Thermal Treatment of Cattle Bone and its Application in Removing Lead from Wastewater

Suporna Paul, Sabrina Mostofa, Shirin Akter Jahan, Samina Ahmed, Nahid Sharmin

Abstract— The main focus of this study was to prepare low cost adsorbent using cattle bone which could be used for the treatment of Pb (II) in aqueous medium. Experimental protocol was particularly confined with the thermal treatment (at 300 °C, 500 °C, 600 °C and 700 °C) of raw bones followed by the investigation of adsorption of Pb (II) on treated bones.Thermally treated bones were characterized using FT-IR, XRD and particle size analyzer. Adsorption study was accomplished considering two factors:(i) adsorbent-substrate solution contact time;and (ii) pH covering both acidic and basic ranges. Cattle bones treated at 300 °C exhibited maximum adsorption capacity. Upholding the pH at 5.72 a maximum adsorption of 88.90% was achieved in 30 min. Observed results revealed that adsorption kinetics of Pb (II) followed pseudo second order model confirming chemisorptions.

Index Terms— Adsorption, adsorption kinetic, cattle bone ash, calcination, chemisorptions, FTIR, hydroxyapatite.

1 Introduction

Heavy metals are toxic for the atmosphere that occurs in industrial wastewater. Therefore, their removal from wastewater is essential to protect human health and environment [1]. Lead (Pb) is one of the heavy metals which has been widely used in building materials, lead-acid batteries, auto exhaust, ammunition, ceramic glass industries and paints and it can damage human nervous (especially children) and reproductive systems [2].

Several methods are commonly used for the treatment of heavy metals, such as adsorption, chemical precipitation, coagulation, flocculation, extraction and reverse osmosis. Most of these process need high capital cost. They have great disadvantage by operating in a succession of steps of heterogeneous reactions, or distribution of substances between different phases which usually requires a lengthy operating period [3].

Adsorption has been shown to be an economical alternative for removing trace of metals from water. Among the numerous materials applied in adsorption processes, activated carbons, primarily due to their low cost and high adsorption ability, are still the most widely used materials for adsorption of impurities.

In this research work, cattle bone ash has been used as an adsorbent which is an available and abundant waste material. The objective of this research work is to evaluate the feasibility of using cattle bone ash as adsorbent for the removal of Pb(II) from aqueous solution. The bones were calcined at different temperatures to find out the optimum temperature for maximum removal of Pb (II). The influence of experimental conditions such as pH and contact time was also studied.

2 Material and Methods

2.1 Thermal treatment of cattle bone: Preparation and characterization of adsorbent

Cattle bones collected from local market were cleaned and washed with plenty of water. It was then boiled for 30 minutes to remove any trace amount of unwanted substances as well as the odour. This step was followed by drying at ambient temperature. Using a high temperature furnace (Nabertherm, LHT 08/16 Germany) dried bones were calcined at different selected temperatures (300 °C, 500 °C, 600 °C and 700 °C). Finally thermally treated bones were ground to fine powder using Mortar and Pastel. Fig 1. shows the calcined bones.

