Removal of Toxic Cation from Aqueous E-Waste Material using ZnO as a Nanoadsorbent by Adsorption Technique

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Received: July 6, 2019; Accepted: July 15, 2019; Published: July 22, 2019

Abstract

The harmful content of E–waste poses a threat to human health and environment. Its toxicity mixed with our environment courses harmful effects in health of living things. Materials such as carcinogenic chemicals, concentrated acids, toxic metals found in E-waste affects in our daily life. E-waste if improperly disposed can leach toxic ions like lead cadmium, chromium, mercury and other harmful substances into soil, surface, and groundwater. A representative sample off E-waste was chosen for the removal of some heavy metals using ZnO as a nanoadsorbent. In the present study investigated the removal of toxic metals [Pb (II), Cd (II), and Hg (II)] from aqueous e waste sample solution by nano adsorbent zinc oxide (ZnO). The values show that adsorption capacity of toxic metals increases with concentration, contact time and solution of pH and then decreases with dosage of adsorbent [ZnO]. The equilibrium time was attained after 30 min for cadmium and mercury. Maximum removal percentage was achieved at an adsorbent loading weight of 0.3 mg/l for Cd (II) and 0.25 mg/l for Hg (II). Equilibrium conditions were found to be at pH 4 and 6 for Cd (II) and Hg (II) while the greatest rate of adsorption of Pb (II) ions was observed at the pH = 4, with adsorbent dosage 0.3 mg/l and equilibrium time one hour on ZnO. Adsorption is an effective purification and separation process used in especially waste water treatment. Freundlich adsorption isotherm model was applied to analyze adsorption data and found to be applicable to these adsorption processes. Experiment was applied for toxic metal ions by Batch adsorption. The adsorption isotherm were determined using Freundlich equation.

Keywords: Electrical waste; Toxic Cations; Nano adsorbent; Environment; Freundlich adsorption isotherm.
Introduction

Electronic products which have damaged unusable, outdated and become non-working, may be called electronic waste. Most of the electronic devices, components, and materials are needed in our useful life. E-waste is constructed from electronic devices, computers, TVs, monitors, mobiles, fax machines, printers, household equipment's like vacuum cleaner, microwave ovens, washing machines, air conditioners etc. and some smart devices such as iPhones, iPads, Digital Watches, Tablet, etc. when these electronics devise are broken and toxic ions such as beryllium, lithium, barium nickel cadmium, mercury and lead are released from that materials. When e-waste containing toxic metals such as lead, copper, cadmium ,barium, mercury, lithium found in discarded mobile phone, torch cells ,vehicles batteries and electronic batteries of computer etc are imperfectly disposed, these toxic metals wash away through the soil and to reached underground water after all run to the surface water.[1] The discharge of wastewater from different industries, and industrial pollutants contain toxic ions including Cd(II), Pb (II) and Hg(II) from electroplating, batteries and paints industries is currently a big environmental problem in the developing society /areas due to toxicity and carcinogenicity of metal ions. Consequently, the removal of such pollutants from aqueous effluents is of significant environmental, technical and commercial importance. Today’s researchers work in this field frequently. [2]

The survival of human being depends on the availability of water and the groundwater. Heavy metals released from e waste affects the plants and animals that exist in the water. When e-waste is warmed up, toxic chemicals are released into the air and damaging the atmosphere. The damage to the atmosphere is one of the biggest environmental impacts from e-west. When electronic waste is thrown away in landfills their toxic materials seep into groundwater, affecting both land and sea animals. This can also affect the health of the people in the developing countries where most of the electronic waste in dumped. Electronic waste is mostly dumped untreated toxic metal present in water bodies on sufficient quantity, can be harmful to marine life and human health. Current methods for such wastewater treatment include precipitation, coagulation/flotation, sedimentation, flotation, filtration, membrane process, electrochemical techniques, ion exchange, biological process, and chemical reaction.

