Preparation of zeolite from incinerator ash and its application for the remediation of selected inorganic pollutants: A greener approach

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Abstract. Zeolites are potential materials and can conveniently be processed as adsorbents for the removal of environmental pollutants. A wide range of commercial zeolites have been marketed but due to high cost are of limited use. The present research offers a green approach for the synthesis of zeolite using Incinerator waste (ash) as precursor. The significance rests on the conversion of hazardous waste into a useful resource (adsorbent). Incinerator ash (IA) was converted hydrothermally under strongly alkaline conditions into zeolite (ZIA). The synthesized ZIA was applied as virgin adsorbent in batch mode for the removal of primary metal pollutants of Cadmium, Chromium and Lead. The residual concentration of each metal was analyzed on Flame Atomic Absorption Spectrophotometer. Each series of batch was conducted at four varying induced concentration of metal salts as a function of time. The synthesized adsorbent was characterized on FTIR spectrophotometer to assess the involvement of functional group in metal binding to adsorbent surface. The results depicted the performance of ZIA (1mg/Kg) in removing 99.5%, 84% and 78% of Cadmium, Chromium and Lead, respectively, upon adsorbate-adsorbent contact for 30 minutes, at lower dose of ZIA. It was also found that higher is the induced concentration, less is the removal efficiency. It may be due to limiting factor of adsorbent dose. Correlation matrix suggests positive relationship of Pb and Cr, Pb and Cd, Cr and Cd. No negative correlation was found. The study recommends the reutilization of Incinerator ash as a potential adsorbent, which can greatly enhance the sustainability of useful resources.

1. Introduction
The discharge of produced water or pollution by textile and petroleum industries has become a significant issue of environmental concern due to importance of this natural resource in the energetic matrix. In most cases, petroleum related pollution is a chronic problem, due to port activities and the outflow of urban and industrial wastewater contaminated with petroleum and its derivatives. Industries discharge pollutants in liquid, solid and gaseous form in the environment. Heavy metal pollution is a problem associated with areas of intensive industry. The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl) and lead (Pb) [1]. Heavy metals are dangerous because they tend to bioaccumulate. In order to treat these inorganic pollutants, various methods and technologies are used. Adsorption is one of the most feasible options available due to its high removal efficiency for inorganic pollutants.
Adsorption process may also provide an advantage over costly and energy-intensive alternative processes [2]. The adsorption process depends upon the type of adsorbent used [3].

Large amount of waste that is generated from the municipal activities can be converted to useful products. The low cost adsorbent is much preferable for the removal of pollutants [4]. The present environmental concerns over municipal solid waste ash disposal have sparked a resurgent interest in its conversion to value added product such as zeolites. Municipal solid waste ash has a tremendous potential for conversion to zeolite and its subsequent utilization as adsorbents for the removal of heavy metals in the industry [5]. In this investigation, hydrothermal processing was employed to recycle IA by converting it to zeolite-like materials through synthesis. More than 100 types of zeolite have been synthesized from various raw materials in the past. For example, coal-fired power plant fly ash has been successfully converted to many types of zeolite such as phillipsite, analcime, and zeolite P . Zeolite synthesis process using municipal solid waste ash as a source for silica and alumina has not been addressed extensively in the literature [6]. Zeolites are hydrated alumina silicates. Their structure consists of primary building blocks of inorganic tetrahedrons of silicon and alumina oxides. These atoms are strongly bonded together via oxygen bridges to form well-defined channels and cavities [7]. Zeolites are negatively charged as a result of the substitution of silica by alumina in the structure. Water molecules and cations, such as Na, K and Ca, are adsorbed on the pore surfaces [8] . These cations balance the negatively charged zeolite structure and are exchangeable species. Simply, any source that can provide a reactive form of silica and alumina can be used to synthesize zeolite under thermal high alkaline conditions [9] . Zeolite has been synthesized massively from pure silica and alumina chemical compounds, such as sodium silicate and sodium aluminates. Other sources including natural clay and fired coal ash have been also investigated [10].

The aim of this study is to find out the removal ability of ZIA using alkali reaction for harmful inorganic ions from wastewater and to find original ways to utilize waste IA.

2. Experimental

In this study the incinerator fly ash was obtained from national cleaner production center (NCPC) in Rawalpindi, Pakistan.