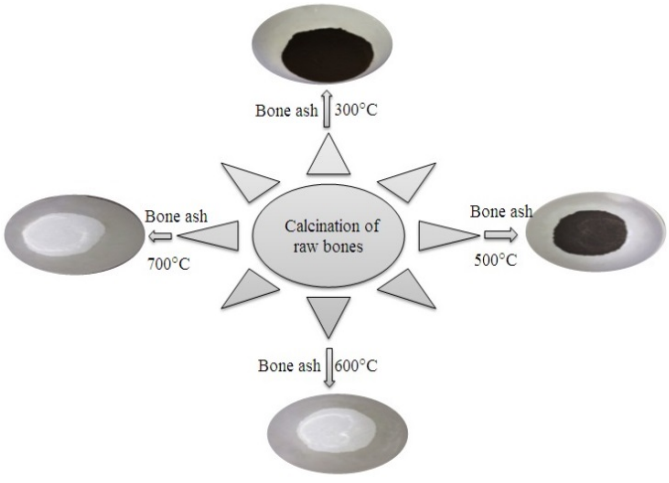

Fig 1.Thermal treatment of bones

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Phase analysis of calcined bones was accomplished by PANalytical (X'Pert PRO XRD PW 3040) X-ray diffractometer (XRD). Using CuKλ (λ = 1.54178°A) radiation, intensity data were collected in 0.02° steps. Observed phases were compared and confirmed using standard JCPDS files. Functional groups were determined by Fourier transform infrared spectrophotometer (FT-IR, Prestige 21, SHIMADZU) following the standard KBr procedure. Particles size distribution of calcined bones was performed using laser diffraction particle size analyzer (MALVERN MASTERSIZER 3000) at room temperature in the range of 10nm up to 3.5mm.

2.2 Adsorption of Pb(II) using bone ash

Batch adsorption process was employed to investigate the adsorption of lead from aqueous medium using thermally treated adsorbents. Prior to the adsorption study a stock solution of **Pb(II)** having a concentration of 1000 ppm was prepared and used throughout the work. Adsorption protocol followed here was customary. However, briefly, **30 mg** of thermally treated (at certain temperature) bone ash was suspended in 30 mL of diluted (5 ppm) Pb(II) solution and the suspension was then placed in a shaking water bath (Stuart SB S40) which facilitated a proper distribution of the adsorbent in the solution. After a fixed time interval the solution was subjected to centrifuge to get clear solution. Concentration of lead in the supernatant solution was measured by Atomic Absorption Spectrometer, AAS [nov AA® 350, Analytik Jena, Germany] coupled with flame mode. Identical experimental procedure was followed for each treated adsorbent. To optimize maximum adsorption condition, primarily adsorbent-substrate solution contact time (upto 60 min) and both acidic and basic ranges of pH (3, 5, 8 and 9) were considered.

pH of the working solutions was controlled using either 0.01 M HCl or 0.01 M NaOH.

The efficacy of the treated bone ash in removing Pb(II) from synthetic wastewater was calculated with the aid of the following Equation [4].

$$\text{Removal Efficiency (\%)} = \frac{C_0 - C_f}{C_0} \times 100 \qquad (1)$$

Where C_0 and C_f are the initial and final concentration (mg/L) of Pb(II) respectively.

3 Adsorption Kinetics

Pb(II) adsorption kinetics was evaluated in terms of pseudo-first order and pseudo-second order kinetic models [4]. Pseudo-first order equation in other words familiar as Lagergren first-order model describes the adsorption rate based on the adsorption capacity. Pseudo-first order model expressed according to the following integrated format (Equation 2) was used to analyze the adsorption data.

$$\log(q_e - q_t) = \log q_e - \left[\frac{K_1}{2.303}\right] t \qquad (2)$$

Where, q_e (meq/g) and q_t are the amount of adsorbed Pb (II) ions on the adsorbent at equilibrium and at time t, respectively.$K_1$is the Lagergrenrate constant of pseudo-first order adsorption (min^{-1}).

The pseudo-second order equation assumes that chemisorption plays the key role in controlling the adsorption mechanism.According to this model rate of sorption is proportional to the square number of unoccupied sites [4]. The linearized form of this model used in to analyze adsorption kinetics is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

Where K_2 is pseudo-second order rate constant (g/meq min).

