

# Removal of Zinc from Aqueous Solution Using Adsorption Phenomena

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**Abstract**— Adsorption is one of the most popular methods for the removal of pollutants from effluents since proper design of the adsorption process will produce high quality treated effluents. The most frequently applied adsorbent for the removal of heavy metal is activated carbon. However it is an expensive material. The use of alternative and perhaps cheaper adsorbents is attractive. In the present study, industrial wastes generated in thermal power plant and in sawmill i.e., coal fly ash and sawdust are used as adsorbents in both active and inactive form, for the removal of Zinc ions from the synthetic zinc solution and to evaluate the adsorptive capacities of the same. Increase in the solution concentration decreases the removal efficiency. The optimum contact time for inactive fly ash, active fly ash, inactive sawdust and active sawdust are 60, 120, 60 and 120 minutes respectively. Increase in mass of adsorbent leads to increase in metal ion adsorption due to increase in number of active adsorption sites. Maximum adsorption at pH 6-7 was observed for sawdust and at higher pH value of 8, adsorption was favorable for fly ash. The Freundlich Adsorption model was best fitted for sawdust and fly ash in active and inactive form for the adsorption of Zinc. The experimental data did not represent best fit for Langmuir Adsorption model. The industrial wastes: Fly ash and Sawdust can be used effectively as adsorbents in removal of zinc.

**Index Terms**— Adsorption, coal fly ash, Freundlich isotherm model, Langmuir isotherm model, sawdust, zinc.

## 1 INTRODUCTION

**W**ATER does not divide; it connects. With simplicity it links all aspects of our existence. Earth was originally allotted a finite amount of water we have no more or no less than that original allotment today. It logically follows that, in order to sustain life as we know it, we must do everything we can to preserve and protect our water supply. We also must purify and reuse the water we presently waste (i.e., wastewater) [1].

Water is typically referred to as polluted when it is impaired by anthropogenic contaminants and either does not support a human use, such as drinking water, and/or undergoes a marked shift in its ability to support its constituent biotic communities, such as fish. Natural phenomena such as volcanoes, algae blooms, storms, and earthquakes also cause major changes in water quality and the ecological status of water [2].

Pollution has been very damaging to aquatic ecosystems, and may consist of agricultural, urban, and industrial wastes containing contaminants such as sewage, fertilizer, and heavy metals that has proven to be very damaging to aquatic habitats and species. Metals, a major category of globally-distributed pollutants, are natural elements that have been extracted from the earth and harnessed for human industry and products for millennia. Metals are notable for their wide environmental dispersion from such activity; their tendency to accumulate in select tissues of the human body; and their overall potential to be toxic even at relatively minor levels of exposure. Today heavy metals are abundant in our drinking water, air and soil

due to our increased use of these compounds. They are present in virtually every area of modern consumerism from construction materials to cosmetics, medicines to processed foods; fuel sources to agents of destruction; appliances to personal care products. It is very difficult for anyone to avoid exposure to any of the many harmful heavy metals that are so prevalent in our environment [3].

## 2 MATERIALS AND METHODOLOGY

### 2.1 Materials

All the chemicals used are of AR grade. Sample solutions was prepared by dissolving 1 g of pure zinc metal in 20 ml 1:1 hydrochloric acid solution in a conical flask. The resulting 20 ml sample was diluted up to 1000 ml in a volumetric flask using distilled water. This solution was stored in glass bottle [4].

The adsorbents, mixed wood saw dust was obtained from a local sawmill and fly ash was collected from Raichur Thermal Power Station, Shaktinagar Raichur, Karnataka, India.

### 2.2 Apparatus and instrumentation

Atomic absorption spectrophotometer (Model - GBC 932 plus) operating with the Air- acetylene (oxidizing) flame type has been used for the determination of the Zinc concentrations in aqueous solution. Different batch experiments were carried out by measuring atomic absorption spectra at wavelength of 213.9 nm with the working range of 0.4-1.5 µg/ml. A priori, a calibration curve has been established, preparing standard Zinc solutions of 0.4, 0.6, 0.8, 1 and 1.2 µg/ml in order to read the residual concentrations of the metal. For the weighing purpose, digital balance were used having uncertainty to weigh up to ± 0.1 mg. Solution pH was measured by using digital pH meter (Model EQ 621, Make - Equip-tronics, India).

