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Removal Of Pb(Ii) Ions From Aqueous Solution Using Waste Foundry Sand And Bentonite Clay

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Abstract: In the present work an attempt has been made to use Waste Foundry Sand (WFS) and Bentonite clay for the removal of lead (Pb(II)) from the aqueous solution. The removal efficiency of the (WFS) and Bentonite clay was studied as a function of dosage, reaction time and pH of the solution along with the reaction kinetics and ion exchange mechanisms. The characterization and mechanism involved in the uptake of lead ion by the Bentonite clay was studied using instrumental techniques such as X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM). The percentage removal of lead was found to increase gradually with an increase in the pH of the solution. The lead removal kinetics study indicated that the overall process was best described by pseudo first order kinetics. The process followed the ion exchange mechanism. The results indicate that Bentonite clay can be used as an effective and low cost material for the treatment of wastewater polluted with Pb(II) ions.
List of abbreviations: Waste foundry sand (WFS),X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), Bureau of Indian Standards (BIS).
Key words: Bentonite clay; Ion exchange; Lead; Waste foundry sand.

1. Introduction

Water pollution and water scarcity are the most urgent environmental issues in the 21^{st} century[1]. The rapid increase in the industrialization has proportionally increased the amount of waste generated in the effluent produced from the industries. The direct exposures of such waste in the environment are imposing negative impact on both aquatic life and human health [2]. Industrial effluent bearing heavy metals like copper (Cu), lead (Pb), zinc (Zn), cadmium (Cd), chromium (Cr), iron (Fe), etc, are hazardous to human health when they exceed their limits [3]. Other sources of the metal wastes include; the wood processing industry where a chromium and copper-arsenate wood treatment produces arsenic containing wastes; inorganic pigment manufacturing process producing pigments that contain chromium compounds and cadmium sulfide; petroleum refineries which generates conversion catalysts contaminated with nickel, vanadium, and chromium; and photographic operations producing film with high concentrations of silver and ferrocyanide [4]. Heavy metals are highly toxic and are not easily degradable and are commonly found in both the industrial and municipal wastewater. Traces of heavy metals are found in soils and earth's waters, due to disposal of wastewater without any treatment. This may lead to chronic health problems such as renal failure, lung damage, neurological or psychiatric symptoms of liver diseases, insomnia, nausea, chronic asthma, rapid respiration, cancer etc. [5]. Many conventional methods have been used in the removal of heavy metal from the industrial effluent such as ion exchange, precipitation, chemical oxidation/reduction, reverse osmosis, membrane filtration and adsorption [4].

A. Lead

Lead has a great environmental importance and also well known for its toxicity. Industries such as storage batteries manufacturing, pulp and paper, ceramics, printing, pigment manufacturing, petrochemicals, electronics, fuel combustion and photographic materials are the major sources of lead in the environment. Water resources pollution has been a worldwide concern due to indiscriminate disposal of wastes containing lead. According to the Bureau of Indian Standards (BIS) IS 10500-2012, the tolerance limit of lead in drinking water is 0.05 mg/L and in land surface water is 0.1 mg/L [6].

Assimilation in human body causes severe damage to the kidneys, liver, brain, and nervous system, while long term exposure may induce impaired blood synthesis, hypertension, sterility and even can cause miscarriage in pregnant women [7][8].

B. General Introduction of Waste Foundry Sand (WFS)

Waste foundry sand is the byproduct of both ferrous (iron and steel) and non-ferrous (copper, aluminum and brass) metal casting industries. It is composed of finely graded sand and clay particles. Some binders are added to the sand in the foundries in order to obtain an effective and strong mould. Based on the binders used foundry sand is classified into two types, green sand and chemically bonded sand. Green sand is also known as clay-bonded sand consists of high-quality silica sand (85-95%), bentonite clay (4-10%) as a binder, carbonaceous additives (2-10%) and water (2-5%). It is generally black in color. Chemically bonded sand also known as resin sand consists of silica sand (93-99%) and chemical binders (1-3%) and it is generally light-grey in color [9].

C. General Introduction of Clay Minerals

Clays are known as hydrous aluminum silicates having a layer structure and are also called as phyllosilicates, forming a sheet lattice structure. They are formed by the deposition of the volcanic ash, having particle size of 0.002 mm. They are mainly composed of silicates, aluminum, magnesium, oxygen and hydroxide. Due its fine particle size, it has a large surface area which has greater influence on the adsorption capacity, ion exchange property and swelling property. All these properties have made clay mineral of a greater commercial value [10][11].