4 Result and Discussion

4.1 Characterization of adsorbent material

4.1.1 FT-IR analysis

Functional groups of adsorbents not only affect the adsorption behavior, but also dominate the adsorption mechanism [5]. However, the peaks appeared in all FT-IR spectra were assigned to various functional groups according to their respective wave numbers. Observed peaks are in well agreement with that of calcium hydroxyapatite (HAP) the principal inorganic component of bone [6]. Bending modes (ν_2 and ν_4) of PO_4^{3-} group are observed at positions 465 - 467 cm^{-1} and ~565 cm^{-1}& ~605 cm^{-1} respectively. Symmetric and asymmetric stretching (ν_1 and ν_3) modes of PO_4^{3-} group are recorded accordingly at 947 – 962 cm^{-1} and ~1045 cm^{-1}. Broad band in the range of 3427-3441 cm^{-1} for cattle bone ash calcined at different temperature attributed to traces of water incorporated in hydroxyapatite (HAP) structure of bone ash. Peak at around 1625 cm^{-1} is due to H-O-H bending mode [7].Fig 2. shows a typical FT-IR spectrum of animal bone ash treated at 700°C and Table 1 summarizes the positions of absorption bands and their corresponding assignments.

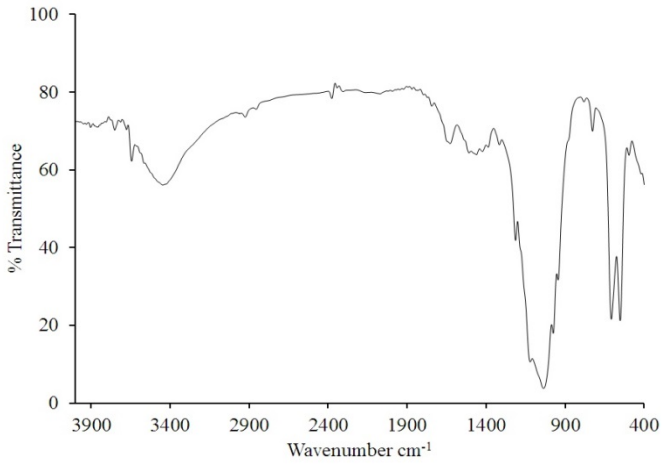

Fig 2.FT-IR sprectrum of thermally treated (at 700 °C) bone.

TABLE 1

FTIR ANALYSIS OF DIFFERENT CALCINED TEMPERATURE CATTLE BONE ASH

Assignments	Band positions of treated bone ash, cm^{-1}			
	300 °C	500 °C	600 °C	700 °C
PO_4^{3-} (ν_2)	465.1	463.2	466.2	467.7
PO_4^{3-} (ν_4)	561.7	567.7	565.4	566.9
PO_4^{3-} (ν_4)	603.5	605.4	603.7	601.5
PO_4^{3-} (ν_1)	947.2	962.2	957.8	945.6
PO_4^{3-} (ν_3)	1040.1	1034.1	1045.6	1040.6
H-O-H bending	1625.6	1629.7	1639.5	1621.9
Structural OH-	3427.4	3431.5	3440.7	3441.4

4.1.2 XRD Analysis

Given in Fig 3., is the typical XRD pattern of cattle bone calcined at various temperatures (i.e. 300, 500, 600 and 700°C). Indexed XRD peaks are in well agreement with the hexagonal HAP reference pattern (JCPDS Card # 9-432). XRD diffractogram had specific peaks (2 1 1, 1 1 2, 2 0 2 and 2 0 0 planes) of HAP as compared with HAP reference pattern [8]. However, in case of 300 °C and 500 °C temperatures, appearance of the peaks in broad fashion provides the information that calcination of bone at these two temperatures result mostly amorphous phase of HAP [9].The effect of calcination temperature became more significant through the growing form of crystallinity which ultimately delivers enhanced crystallite size when thermal treatment was accomplished at 600 °C and 700 °C. This is because higher temperature facilitates the small sized grains to be in fused state making larger aggregates.