2.1. Samples preparation

Before the synthesis Zeolite, incinerator fly ash was characterized by FTIR. The total content of heavy metals was also determined on Flame atomic absorption spectrophotometer by US EPA 3050 method. The sample was pre treated and dried in oven at temperature 110 °C then milled until 80% of the sample passed through 40 micrometer sieve. The sieved sample was then subjected to treat hydrothermally.

2.2. Experimental setup

Zeolite synthesis process was performed by placing 5 grams of ash samples in a 50 ml conical flasks, then 50 ml of deionized water was added to the ash samples to obtain solid/ liquid ratio , sodium hydroxide was added in different ratios to obtain 1.5N and 2.5N solutions. Then the flasks were sealed and placed in hot plate that was maintained either at 60 °C or at 100 °C for different periods of times including 6, 24 and 72 hours. Conditions that are mentioned above were used for another set of ash samples . After the hydrothermal process is completed the reacting solution was decanted and samples were washed three times with deionized water, the residue was separated from samples by using what man filter paper 60.[11].

2.3. Characterization of synthesized product

The synthesized products were characterized by the properties listed as follows: (1) Functional group identification, Spectra of adsorbent recorded from 4000cm-1 to 400 cm-1 on FTIR spectrophotometer (FTIR 8400, Shimadzu, Japan) ; (2) mineral species, by X-ray diffraction –XRD analysis using Cu anode material, 45 kV, 40 mA, and a scanning rate of one degree per second . The results of determined d-spacing and relative intensities for corresponding 2u values were analyzed by Xpert
High score PANalytical Malaysia (; (3) TGA and (4) SEM of sample to identify particle size. So doing, each of the mineral species including zeolite-like materials was identified according to the major and minor peaks. Due to the complexity of crystalline phases, the overlapping of peaks for different mineral species is a commonplace.

2.4. Preparation of Stock Solutions

2.4.1. Preparation of 1000 mg/L stock solution of Lead Nitrate
A salt of 0.1599 grams of Pb (NO₃)₂ was dissolved in 10 mL of deionized water and transferred to a 100 mL volumetric flask. The volume is made up to 100 mL with deionized water. The 1000 mg/L stock solution is prepared.

2.4.2. Preparation of 1000 mg/L stock solution of Cadmium Nitrate
A salt of 0.2744 grams of Cd (NO₃)₂.4H₂O was dissolved in 10 mL of deionized water and transferred to a 100 mL volumetric flask. The volume is made up to 100 mL with deionized water. The 1000 mg/L stock solution is prepared.

2.4.3. Preparation of 1000 mg/L stock solution of Chromium Nitrate
A salt of 0.7695 grams of Cr (NO₃)₂.9H₂O was dissolved in 10 mL of deionized water and transferred to a 100 mL volumetric flask. The volume is made up to 100 mL with deionized water. The 1000 mg/L stock solution is prepared.

2.5. Batch adsorption studies
The laboratory scale experimental studies were conducted using synthetic solutions prepared using deionized water with constant metal concentration for each of Cd, Cr and Pb separately. The uptake of heavy metals on the zeolite was carried out using the batch method. Batch adsorption experiments were conducted using 1 mg dose of zeolite with 10 mL of solutions containing heavy metal ions of desired concentrations (50, 100, 150 and 200 mg/L) for each metal at ambient conditions. The solutions were placed for 60 min. The applied time intervals were 10, 20, 30, 40, 50 and 60 min. and after that solutions containing heavy metals were filtered through Whatman 40 filter paper.

3. Results and Discussion

3.1. Characteristics of incinerator ash
After digestion of raw material, it was run on Flame atomic absorption spectrophotometer to check the metal concentration of Lead, Cadmium, Chromium, Copper, Nickel and Zinc. The metal concentrations of raw material are reported in Table 1.

| Table 1: Metals concentration in incinerator ash |
|------------------------------------------------|
| **Metal** | **Concentration (mg/L)** |
| Lead      | 2.4268                 |
| Cadmium   | 0.0423                 |
| Chromium  | 2.8387                 |
| Copper    | 12.1336                |
| Nickel    | 2.2327                 |
| Zinc      | 7.887                  |

3.2. Characteristics of synthesized product
The characterization of adsorbent material ZIA is done by using FTIR and XRD analysis.