D. Ion Exchange Capacity of Clays

The characteristic property of clays is their ion exchange capacity. This is the property of clays to adsorb certain anions and cations and their capacity to retain them in exchangeable state. In other words, the adsorbed ions are exchanged for other anions and cations in an aqueous solution, though such an exchange reaction can also take place in non-aqueous environment. The exchangeable ions are held around the outside of the silica-alumina clay mineral structural units, and the exchange reaction generally does not affect the structure of the silica-alumina packet. Ion exchange capacities are determined based on the pH of the aqueous solution [12

2. Materials & Methodology

A. Preparation of Synthetic Solution

Chemicals used in the present experimentation are: lead metal powder Pb (II) (Nice chemicals, 99.5%, AR grade), Nitric acid (HNO_3) (Nice chemicals, 70%, LR grade), 0.1 N NaOH solution.

The synthetic solution (250 mg/L) was prepared by mixing 51.8 gram of lead metal powder in 150 mL of 6 N nitric acid. The mixture is diluted to 1000 mL in a volumetric flask; this is known as the stock solution. Standard solutions of different concentrations were prepared by diluting a known ml of stock solution with distilled water.

B. Preparation of Raw Materials

The waste foundry sand (WFS) and bentonite clay used in the present experimental study was obtained locally from Aqua Alloy Pvt.Ltd. Waste foundry sand containing bentonite clay obtained from the industry was directly used in the experimental work, because the fine particles of the clay were necessary for the experimentation. Physical properties of waste foundry sand are shown in **Table. 1**.

Table 1: Physical properties of WFS

Sl No	Properties	Values
1	Specific gravity	2.48
2	Moisture content	0.14
3	Coefficient of permeability	10-3 to 10-6
4	Plasticity	Non-plastic

The Bentonite clay is derived from the volcanic ash and is a sub group of Smectite mineral and predominantly consists of Montmorillonite minerals. The Bentonite clay has the general formula $Al_2O_34SiO_2$ (H_2O) and is known as hydrated aluminum silicate. It may include gypsum, dolomite, calcite, feldspar, crystoballite, quartz and ferruginous compound. Bentonite clay is used in pharmaceuticalindustry, foundries, as adsorbent and catalyst in the chemical process industries. Based on the composition bentonite clay is classified as sodium Bentonite or sodium Montmorillonite and calcium Bentonite or calcium Montmorillonite[13] [14].
Natural Raw Bentonite Clay was used in present experimentation. The finely powdered sample was sieved to obtain a particle size less than 75µm. This was used for the batch studies and its physical properties are given in the **Table.2**.

C. Analytical Tools

The experiments were conducted for different dosages of samples weighed using, weighbalance (Citizen CY 220). All the experiments were carried out in borosilicate glass vials (Borosil) of 30 mL capacity. To provide proper mixing of the adsorbent and lead solution the vials were rotated to provide end to end mixing using rotary mixer at 30 rpm. After providing sufficient contact time the vials were taken out and the contents were centrifuged using centrifuge (Remi R-4C). The supernatant was collected and pH of the solutions was checked using digital pH meter (Systronics). The lead ion concentration was analyzed in Atomic Adsorption Spectrophotometer (AAS) (GBC 932 plus). XRD and SEM analysis were carried for the samples which gave the best results. XRD analysis was done using D2-Phaser diffractometer. SEM analysis was done using JEOL JSM-6360.

D. Experimental Work

Batch experiments were performed to study the lead removal efficiency from the synthetic solution using WFS and Bentonite clay, by varying the parameters such as contact time, WFS/Bentonite clay dosage and pH. In every experimental set up only one parameter was changed at a time keeping all other parameters constant. Initially 0.5 gram of WFS was added to the glass vials, containing lead ion concentration of 20 mg/L, continuous end to end mixing was provided with the help of rotary mixer at 30 rpm. After providing sufficient mixing, the mixture was transferred to the centrifuge for 5 minutes at 500-800 rpm. The supernatant was collected and stored at 4^oC until lead was analyzed in AAS. The same experiments were carried out for the bentonite clay.