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## 2.3 Preparation of Adsorbents

- A. **Inactive Sawdust:** Locally available sawdust was collected and cleaned to remove dust and extraneous for laboratory use. The samples were then dried in an oven at 105 °C for 24 hrs. The sawdust powder was sieved to obtain a fraction of 150µm. These were used in experiments as inactive sawdust after drying in an oven at 105° C for 2-3 hrs [5].
- B. **Active Sawdust:** Sawdust was earlier dried and sieved to obtain a fraction of 150µm. Activation of sawdust was carried out with phosphoric acid in a ratio of 4:1.5. The acidified mixture was kept in an air oven, maintained at 150±5° C for 12 hr. The resulting char was washed with distilled water and then soaked overnight in 1% sodium carbonate solution to remove the residual acid. The soaked material was then washed with distilled water. Final material was dried at 105° C for 24 hr before conducting adsorption experiments [6].
- C. **Inactive Fly ash:** Fly ash was collected from Raichur Thermal Power Station, Shaktinagar Raichur. Collected fly ash sample was cleaned and oven dried at 105°C for 2 hrs. The sample was ground and sieved to a particle size of 150 µm and was stored in polypropylene container. Before using, sample was oven dried at 105° C for 2-3 hrs [7].
- D. **Active Fly ash:** The fly ash was earlier dried and sieved to obtain a fraction of 150 µm. Activation was carried out by treating it with concentrated sulphuric acid in 1:1 weight ratio. Sample was kept in an oven maintained at a temperature of 150° C for 12 hours. After taking out from oven, sample was washed with distilled water to remove the residual acid. It was dried at 110° C for 5 hours before using in experiment [8].

## 2.4 Batch Adsorption Experiments

The study of adsorption process on zinc removal was conducted considering four cases. Parameters considered for the study were: solution concentration, adsorbent dosage, pH and contact time. In each case one parameter was studied varying its values, while keeping other parameters constant. Detailed methodology of these cases is as follows:

### A. Varying zinc concentration

- a) In this case, concentration of the solution was varied as 1,2,4,8 & 16 mg/l, while keeping the values constant for pH, dosing rate and contact time. The experiments were conducted at laboratory temperature.
- b) 100 ml of diluted solution was taken in 5 beakers labeled from 1 to 5 containing varying zinc concentrations (1, 2, 4, 8 & 16 mg/l) respectively. The pH of aqueous solutions was adjusted to optimum value of 6 by adding required amount of 0.25N NaOH [9]. 2gm of inactive sawdust was added to each of the above 5 beakers. All the samples were agitated for 60 minutes [10]. After providing mentioned contact time, solutions from each beaker were filtered to conical flask using

Whatman 40 filter paper. The filtered samples were then stored in polypropylene bottle at 4° C. Zinc concentrations of these filtered samples were measured using Atomic Absorption Spectrophotometer.

- c) The procedure was repeated for the other three adsorbents activated sawdust (ASD), inactive fly ash (IFA) and activated fly ash (AFA), by maintaining the pH of the solutions as 7, 8 and 8 , 5, 5 and 2.5 gm of adsorbents were added and contact time of 120, 60, 120 min was provided respectively [8], [11], [12], [13].

### B. Varying contact time

- a) In this case contact time was varied as 30, 60, 90, 120 and 150 minutes while keeping the values constant for metal concentration, adsorbent dosage and pH. The experiments were conducted at laboratory temperature.
- b) 100ml of diluted solution was taken in 5 beakers labeled from 1 to 5 containing zinc concentration of 16 mg/l. The pH of aqueous solutions was adjusted to optimum value of 6 by adding required amount of 0.25N NaOH [8]. 2 grams of inactive sawdust was added to each of the above 5 beakers. Samples were then agitated at time intervals 30, 60, 90, 120 and 150 minutes respectively [9]. After providing mentioned contact time, solutions from each beaker were filtered to conical flask using Whatman 40 filter paper. The filtered samples were then stored in polypropylene bottle at 4° C. Zinc concentrations of these filtered samples were measured using Atomic Absorption Spectrophotometer.
- c) The procedure was repeated for the other three adsorbents i.e. ASD, IFA and AFA, by taking initial zinc concentration as 8, 16 and 4 mg/l, pH of the solutions were maintained to the values of 7, 8 and 8, 5, 5 and 2.5 gm of adsorbents were added to the beakers respectively.