3.2.1. FTIR characterization of adsorbent
The FTIR characterization of these adsorbent is showed in figure. In it the major peaks and band were taken and studied to find out the functional group present in Zeolite. Compare these spectrums to the
standardized FTIR spectrum table. In all type of Zeolite the following functional groups exist showed in Table 2 (FTIR 8400, Shimadzu, Japan).

| Wave number (cm⁻¹) | Assignment                           |
|-------------------|-------------------------------------|
| 3600 - 3650 cm⁻¹  | Hydroxyl group                      |
| 1640 cm⁻¹         | Adsorbed H₂O                        |
| 1438 - 1452 cm⁻¹  | Aluminum containing entities; AlₓOᵧⁿ⁺ |
| 1250 - 920 cm⁻¹   | Tetrahedral SiO₄/₂ / AlO₄/₂          |
| 650 - 500 cm⁻¹    | Si-O / Al-O bend; external linkages  |
| 200 - 500 cm⁻¹    | Cationic vibration; far infrared region |

Vibrations of the frameworks of zeolites in following figure give rise to typical bands in the mid and far infrared. A distinction is made between external and internal vibrations of the Si or Al O₄/₂ tetrahedral. The original assignments of the main IR bands in zeolite adsorbent ZIA is as follows: internal tetrahedral 1250 - 920 cm⁻¹, asymmetrical stretch (n_asym); 720 - 650 cm⁻¹, symmetrical stretch (n_sym; 500 - 420 cm⁻¹, Si/Al-O bend; external linkages: 650 - 500 cm⁻¹, double ring vibrations; 420 - 300 cm⁻¹, pore opening vibrations; 1150 - 1050 cm⁻¹, asymmetrical stretch; 820 - 750 cm⁻¹, symmetrical stretch. The positions of bands due to vibrations of external linkages are often very sensitive to structure [12].

Figure 1. FTIR characterization of Adsorbent ZIA

3.2.2. X-ray diffraction analysis
Results of X-ray diffraction analysis have proved that hydrothermal processing is capable of converting IA into zeolite like materials. After synthesis several types of zeolite have been identified on basis of different conditions. XRD powder pattern for the synthesized product resulted from various IA mineralizer ratios are similar, but different in relative intensities for various mineral species [13].
Table 3. XRD identified pattern of compounds in hydrothermally treated Zeolite at 2.5N NaOH at 100°C

| Visible | Ref. Code   | Score | Compound Name                     | Displacement [°2Th.] | Scale Factor | Chemical Formula |
|---------|-------------|-------|-----------------------------------|----------------------|--------------|------------------|
| *       | 01-086-2335 | 58    | Magnesium Calcium Carbonate       | 0.000                | 0.820        | (Mg.064 Ca.936 ) (CO₃) |
| *       | 01-083-2467 | 39    | Silicon Oxide                     | 0.000                | 0.277        | SiO₂              |

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| *       | 98-017-0486 | 27    | Zeolite                            | 0.000                | 0.133        | O₂Si₁             |
| *       | 01-078-1254 | 41    | Silicon Oxide                     | 0.000                | 0.238        | SiO₂              |

On the other hand, different types of compounds were identified when 1.5 N NaOH was used; whereas magnesium calcium carbonate and silicon oxide present which shows the existence of zeolite shown in fig 3[14].

3.2.3. TGA of synthesized product
The number of water molecules attached with the hydrothermally synthesized zeolite and its thermal stability was investigated using TGA. Upon heating the sample from room temperature a continuous weight loss of 55% is clearly observed in TGA. This weight loss is may be due to the dehydration of physically adsorbed water. When the sample is further heated in the temperature range of 200 to 700°C the weight loss observed is attributed to desorption of remaining water enclosed in the material matrix. Reduced weight loss in this region was observed with increase in crystallization of the sample which is consistent with the fact that zeolite becomes more hydrophobic as the Al content decreases [14].
Figure 2. Pattern of X-ray diffraction of hydrothermally treated zeolite at 2.5N NaOH with at 100°C

Figure 3: TGA of synthesized I.A
3.2.4. SEM of synthesized product

The synthesized product as examined under an electronic microscope. The micrograph is presented in Figure 4 by using different magnifications. The sample revealed the presence of some cubic crystal of zeolite. The micrograph indicated a plate like structure which is an indication that the silica and alumina are sliding over one another. Some partial damage of the plate like structure was observed in the synthesized sample. The SEM image revealed a uniform particle size of the sample with a regular shape. The synthesis SEM results give a narrow distribution of particle size with average crystal size of 1µm [14].