Table 2: Physical properties of Bentonite clay

Sl. No	Parameters	Results
1	Sieve analysis	100% passing through 75µm sieve
2	Specific Gravity	2.7
3	Liquid limit	118.5% (good water holding capacity)
4	Plastic limit	48.57% (good water holding capacity)
5	Swelling index	560% (good water holding capacity)
6	Shrinkage limit	2.11% (less development of cracks)
7	Compaction test	More the compaction lesser is the permeability
8	Permeability test	Highly impervious soil

E. Percentage Removal of Metal

During the batch experiments a known quantity of WFS and Bentonite clay was added to the predetermined heavy metal solution and the mixture was mixed well. The samples were then centrifuged to obtain the supernatant solution to analyze the reduction in the concentration of the heavy metal solution. The percentage removal of the heavy metal from the solution was given by Eq. (1),

$$\text{Pb removal (\%)} = \frac{\text{Co}-\text{Ci}}{\text{Co}} \text{............} \quad (1)$$

Where: C_o = Initial concentration of lead in mg/L
C_i = Final concentration of lead in mg/L

3. Results & Discussions

A. Effect of Reaction Time on Removal of Lead Using WFS

The effect of reaction time on the removal of lead was investigated with initial lead concentration of 20 mg/L, with dosage of 0.5 gram of WFS in each glass vial along with the controls which contained only the lead solution. The contact time maintained was 60 minutes and pH range 1-2. **Fig.1**shows the lead removal efficiency of WFS with respect to time. Similar experiment was carried with 0.5 gram of bentonite clay.

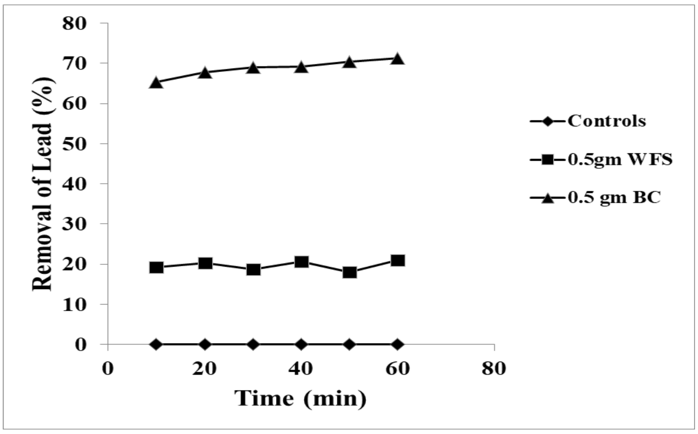

Fig.1: Removal of lead metal ions with different reaction time using WFS and Clay.

B. Effect Of Change Of WFS Dosage On Removal Of Lead Ions

The effect of WFS dosage on the lead removal efficiency was carried out with initial lead concentration of 20 mg/L, with different reaction time, in a pH range of 1-2. **Fig. 2** shows the efficiency increased from 20 % to 30 % for WFS dosage 0.5 gram to 1.0 gram. This clearly demonstrates that with an increase in dosage of WFS, the Pb removal efficiency also increased.

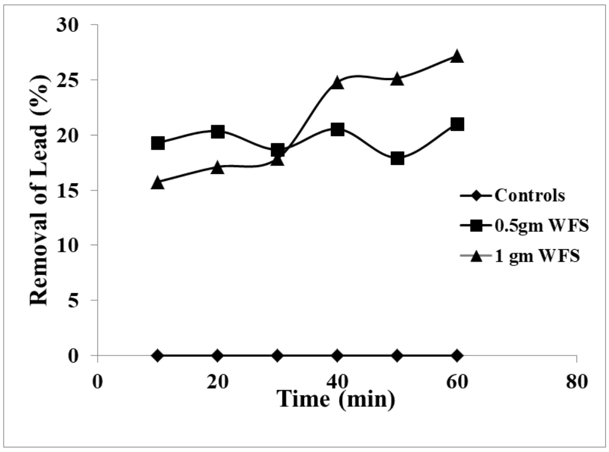

Fig.2: Removal of lead metal ions with varying the dosage of WFS.

C. Effect of Change of Clay Dosage On Removal Of Lead Metal Ions

The effect of bentonite clay on the removal of lead ions was studied with different reaction time, initial lead concentration of 20 mg/L in a pH range of 1-2. **Fig 3** represents the effect of clay dosage on percentage removal of lead ions; it can be observed that the removal efficiency increased from 50 % to 70 % with an increase in the dosage of clay from 0.1 gram to 0.5 gram.

D. Effect of pH on Reduction of Lead Ion Concentration

Initially the pH of the lead solution was between 1-2, to study the effect of pH on the removal of lead (II) ions, the pH of the lead solution was maintained between 4 -5 using 0.1 N NaOH solutions, with 0.1 grams of clay and total reaction time of 60 minutes.

Fig. 4 represents the lead removal efficiency of bentonite clay in the pH range of 1-2; it can be observed that the removal efficiency of the lead was increased with an increase in the pH value. As the pH was increased from 4-5, the removal efficiency was increased from 50% to 99 % while all other parameters were maintained constant.