### C. Varying Dosage

- a) In this case adsorbent dosage was varied as 1, 2, 3, 4 and 5 g, while keeping the constant values for metal concentration, pH, and contact time. The experiments were conducted at laboratory temperature [14].
- b) 100ml of diluted solution was taken in 5 beakers labeled from 1 to 5 containing initial zinc concentration of 16 mg/l. The pH of aqueous solutions was adjusted to optimum value of 6 using 0.25N NaOH [8]. Inactive sawdust was added to each of the beakers by varying dosage as 1, 2, 3, 4 and 5 grams respectively. All the samples were agitated for 60 minutes [9]. After providing mentioned contact time, solutions from each beaker were filtered to conical flask using Whatman 40 filter paper. The filtered samples were then stored in polypropylene bottle at 4° C. Zinc concentrations of these filtered samples were measured using Atomic Absorption

Spectrophotometer.

- c) The procedure was repeated for other three adsorbents i.e. for ASD, IFA and AFA. The initial zinc concentration in the beakers were 8, 16 and 4 mg/l, the pH values were maintained at 7, 8 and 8 and the contact time of 120, 60 and 120 min was provided respectively.

#### D. Varying pH

- a) In this case pH of the solution was varied as 2, 4, 6, 8 and 10 while keeping the values constant for metal concentration, adsorbent dosage and contact time. The experiments were conducted at laboratory temperature.
- b) 100ml of diluted solution was taken in 5 beakers labeled from 1 to 5 containing zinc concentration of 16 mg/l. The pH of aqueous solutions was varied over the range from 2 to 10 by adding required amount of 0.25N HNO<sub>3</sub> and NaOH [8]. 2gm of inactive sawdust was added to each of the above 5 beakers. All the samples were agitated for 60 minutes. After providing mentioned contact time, solutions from each beaker were filtered to conical flask using Whatman 40 filter paper. The filtered samples were then stored in polypropylene bottle at 4° C. Zinc concentrations of these filtered samples were measured using Atomic Absorption Spectrophotometer.
- c) The procedure was repeated for ASD, IFA and AFA. The initial concentration of the solutions were taken as 8, 16 and 4 mg/l, pH values were varied in the range of 2 - 10, dosage provided was 5, 5 and 2.5 gm with the contact time of 120, 60 and 120 min respectively.

at the beginning. That is probably due to the larger surface area of the sawdust being available at beginning for the adsorption of metals. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. The rate of zinc removal was attained after approximately 2 hours stirring, with further increase in contact time the efficiency decreased slightly. Therefore, contact time of 120 minutes and 60 minutes was selected for further studies for activated adsorbents and adsorbents in inactive form respectively.

#### 3.3 Effect of Adsorbent dosage

The effect of adsorbent dosage on removal of zinc is depicted in Fig. 3. The study was carried out with by keeping the solution concentration as 8, 16, 4 & 16 mg/l, pH value of 7, 6, 8 & 8 and contact time of 120, 60, 120 and 60 minutes for all the adsorbents. It can be inferred from the graph that, increase in adsorbent dosage increases the removal efficiency; maximum removal is obtained at 5 g but gradually the equilibrium is reached in the range of 3 to 5 g. This is because of the availability of active sites at higher dosage. The equilibrium is reached because most of uptake of the metal ions is obtained below 5 g of adsorbent dosage.

#### 3.4 Effect of pH

The biosorption capacity is influenced most by the pH of the solution. The pH of the solution affects the surface charge of the adsorbent, degree of ionization and speciation of the adsorbate species, which may lead to change in kinetics and equilibrium characteristics of the adsorption process. It is clear from Fig. 4 that in pH range of 2-4, there is little or no sorption. The percent adsorption increases in the pH range of 6-8, showing the maximum adsorption at pH 7. The highest increase in the sorption rate of Zn on sawdust was observed in a pH range from 6 to 8. The sorption of metal ions is primarily affected by the surface charge on the sorbent, which is directly influenced by solution pH. The low sorption percent at low pH may be explained by the competitive sorption between proton and Zn ions. As the solution pH increases, the number of negatively charged sites increases which favor the sorption of metal cations. The nature of the adsorption depends on several parameters related to the adsorbent ionic charge, solution pH and the chemistry of metal ion, ability to be hydrolyzed and to form poly nuclear species.

