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Continuous Column Performance in Lead Removal from Aquatic Environment Using Fixed Bed of Goat Hoofs

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Abstract:- The current work aims to evaluate the potential of Goat Hoofs, in a continuous flow removal of lead ions from aqueous and real effluents with more successive capability and regeneration cycles. The influential parameters obtained in a batch equilibration method are used to scale-up the process of short term and long term column studies. The fixed bed study is conducted in a column with the constant flow rate of 50 mL/ 5 min, 0.71 mm particle size and at the initial concentration of 70 – 100 mg/ L. The long term analysis at the laboratory levels, reveal 98% and 92% lead removal from aqueous and industrial leachates. Fabric Reinforced Polymer is designed for column studies for industrial effluents, later extended to the effluent discharge plants where the assessed performance indicated 100% removal of Pb(II) ions from Paint factory wastewaters.

Keywords: *lead, fixed bed column, adsorption, goat hoof.*

1. Introduction

Industrial wastewater polluted with heavy metals has endangered the human health and ecosystem. Lead is one of the most extensive toxic metals[1,2] in the paint industries operated in Coimbatore are reported under Red category list, their main source of pollution being leaching into soil and aquatic streams.

Adsorption process is one of the efficient methods in trapping toxic metal ions, due to its simplicity, sludge-free operation, easiness in handling, availability of various adsorbents [3] and also efficient removal of metals at lower-concentration levels. Batch operations are very easy to operate on the laboratory scale but these are not convenient for the field applications [4,5]. Batch equilibration experiment shows the adsorption capacity of the sorbent, which provide fundamental information about the effectiveness of adsorbent - adsorbate system[6].However, the adsorption capacity data obtained from batch studies provide adequate scale-up information regarding the column operation systems [7].

In the industrial point of view, the removal of pollutants including dyes, heavy metal ions etc. using continuous flow systems is found to be very useful and reliable. The continuous flow system is an effective process for the treatment of large-scale wastewater volumes and cyclic adsorption/ desorption practices [3].

However, continuous flow mode studies have been reported in the literature on the removal of lead and other pollutants. In this investigate, the column bed adsorption experiments for Pb(II) removal from aqueous and industrial effluents using Goat Hoofs [8]. This low/ no cost materialis reported to have excellent sorption potential that are affordable and eco-friendly [9,10].

2. Materials and Methods

Collection/ Preparationof adsorbent material

Goat Hooves (GH) were collected in bulk, from the butcher shops located at market places in Coimbatore, Tamil Nadu, washed well with distilled water to eliminate macroscopic impurities, shredded into smaller pieces and sun dried for a week. The shredded Goat Hooves (GH) were soaked in 0.2N NaOH for 3 hours, washed, adjusted to pH 9,dried, sieved into varied mesh sizes using Scientifically Tested Molecular Sieves, (JAYANT Scientific Instruments Co., Mumbai), stored in air tight containers and referred as TGH [8]. Fig 1a and 1b depicts the pictorial representation of the Purchased Goat Hoofs and Sieved Goat Hoof – 0.18 mm

Fig 1a: Purchased Goat Hoofs

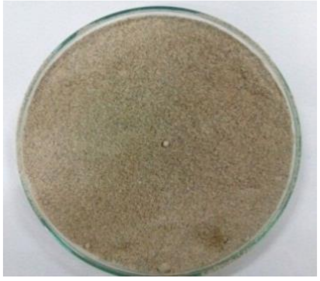

Fig 1b: Sieved Goat Hoofs – 0.18mm

Chemicals

Stock solutions (1000 mg/L) of Pb(II) were prepared using $Pb(NO_3)_2$ salts and aliquots standard of varied concentrations were prepared from the stock solution. pH environments were adjusted by and large with 0.1N HCl / 0.1 N NaOH.