E. Characterization of Clay Samples

The XRD analysis was carried out for the bentonite clay used in the present study. The **Fig. 5** shows the XRD peak of bentonite clay before reaction and after lead reduction reaction, all these peaks were matched with standard JCPDS card numbers. However there was one new peak in used bentonite clay at 2θ value of 29.3° which matched with standard JCPDS card number 76-1791, which is of lead oxide. This clearly shows that lead is taken up by bentonite clay.

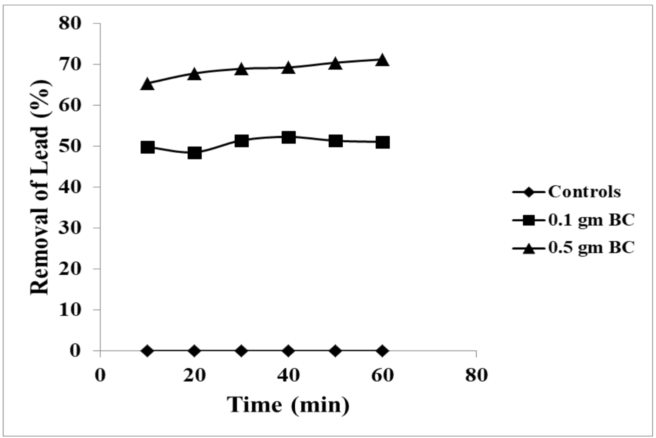

Fig.3: Removal of lead metal ions with varying the dosage of Bentonite clay.

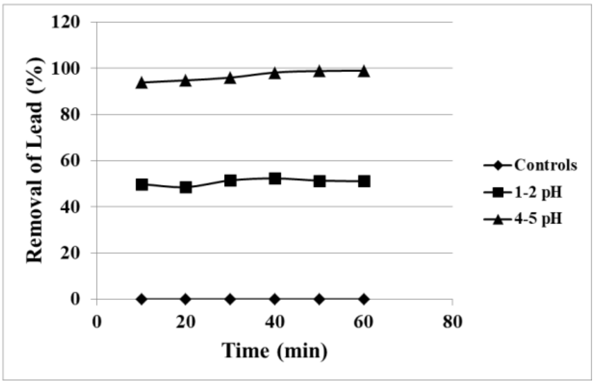

Fig.4: Removal removal of lead metal ions with varying pH range.

SEM is a tool used to study the morphology and variation in the texture of the bentonite clay before and after lead reduction reaction. The images of raw bentonite clay and used bentonite clay are shown in the **Fig. 6**(a), (a_1), (b), (b_1) at different magnifications.

From the results of the SEM images it can be observed that the particles of the raw bentonite clay are dispersed and formed into clumps like structure. The raw clay has a characteristic of flatter and flaky surface area, clear outline shape and are separated from irregular pores whereas in case of used bentonite clay, the particles are clubbed together to form an aggregate like structure and the surface is seen eroded, which are clearly observed from the images obtained at different magnifications.

F. Kinetics and Removal Mechanism

The solution containing only bentonite clay at specified amount had a pH range of 4-5. Since the predominant species at this pH range is Pb^{2+}. Assuming that the proportional ion exchange reactions take place between Pb^{2+} and Ca^{2+} or Mg^{2+} ions in order to maintain the charge balance. Fig. 7: shows the mechanism of cation exchange taking place between Pb^{2+}, Ca^{2+} and Mg^{2+} ions without disturbing the structure of the mineral.

Pseudo first order kinetic was used in the work, significant Pb (II) removal was observed at the pH range of 4-5 with a k value of 0.88 and 1.82, from the "*k*" values obtained it can be observed that the rate of reaction was rapid at the beginning and slowed down as the time increased. About 98-99% of Pb (II) was removed within 40 minutes, and the reaction reached equilibrium. Meanwhile Ca^{2+} and Mg^{2+} ions were released from the clay layers with the uptake of Pb (II) ions. This indicates a stoichiometric replacement induced by an ion exchange reaction.

To investigate the removal mechanism further, XRD analysis was performed and from the XRD data, it was observed that the peaks obtained for the used bentonite clay was similar to that of the peaks obtained for the raw bentonite clay. The peak obtained at 29.3° 2θ in case of used clay was found missing in the raw clay which indicated that the clay has played a major role in the intake of Pb (II) ions through ion exchange mechanism.