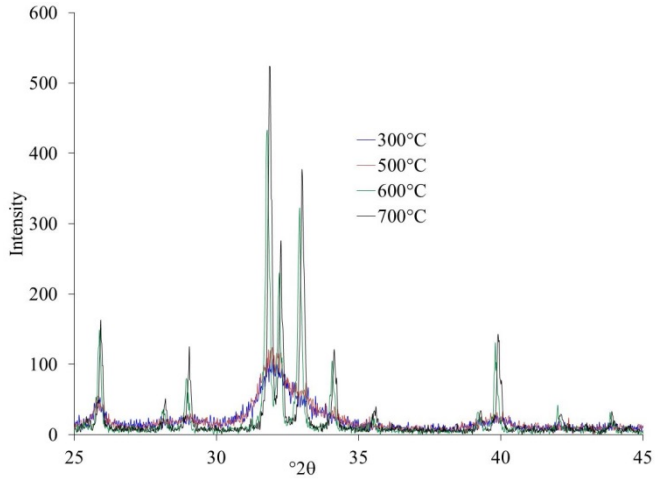

Fig 3. XRD patterns of cattle bone ash at various temperatures.

The crystallite sizes for treated bone ash samples were calculated from Scherrer's relationship:

$$D = \frac{79.5}{\Delta \cos\theta} \qquad (4)$$

Where D = crystal size (Å), Δ = Full width at half maxima (FWHM) in degree.The Bragg reflections at 211 plane was considered to compute the crystallite size.

The lattice parameters and surface area of treated bone samples were calculated using equations 5 and 6 respectively. Measure crystallite size, lattice parameters and surface area of all treated samples are tabulated in Table 2.

$$\frac{1}{d^2} = \frac{4}{3}\left[\frac{h^2 + hk + k^2}{a^2}\right] + \frac{l^2}{c^2} \qquad (5)$$

$$\text{Surface area} = \frac{6 \times 10^3}{\rho D} \qquad (6)$$

Where ρ = density of cattle bone (7.08×10^3g m^{-3}) and D = crystallite size

TABLE 2
CRISTALLINE SIZE, LATTICE PARAMETERS AND SURFACE AREA CALCULATED USING XRD DATA

Parameters	Cattle bone treated at			
	300 °C	500 °C	600 °C	700 °C
Crystallite size, nm	15.01	21.00	41.10	46.68
Lattice parameters	a = 9.39 Å	a = 9.42 Å	a = 9.40 Å	a = 9.39 Å
	b = 6.89 Å	b = 6.90 Å	b = 6.89 Å	b = 6.87 Å
Surface area, m^2 g^{-1}	126.50	90.42	45.10	40.68

It is clearly evident from Table 2 that the values of lattice parameters are very close to those values obtained from the JCPDS (ref. code: 89-6439) standard data of hydroxyapatite [8].However, observed crystallite size increases with the increase of sintering temperature. Surface area values also varied and the highest surface area has been obtained at 300 °C. This indicates the higher activity of this sample compare to the other treated samples.

4.1.3 Analysis of particles size of treated bone

The results obtained from particle size analyzer given in Table: 3 and fig 4.

TABLE 3
PARTICLE SIZE OF DISTRIBUTION OF CATTLE BONE ASH

Result units	300 °C	500 °C
	Volume (µm)	
D_v (10)	3.35	2.79
D_v (50)	19.2	10.9
D_v (90)	79.2	28.3

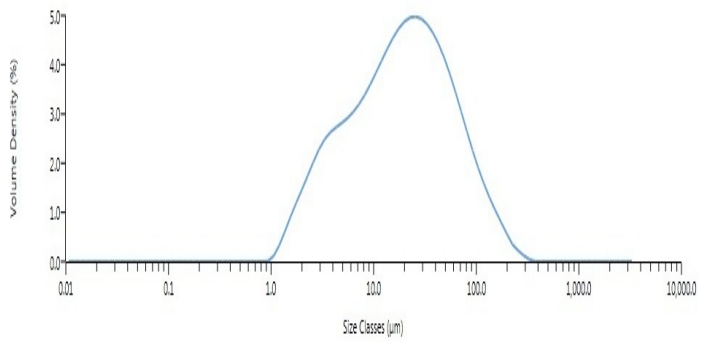

Fig 4.Particles size distribution of cattle bone treated at 300°C.