### 3 RESULTS AND DISCUSSIONS

#### 3.1 Effect of Zinc Concentration

The effect of concentration of zinc ions was investigated for ASD, ISD, AFA and IFA with constant contact time of 120, 60, 120 & 60 min, pH value of 7, 6, 8 & 8 and a fixed adsorbent dosage of 5, 2, 2.5 & 5 grams respectively. From the graph Fig. 1 it can be inferred that, the removal efficiency increased gradually for first two concentrations and with further increase in concentration it almost reached equilibrium. The metal uptake mechanism is particularly dependent on the initial heavy metal concentration; at low concentrations, metal ions are adsorbed by specific active sites, while with increase in the metal concentrations the binding sites become saturated, and the removal efficiency gradually decreases as the amount of biomass remains constant. Therefore 8, 16, 4 & 16 mg/l for sawdust and flyash in active and inactive form were opted as metal concentration for further studies.

#### 3.2 Effect of Contact time

The effect of contact time on zinc removal was investigated by varying the time as 30, 60, 90, 120 and 150 minutes for all the mentioned adsorbents with solution concentration of 8, 16, 4 & 16 mg/l with other parameters being constant. The Fig. 2 reveals that the rate of the percentage of zinc removal is higher

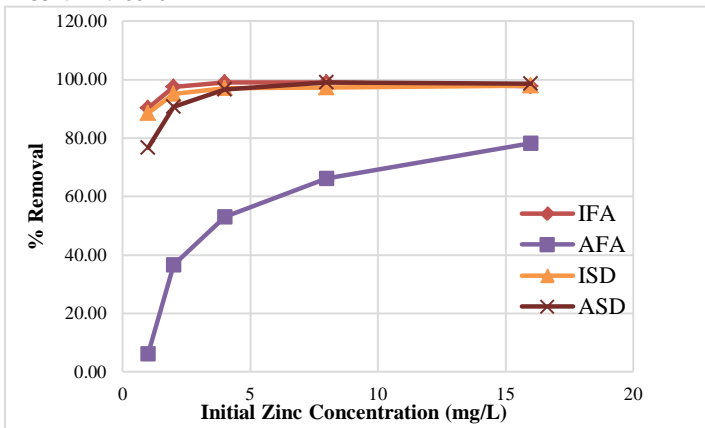


Fig. 1 Adsorption efficiency with varying zinc concentration using different adsorbents