The adsorption process with metal oxides has attracted scientists because of cost effectiveness and less time taken. Recently different methods are used for the removal of toxic metals such as Ion exchange, co-precipitation, membrane filtration, adsorption etc. [3][4]. Among these methods, adsorption is presently considered to be very suitable for wastewater purification because it has very simple low maintenance, and is power efficient and cost effective. Therefore it is commonly used for the removal of toxic metal ions from aqueous solution. [5] [6]. In this present investigation the performance of heavy metals removal by adsorption techniques has been carried out using Freundlich adsorption isotherms.

Components and Composition of E-Waste

<table>
<thead>
<tr>
<th>SN</th>
<th>ITEMS</th>
<th>Acids</th>
<th>Metals</th>
<th>Plastices</th>
<th>Rubber</th>
<th>Glass</th>
<th>Wood</th>
<th>Paints</th>
</tr>
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<tbody>
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<td>√</td>
<td>√</td>
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<td>√</td>
</tr>
<tr>
<td>3</td>
<td>vehicles batteries</td>
<td>√</td>
<td>√</td>
<td></td>
<td>√</td>
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<td>5</td>
<td>Cables</td>
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<td>√</td>
<td></td>
<td>√</td>
<td>√</td>
<td>√</td>
<td></td>
</tr>
</tbody>
</table>
Lead is used as a soldering agent in circuit boards and other components. Glass panels in computers are also made of lead. Nervous system is severely damaged when exposed to the highly toxic lead. Besides affecting the blood systems, kidney and reproductive system in humans, it also affects the various functioning systems among children. The damaging effects on plants, animals and microorganisms are a well-established fact [7]. Cadmium and its compounds which are widely used in electrical and electronic products have found their way into the soil harming microorganisms and disrupting the soil ecosystem [8]. The metal slowly builds up in the surface of contaminated soils, showing no downward migration. Some older cathode ray tubes contain cadmium. Very soon the toxic metal enters the food chain through bio-accumulation and ultimately the liver, kidney gets affected [7]. The heavy metal, mercury is found in many electronic appliances used in our homes. It severely contaminates the environment because it does not filter quickly. Though not used as much as it used to be, it is still used in batteries, relays, switches, medical equipment, lamps, and mobile phones. Its use will likely to increase as it replaces cathode ray tubes. It specifically affects the central nervous system and the developing fetus [7]. Although all forms of mercury can accumulate, methylated mercury bio-accumulates in living organisms and concentrates maximum in fish [8]. Mercury decreases the chlorophyll content of plants and may also cause death in certain vegetation.

**Formation of ZnO Nanoparticles by Precipitation method**

Zinc nitrate Zn(NO$_3$)$_2$.6 H$_2$O of 0.2 M was prepared by dissolving 7 g of zinc nitrate in 200 ml distilled water. 25 ml of this solution diluted with 50 ml of distilled water, was used as the mother solution of zinc nitrate for the present work. 0.4M solution of potassium hydroxide was prepared by dissolving 4.48 g of KOH in 100 ml of distilled water. Then 25 ml of the alkali solution was added at an approximate rate of 5 ml/min to the mother solution, with continuous stirring resulting in a white suspension. During this reaction, pH of the mixture was controlled at 12 providing a basic environment necessary for the formation of ZnO nanoparticles [9]. Under the operating conditions of 3000 rpm, the resultant product was centrifuged for 20 min and washed with deionized water and finally with absolute alcohol to obtain a precipitate which was calcined at 500°C in air atmosphere for 3 hr. [9].
Characterization of zinc oxide

The structural properties of synthesized sample were investigated using powder X-ray diffraction (XRD). The scanning was done in the 2θ range from 10° to 70° and scan step time of 22.04s.