4.2 Adsorption of Pb(II) on treated bone ash

4.2.1 Effect of contact time

Substrate solution-adsorbent contact time plays an important role in controlling the adsorption efficiency. Fig 5. shows adsorption efficiency of all the treated bones as a function of time. There is a general increase in the % adsorption of Pb(II) with time (Fig 5.). Clearly it is evident from Fig 5. that for all cases maximum adsorption was achieved within 5 minutes then the process became slow and reached to equlibrium by 40 min. The plausible reason for such behaviour could be the prompt involvement of available active sites of the adsorbent and Pb(II) interacts easily with these sites [10]. However, cattle bone treated at 300 °C showed highest effciency because of its amorphous nature and high surface area (as observed from XRD)

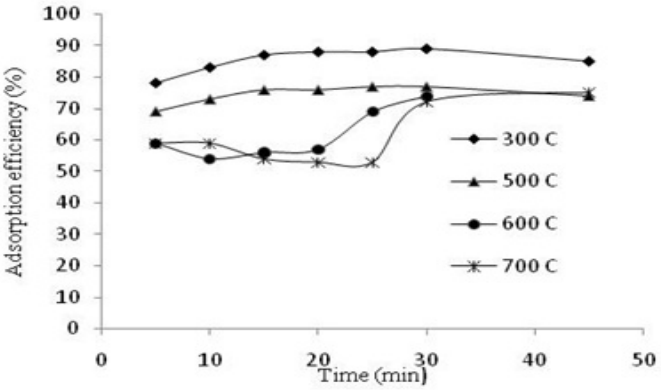

Fig 5.Effect of contact time

4.2.2 Effect of pH

Fig 6. shows that best adsorption occurs when the solution pH was 6. pH of solution affects the surface of the adsorbent and the degree of ionization of adsorbate. At low pH, the amount of protons H^+ is important that prevents the formation of a bond between Pb(II) and the active site. On the other hand, at high pH, the Pb(II) ions becomes precipitated in the form of $Pb(OH)_2$, $Pb(OH)_3^-$, $Pb2(OH)^{3+}$, $Pb_3(OH)_4^{2+}$, and $Pb_4(OH)_4^{4+}$ which prevents adsorption of Pb(II) on active sites [11].

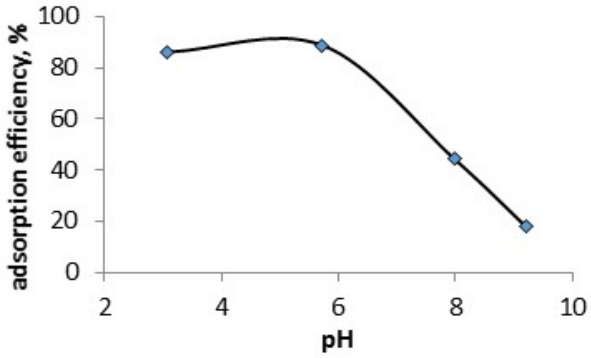

Fig 6.Effect of adsorption efficiency on pH of adsorbent fired at 300 °C

4.3 Kinetics of adsorption process

In order to get a better understanding of the adsorption process, adsorption kinetics of Pb(II) ions were investigated using pseudo-first-order and pseudo-second-order kinetic models.