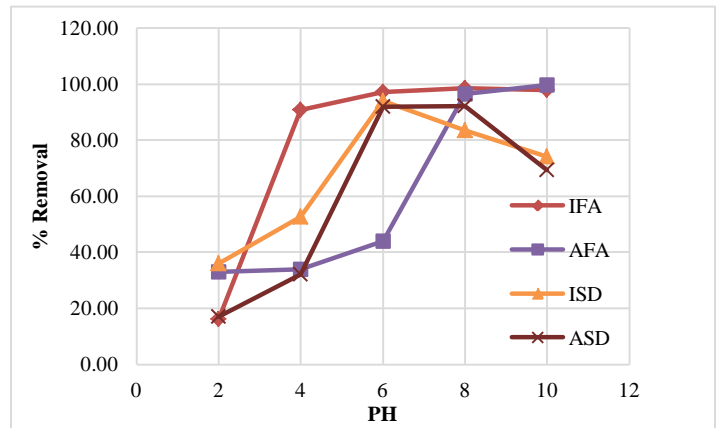


Fig. 4 Effect of varying pH on removal of zinc

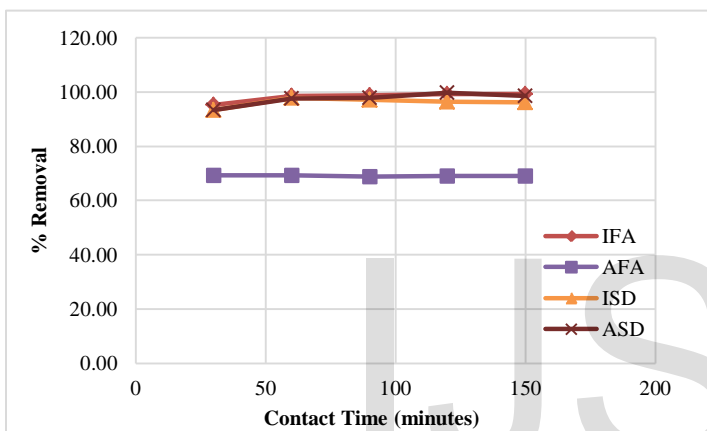


Fig. 2 Effect of Contact time on removal of zinc

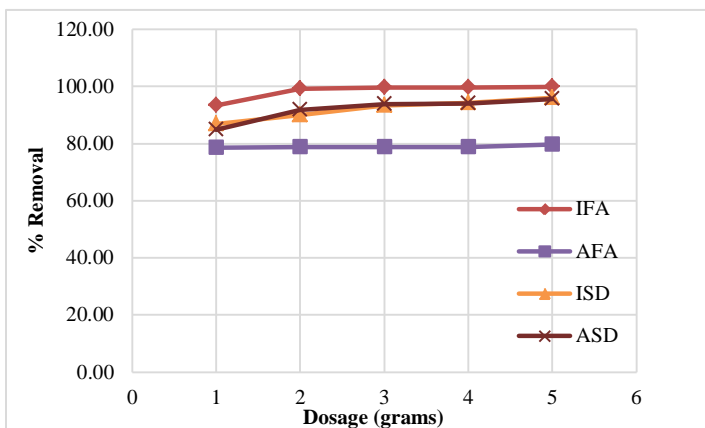


Fig. 3 Effect of varying dosage in removal of zinc

### 3.5 Adsorption Isotherms

In a solid-liquid system adsorption results in the removal of solutes from solution and their accumulation at solid surface. The solute remaining in the solution reaches a dynamic equilibrium with that adsorbed on the solid phase. The amount of adsorbate that can be taken up by an adsorbent as a function of both temperature and concentration of adsorbate, and the process, at constant temperature, can be described by an adsorption isotherm according to the following general Eq.1

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

Where  $q_t$  (mg/g) is the amount of adsorbate per mass unit of adsorbent at time  $t$ ,  $C_0$  and  $C_t$  (mg/L) is the initial and at time  $t$  concentration of adsorbate, respectively,  $V$  is the volume of the solution (L), and  $m$  is the mass of adsorbent (g).

Taking into account that adsorption process can be more complex, several adsorption isotherms were proposed. Among these the most used models to describe the process in water and wastewater applications were developed by, (i) Freundlich (ii) Langmuir and (iii) Brunauer, Emmet, and Teller (BET).

The Langmuir adsorption model is valid for single-layer adsorption, whereas the BET model represents isotherms reflecting apparent multilayer adsorption. So, when the limit of adsorption is a monolayer, the BET isotherms reduce to the Langmuir equation. Both equations are limited by the assumption of uniform energies of adsorption on the surface. The Langmuir isotherm is described by the Eq. 2

$$q_e/q_m = \frac{bC_e}{1+bC_e} \quad (2)$$

Where  $q_e$  (mg/g) is the amount of adsorbate per mass unit of adsorbent at equilibrium,  $C_e$  is the liquid-phase concentration of the adsorbate at equilibrium (mg/L),  $q_m$  is



the maximum adsorption capacity (mg/g) and b is the Langmuir constant related to the energy of adsorption (L/mg).

The adsorption experimental data for the adsorbents used in the study did not represent the best fit for the Langmuir adsorption model.