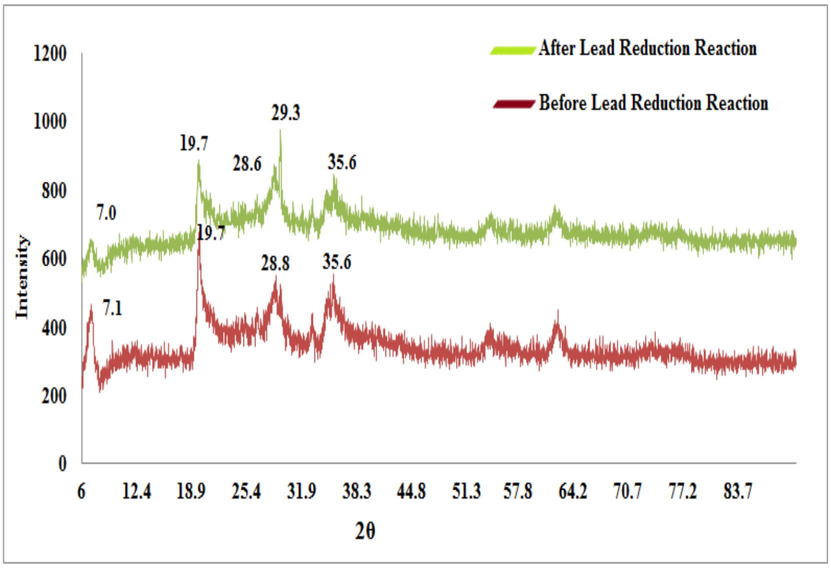

Fig.5: XRD pattern of bentonite clay before and after lead reduction reaction.

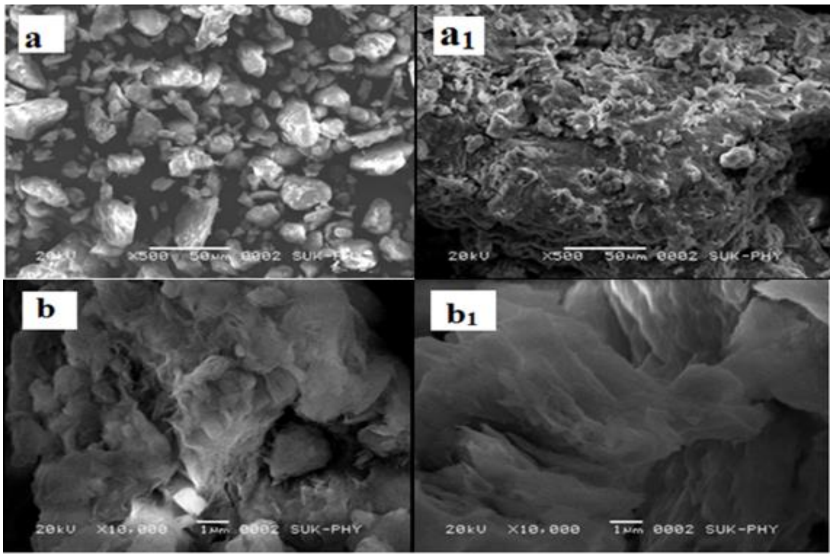

Fig.6: SEM images of (a) raw bentonite clay and (a_1) used bentonite clay at 500X magnification, (b) raw bentonite clay and (b_1) used bentonite clay at 10000X magnification.

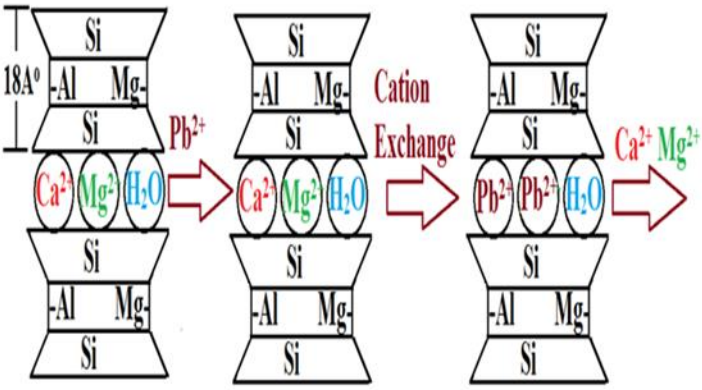

Fig.7: Lead removal mechanism.

6. Concluding Remarks

The following conclusions can be drawn based on the experimental results carried out on lead removal using WFS and bentonite clay from the synthetic wastewater containing lead.

1. In the present experimental work the composition of WFS and structure of different types of clay minerals were studied.
2. Physico-chemical properties of the bentonite clay present in the WFS were analyzed and it was seen that bentonite clay has a very good water holding capacity.
3. Based on the properties of clay minerals, Bentonite clay can be used for the removal of lead metal ions from the aqueous solution.
4. Cation exchange mechanism was developed for the removal of lead metal ions using the bentonite clay.

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Conflict Of Interest

The authors have declared no conflict of interest.

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