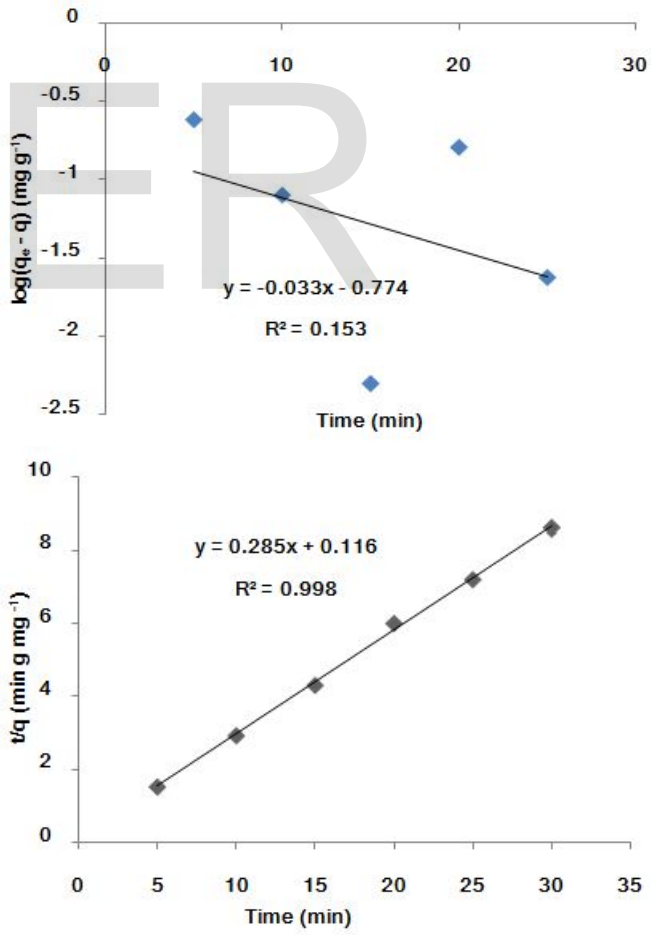

Fig 7.Pseudo-first order kinetic model (a) and Pseudo-second-order kinetic model (b)

Pseudo-first order and pseudo-second order rate constants

and q_e were calculated from the slope of the respective graphs. Calculated values are summarized in Table 3. The value of R^2 in pseudo-first order is 0.153 which is not satisfactory. In case of pseudo second order kinetic model a linear representation with R^2 = 0.998 indicates that this model is favourable for adsorption of Pb(II) ions according ot the present experimental protocol. However, from the Table 4, it is clear that here the adsorption kinetics model follows pseudo second order which confirms chemisorptions [4].

TABLE 4
PARAMETERS OF PSEUDO-FIRST-ORDER, PSEUDO-SECOND-ORDER

Kinetic model	Experimental q_e mg g^{-1}	Calculated q_e mg g−1	R^2	K_1 min^{-1}	K_2 gmg^{-1} min^{-1}
Pseudo first order	3.481	0.168	0.153	0.076	-
Pseudo second order	3.481	3.509	0.998	-	0.700

5 Conclusion

From the overall analysis, it can be concluded that cattle bone ash is an efficient low cost adsorbent which can be used for removing Pb (II) ions from aqueous solution. In this experiment, only the effect of calcination temperature, contact time and pH on adsorption was investigated.

The animal bone ash calcined at 300 °C found the best adsorption efficiency to remove Pb (II) metals ions from aqueous solutions. According to the XRD analysis of 300–700 °C bone ashes, a decrease of surface area was noticed from 126.50 to 40.68 m^2 g^{-1}, similarly from particle size analysis it was observed that 90% of bone ash calcined at 300 °C was 79 µm which also reduces with temperature. As higher surface area obtained at 300 °C, it explains it's higher adsorption. Adsorptions of Pb (II) metals ions from aqueous solutions found to dependent on pH and contact time. The highest adsorption took place for the Pb (II) metals within 30 minutes at pH 5.72. The adsorption kinetics model of Pb(II) was better described with pseudo second order rate equation which confirms the chemisorptions. However it is suggested to study more parameter such as initial concentration of Pb(II), adsorbent dose and solution temperature to determine optimum condition to remove Pb(II) metals ions at maximum percentage.

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