(III) and Pb(II) adsorption obtained using equation (10) are in between 0 and 1 which is in agreement with the favorable adsorption.

From the Langmuir and Freundlich parameters, the adsorption of As(III) and Pb(II) as a function of equilibrium concentrations of both ions is shown in Figure 9, where the curves indicates that experimental data followed very well with Langmuir model.

Mechanisms of As(III) and Pb(II) adsorption

Mechanisms and rate controlling steps affecting the kinetics of adsorption. The kinetic results are fitted to Weber-Morris equation[42]:

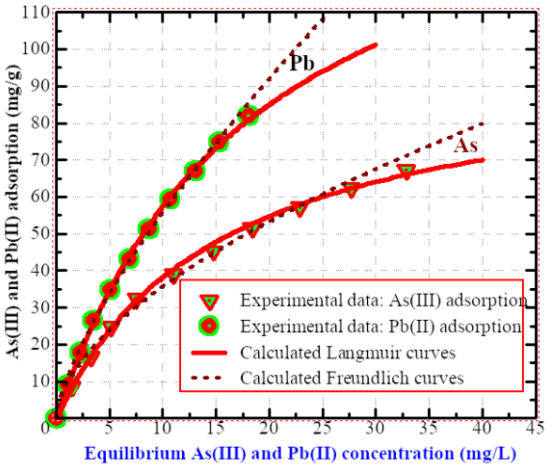

Figure 9: The adsorption isotherms of As(III) and Pb(II) onto adsorbent CBAM-NS.

$$Qt = K_{id}t^{0.5} + C \quad \cdots\cdots (12)$$

Where C is the intercept and K_{id} (mg/g $h^{0.5}$) is the intraparticle diffusion rate constant, which can be evaluated from the slope of the linear plot of Q_t versus $t^{0.5}$. The intercept of thus obtained plot reflects the boundary layer effect. The larger the intercept, the greater is the contribution of the surface adsorption in the rate-controlling step. If the regression of Q_t versus $t^{0.5}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step otherwise there is some degree of boundary layer control and the intraparticle diffusion is not the only rate-determining step but other kinetics models may also control the rate of adsorption.

The graphical relationship between the amount of As(III) and Pb(II) adsorbed (mg/g) as a function of square root of time (√t) is shown in Figure 10.

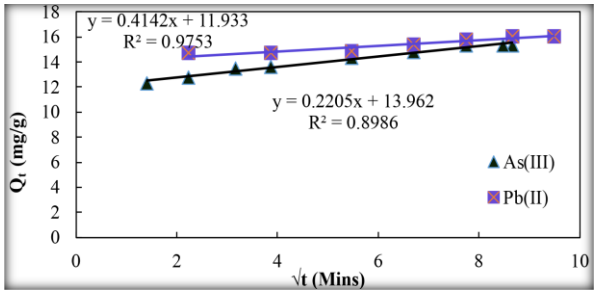

Figure 10: Plot of Q_t verses √t for the adsorption of As(III) and Pb(II) on adsorbent CBAM-NS.

The plot of Q_t verses √t does not pass through the origin and indicates that the intra-particle diffusion model was not the rate limiting step.

Conclusions

Three different types of low- cost adsorbent materials were prepared by pyrolysis of chicken bone in open air, nitrogen gas and nitrogen gas plus water steam at 700 °C. These were characterized by FTIR, XRD analyses and methylene blue adsorption method.

The XRD analysis showed the strong evidence for the formation of activated carbon and hydroxy apatite. The FTIR analysis concluded that the hydroxyl and carboxyl group could bind Pb(II) and As(III) ions with adsorbent. The specific surface areas of CBAM-O, CBAM-N and CBAM-NS were 126.73, 129.977 and 206.30 m^2/g, respectively.

The optimum pH was found to be 5 for both As(III) and Pb(II) ion adsorption. The equilibrium contact time of As(III) and Pb(II) were 40 minutes following the pseudo-second order kinetic model with the rate constant values 0.0449 and 0.0354 g/(mg.min) for As(III) and Pb(II) ions adsorption respectively. Adsorption isotherm studies of As(III) and Pb(II) showed that the Langmuir model fitted better. The maximum adsorption capacity of As(III) and Pb(II) were 100 and 163.934 mg/g respectively.

The ΔG values revealed the spontaneous nature and feasibility of the adsorption process and was favoured by physio-chemical-adsorption. The adsorption capacity of Pb(II) was greater than As(III) due to its larger ionic radius. The values of χ^2 for the adsorption of As(III and Pb(II) indicates to follow Langmuir model while The K_L values revealed good adsorption of As(III) and Pb(II) onto CBAM-NS.

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