Collection of Effluent Samples

Wastewaters containing Pb(II) and Cr(VI) ions above the tolerance levels were found at Paint industry located in Annur road, Coimbatore. The effluent samples were collected in pre cleaned Can/ PET bottles and analyzed for Pb(II) and Cr(VI) ions of initial concentrations (Fig 2: AAS - *Atomic Absorption Spectrophotometer:Shimadzu (AA 6200)*) after digestion with 0.1 N HNO_3, Pb(II): 70 - 100mg/L, Cr(VI): 16.7 mg/L. The pH and conductivity values of the samples were also recorded using LABTRONICS pH meter and conductivity meter respectively

**Fig 2: Atomic Absorption Spectrophotometer
Shimadzu (AA 6200)**

Batch equilibration studies

50ml volume of Pb(II) and Cr(VI) aqueous solutionswith Goat Hoofs were experimentally verified in a mechanical shaker (KEMI) to define the role of various factors viz., particle sizes (0.18mm, 0.24mm, 0.30mm, 0.42mm and 0.52mm) and dosages(100 mg -500mg: 100 mg interval) of the treated sorbent, initial concentrations of the aqueous Pb(II) and Cr(VI) solutions (50- 250mg/L: 50 mg/L interval),preset time intervals between the sorbent and sorbate species (5 - 30 min : 5 min interval) and pH of the medium (3, 5, 7, 9 and 11) at room temperature to assess the sorption capacityunder laboratory circumstances. The agitated samples were filtered and the residual metal ion (Cr(VI) and Zn(II)) concentrations were analyzed using Atomic Absorption Spectrophotometer. The percentage removal and amount adsorbed were calculated as follows:

$$\text{Removal percentage (\%)} = (C_1 - C_2) / C_1 \times 100$$
$$\text{Amount adsorbed (mg/g)} = (C_1 - C_2) \times V/M$$

where, C_1= initial metal concentration (mg/L), C_2= final metal concentration (mg/L), V= volume (ml) and M= mass of adsorbent (mg).

Column Studies

Batch studies are the basic pilot studies performed to screen the adsorbents before adopting the adsorption method to the field levels [12]. Based on the batch results, column studies were carried out to quantify the practical applicability of the chosen sorbentin the continuous flow mode. The objective of the column schemes is to quantify the parameters which are extended to design the industrial scale fixed bed adsorption columns [13,14].

Regeneration of the Adsorbent

Regeneration andreusability of the adsorbent are an important significance in economic and environmental point of view. Desorption through traditional methods like thermal activation, incineration, and land disposal were not used to restrict the environmental pollution. Regeneration of TGH was done by 0.01 N HCl as desorbing agent, later washed with DD water at the collection rate being fixed as 50 mL/5mins and the experiment was done by repeating the adsorption-desorption cycles[6], for five times. The resultant desorption phenomenon observed in 0.01 N HClmight be attributed to the ion exchange type interaction rather than chemical sorption for Pb(II) – TGH system. Desorption efficiency was calculated using the following formula:

$$\text{Desorption efficiency (\%)} = \frac{\text{Residual metal concentration}}{\text{Initially sorbed metal concentration}} \times 100$$

3. Result and Discussion

Batch Equilibration Studies

The optimized conditions resulted from the batch studiesof Pb(II)-TGHsystem: 0.18 mm, 300 mg, 100 ppm, 5 min, pH 5 , 30^0C ;Cr(VI)-TGH system:0.18 mm, 500 mg, 100ppm, 25 min, pH 2,30^0C. Further increase in agitation time, beyond the attainment of equilibrium, registered least changes in the residual concentrations of the metal ions.The maximum removal of 97 % and 81 % observed for aqueous Pb(II) and Cr(VI) solutions respectively, whereas 84% for Pb(II) and 68 % for Cr(VI) removal for paint industry leachates. The highest uptake value of Pb(II) corresponds to the lower hydrated ionic diameter of Pb(II) ions (0.802nm), compared with Cr(VI) (0.922 nm), also higher charge density favours attractive electrostatic interactions between the TGH and Pb(II) ions.

Column Studies

Fixed bed column studies for Pb(II) removal from water and wastewaters by Goat Hoofs were conducted using short term, long term, pilot scale set-up and prototype device column represented in the Figure 3a, 3b, 3cand 3d respectively. The column was packed with TGH between the two supporting layers of glass wool in order to improve the mechanical strength and prevent the sorbent dispatching. Later, the column was charged with Pb(II) bearing solutions with a volumetric flow rate of 50 mL/ 5 min at room temperature and the initial concentration of 70 – 100 mg/L. The samples were collected at certain time intervals and analyzed using Atomic Absorption Spectrophotometer (AA 6200, Shimadzu).