The data related to adsorption from the liquid phase are fitted better by Freundlich isotherm equation. It is a special case for heterogeneous surface energies. Freundlich isotherm is described by the Eq.3.

$$q_e = K_f C_e^{1/n} \quad (3)$$

Where  $K_f$  (mg/g) (L/mg)  $1/n$  is the Freundlich capacity factor and  $1/n$  is the Freundlich intensity parameter. The constants in the Freundlich isotherm can be determined by plotting  $\log q_e$  versus  $\log C_e$ . The Freundlich isotherm constants  $K_f$  and  $n$  are constants incorporating all factors affecting the adsorption process such as of adsorption capacity and intensity of adsorption. The amount of adsorbent required to reduce any initial concentration to predetermined final concentration can be calculated. The values of  $n$  between 1 and 10 (i.e.,  $1/n$  less than 1) represent a favorable adsorption [14].

The plot of  $\log q_e$  versus  $\log C_e$  is given in figure 5 for the adsorption of Zinc using ISD, ASD, IFA and AFA respectively. Table 1 shows the values of Freundlich capacity factor and Freundlich intensity parameter and Regression coefficient for the different adsorbents. From the table it is inferred that Freundlich isotherm model gave the best fit for the data given.

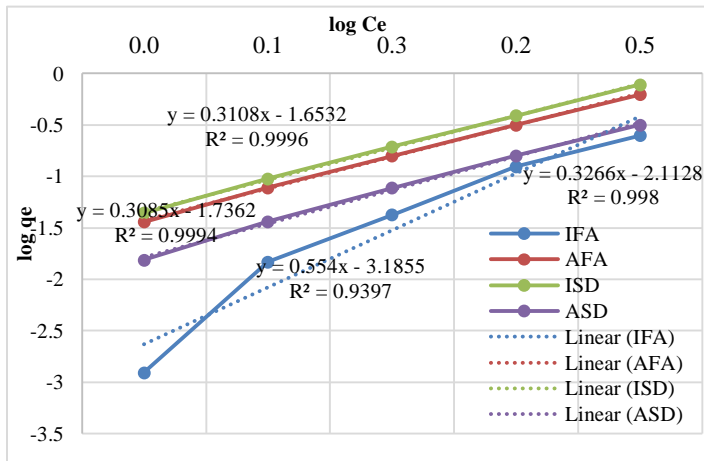


Fig. 5 Freundlich Isotherm for Zinc adsorption on adsorbents

Table 1. Freundlich constants and regression coefficient for different adsorbents

Adsorbent	$K_f$ in L/g	$1/n$	$R^2$
ISD	0.02223	0.3099	0.990
ASD	0.0077	0.3260	0.998

IFA	0.00065	0.5540	0.939
AFA	0.0183	0.3080	0.999

#### 4 CONCLUSIONS

- A. It can be observed from the adsorption experiments for varying zinc concentrations that the removal efficiency increased gradually for first two concentrations and any further increase in concentration it almost reached equilibrium. This effect can be explained as, at low metal ion/adsorbent ratios, metal ion adsorption involves higher energy sites. As the metal ion/adsorbent ratio increases, the higher energy sites are saturated and adsorption begins on lower energy sites, resulting in decreases in the adsorption efficiency.
- B. The larger surface areas of the adsorbents are available at beginning for the adsorption of metals. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. The optimum contact time for IFA, AFA, ISD and ASD are 60, 120, 60 and 120 minutes respectively.
- C. Increase in mass of adsorbent leads to increase in metal ion adsorption due to increase in number of active adsorption sites. But in case of AFA and ISD a gradual decrease in removal efficiency was observed, this is because of the saturation of the available active sites.
- D. The pH experiments showed that the governing factors affecting the adsorption characteristics of all adsorbents are competition of the  $H^+$  ions with metal ions at low pH values, maximum adsorption at pH 6-7 was observed for sawdust and at higher pH value of 8, adsorption was favorable for fly ash.
- E. The optimum removal efficiencies (%) obtained for ISD, ASD, IFA and AFA are 97.92, 99.70, 99.68 and 99.78 respectively.
- F. The Freundlich Adsorption model was best fitted for the adsorbents ISD, ASD and AFA for the adsorption of Zinc but, for IFA a more precise preparation of adsorbent can give the best fit. The experimental data did not represent best fit for Langmuir Adsorption model.
- G. It can be inferred from the above study that industrial wastes: Fly ash and Sawdust can be used effectively as adsorbents in removal of zinc.

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