![SEM images](image)

**Figure 4**: SEM of adsorbent at different magnifications (a) 10,000 X, (b) 15,000 X, (c) 22,000X and (d) 95,000X

3.3. Adsorption of heavy metals

3.3.1. Effect of contact time

The studies of different contact time helps in determine the removal of heavy metal from constant mass of adsorbent (1mg) at different time intervals of 10, 20,30,40,50 and 60 min. The results given in Figure showed that the adsorption of the studied heavy metals has gradual increase with contact time because ions has maximum time to hold on to the surfaces of zeolite by physical or chemical bonding until 50 min then the removal percent became constant i.e. equilibrium is attained[15]. From the calculated removal percentage, the efficiency of IA-Z is 99.5 %, 84% and 78% of Cadmium, Chromium and Lead, respectively at optimum contact time although. This may be attributed to the fact that both Zeolite can act as ion exchanger. Accordingly, the pore diameter is not effective but the
operating capacity depends up on other parameters such as concentration of adsorbent, contact time and particle size [16].

![Graph](image)

**Figure 5:** Removal of Metals using zeolite as an adsorbent at different contact time (optimum operating conditions).

3.3.2. Effect of induced concentrations

Four different concentrations (50, 100, 150, 200mg/L) of Heavy metals solution were introduced on Zeolite adsorbent with different contact time. It is investigated from data that change in induced concentration has significant impact on adsorption process. It is deducted that adsorbent showed the decreasing trend of adsorption with increase in induced concentrations of metal solutions. The reason behind decrease in adsorption is attributed to the less number of available adsorption active sites as compared to heavy metal concentrations [17]. From the result showed in Figure the percentage removal at initial concentrations of the heavy metals are high, particularly for Lead, Cadmium and Chromium whereby the ability to absorb Pb, Cd and Cr cations at higher concentrations is less because it involved energetically less favorable sites of zeolite in the uptake of heavy metals. The higher metal uptake at low concentration is due to the availability of greater surface area with active centers on the adsorbent for lesser amounts of adsorbate ions [18].

![Graph](image)

**Figure 6:** Removal of Metals (a) Lead, (b) Cadmium and (c) Chromium using ZIA adsorbent at different induced concentration.
3.3.3. Batch Adsorption studies for Industrial Effluents
Industrial effluents were collected from point source of Plastic factory (PE) located on Millet road (Sargodha road), Textile I (TE-I) and Textile II (TE-II) located on Bawachuk, Manawala, Faisalabad. Water samples were also collected from D- separator (D-S) and C- separator (C-S) of Attock oil refinery limited located in Morgah, Rawalpindi. The industrial effluents were subjected to batch removal for the removal of metals and azo dyes using zeolites synthesized from incinerator ash under varying experimental parameters. The results were analyzed on FAAS. The 1 mg dose of zeolite was placed in each effluent taken from different industries. The effluents were placed for 60 minutes for the removal of metals. The samples were then filtered and analyzed. The results are shown in following figure 7. The results are quite similar to the synthetic solution batch experiment performed in lab. The Sequence of removal efficiency of IA-Z is Cd > Cr > Pb > Cu > Ni > Zn. Along with the heavy metals Cu, Zn and Ni removal from effluents are also investigated.

Figure 7: Removal of Metals by using CFA-Z adsorbent from industrial effluents (a) PE, (b) TE-I, (c) TE-II, (d) D-S and (e) C-S
4. Conclusion
The zeolitic type materials synthesized by hydrothermal conversion of incinerator ash demonstrated promising adsorption performance for the three heavy metal contaminants tested (Cd$^{2+}$, Cr$^{2+}$ and Pb$^{2+}$).

The key findings of this study are:
- Adsorption studies indicated higher affinity for Cd, Cr and Pb for ZIA.
- The adsorption performance of ZIA was generally superior to that of the natural zeolite for both synthetic heavy metal solutions and contaminated industrial effluents. ZIA achieved 99.5%, 84% and 78% of Cadmium, Chromium and Lead respectively from 1 mg sorbent dosage.
- The Sequence of average removal of metals at optimum operating conditions on ZIA as Cd > Cr > Pb

Given the positive results found in this study, further work aims to optimize the performance of the ZIA. The affinity of this material for heavy metals, its flexibility and low-cost, also open the possibility for its application in other industrial processes, including chemical and catalyst synthesis. In any case, the reutilization of incinerator ash achieves the goal of reducing the burden of industry on its safe disposal and improves the sustainability of waste incineration technology.

5. References
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