Short Term Analysis

On the trial basis, 2 g of 0.18 mm TGH was filled in the 20 cm column with the diameter of 3 cm and the Pb(II) solution passed from the top of the column at a flow rate of 10 mL/ 5 min. The result shows 95% removal of Pb(II) ions for 3 litres but the column gets clogged in the short duration due to the smaller particle size (0.18 mm) of the TGH.

Long Term Analysis

The experiments were carried out with a dose of 40 g TGH (0.71 mm) packed in the column having a diameter of 5 cm, 50 cm height, 10 cm bed depth, 100 mg/ L initial Pb(II) concentration and at the flow rate of 50 ml/ 5 min. The sequestering percentages of aqueous Pb(II) solution on TGH was recorded as: 94, 90, 81, 75, 58 % for the respective five cycles and the corresponding desorbed percentage observed to be 95, 90, 88, 77 and 48 %, exposing its better regenerating capacity.

Similar column performances had been performed for paint industrial effluents with the metal ion concentrations of Pb(II)- 83.4 % and Cr(VI)- 16.7%. In first cycle,79 % and 53 % removal was achieved and declined to 18% and 11% for Pb(II) and Cr(VI) ions respectively in the end of third litres. After desorption, the removal efficiency of Pb(II) -48% and Cr(VI) -12%, wherein the retention capacity is reported as 61% for both the metal ions.

Pilot Scale Column Experiments

Pilot scale set-up was performed in a 7.5 cm diameter glass column packed with 150 g TGH in the depth of 4 cm bed height at the flow rate of 50 mL/ 5 min and the paint effluent concentration [Pb(II)] of 78.6 mg/ L. The results implies that the removal efficiency of consecutivethree cycles 86, 71, 48%, where exhausted in the end of 9th, 5th, 3rd litres respectively and the corresponding retaining capacity perceived to be 82, 67 and 39 % for Pb(II) – TGH system. Later, the column schemes are to the effluent discharges with prototype device set-up.

Fibre Reinforced Polymer Column

Based on thepilot scale set up results and optimized conditions observed for both at the laboratory and field levels effluent analysis, Fibre Reinforced Polymer (FRP) Column has been fabricated and examined for the metal leachates from paint industry.

FRP Column	**TGH**
Volume:**1.5 Litrecapacity**	Dosage: **300 g - Pb(II)** removal
Diameter:**3”**	Particle Size: **0.18mm**
Height:**10”**	Column Bed: **4 cm**
Max. Flow rate: **50 mL/ 5 min**	

The performance of the FRP Column packed with 300 g has been assessed by the passage of effluent [Pb(II)] into the inlet of the column with the initial concentration of 70- 100mg/ L and the treated samples were collected through the outlet at a flow rate of 50 mL/5 minutes. The analysis concludes that the removal percentage recorded as 93, 84, 69% where the column exhausted at the end of 11th, 9th, 6th litres respectively and the regeneration ability of three cycles are 91, 82, 60%.

			
Fig 3a: Pb(II) - TGH	**Fig 3b: Effluent - TGH**	**Fig 3c: Pb(II) – TGH Pilot Scale Set-up**	**Fig 3d: Fibre Reinforced Polymer Column**

4. Conclusion

This study was carried out to investigate the practice of fixed bed adsorption to treat aqueous and metal leachates of Pb(II) ions using an eco-based byproducts. The exhausted TGH material of the column was desorbed using 0.01N HCl medium. Long term column experiments were performed using a glass column with a 40 g of TGH registered a maximum efficiency of 94, 79% removal, where exhausted at 12th, 3rd litres of aqueous and industrial effluents respectively. In pilot scale studies, 150 g of TGH packed in a glass column shows the prominent efficiency of 86%, wherein the retention capacity is reported as 82%. The performances of the FRP device filled with 300 g of the TGH recorded a good sorption ability of 93%, where exhausted at 11th litre with the desorption capacity of 91%. The column result shows that the increase of sorbent dose enhances the adsorbent capacity of the fixed bed capacity. Also, the removal efficiency decreases as cycle proceeds because the use of acid solution as desorbing agent may destroy the binding sites of the TGH or insufficient acid solution may allow the lead ion to remain in the binding sites.rom the recorded reports made, it is concluded that slaughterhouse waste (TGH) can serve as an effective alternativefor the removal of lead ion in continuouscolumn mode with excellent regeneration.

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