![Sample XRD pattern](image1) ![Standard XRD pattern](image2)

**Figure 1:** XRD of ZnO nanoparticles.

Figure 2 shows the SEM pictures of ZnO nanoparticles at different magnifications. Formation of ZnO nanoparticles is confirmed by these images. These pictures substantiate the approximate spherical shape of the nanoparticles exhibit some faceting. The size of the nanoparticle is less than 50 nm which was in nicely agrees with the particle sizes (20 nm) derived from the Debye-Scherrer formula.

$$d = \frac{0.89 \lambda}{\beta \cos \theta}$$

![SEM Images of ZnO nanoparticles](image3)

**Figure 2:** SEM Images of ZnO nanoparticles

Materials and Methods

In this present study 05 units of computer batteries, 04 units mechanical doorbells, 02 units electronic board, 02 units of Cathode rays tubes, 02 units of mobile phone, 08 units torch cell, 02 units of Vehicle’s batteries and 05 units of switch boards, 05 units of AC
remotes 06 units of cables, 04 units of computer mouse, 05 units of iron screw were collected from different electronic repairs shops and used in this study. Electronic components were carefully breakup and classified into two major parts:

- **Millable parts**: Wire boards, electronic Switchboard monitor, and CRT
- **Non-Millable parts**: Metal frames, torch cell and Batteries
- **Other metal parts**: Iron screw, heating rods

Millable devices were separate and cut into small pieces, followed by crushing in a heavy mill and finally passed in to sieve for filtration. Wood chips were used to clean the milling apparatus after each sample milling, and served as blanks to assess cross-contamination. Milled samples were thoroughly mixed to achieve homogeneity before removing aliquots for testing.

**Digestion of sample**

Initially one gram of the mixed sample was weighed and transferred into a digestion chamber. To this representative sample, 10ml of 1:1 HNO₃ was added to make slurry, which was thoroughly mixed. The resultant was refluxed for 15 minutes and then allowed to cool. After addition of 5ml of concentrated HNO₃ the solution was again refluxed for another 30 minutes. This step was repeated until the brown fumes ceased. The refluxed sample was then heated at 95°C in a water bath for two hours, and finally allowed to cool. Following this the peroxide reaction accompanied with heating occurred by adding 2 ml of de-ionized water and 3ml of 30% H₂O₂ to the sample. It was ensured that losses do not occur due to excessive vigorous effervescence. 30% of H₂O₂ up to a maximum of 10 ml was added until the appearance of the sample remain unchanged. The product was covered with a watch glass and heated at 95°C without boiling for two hours. After a substantial time, 10ml concentrated HCl was added to the digest above, and heated at 95°C for 15 minutes. The digest was finally allowed to cool and was subsequently filtered and filtrate was collected in a 100ml volumetric flask.

**Instrumental analysis and Quality assertion**

The analysis for lead cadmium and mercury in all the sample solutions was carried out with atomic absorption spectrophotometer using appropriate resonance wavelengths of the metals. Before the measurement took place, the spectrophotometer (Systronic make) was calibrated using standard metal solutions. The appropriate wavelengths for cadmium, lead and mercury were 228.80nm, 283.2 nm, 253.7nm respectively. All chemicals used were of analytical grade: HNO₃, H₂O₂ and HCl. The grinder was washed with deionized water and 5 percent nitric acid, and acetone and air dried for 1 day. After sample processing of each component, the grinder was cleaned air blasted into it to ensure that it was completely free of sample particles or wood chips. All plastic and glassware were carefully cleaned by washing, rinsing severally with tap water, and then soaking in 30% HNO₃ solution for a minimum of 48h. Blank determinations with reagents were used to correct the instrument readings.

**Batch Method and Adsorption studies**

The batch experiments were carried out at room temperature (27°C). For each individual metal compound, batch adsorption studies were carried out to investigate the effect of different operating parameters such as adsorbate concentration, adsorbent dose, agitation time and pH. Solution containing adsorbate and adsorbent was taken in 250 mL capacity beakers and agitated at 160 rpm by a mechanical shaker at fixed time intervals. The adsorbate was decanted and separated from the adsorbent using what man No. 1 filter paper. Pretreating the container with respective adsorbate helps in lessening the chances of adsorption of adsorbate on the container walls. The percentage removal of the metal ion was calculated by the following equation [10].

\[
\text{% removal} = \left(1 - \frac{C_e}{C_o}\right) \times 100
\]
Where \(Co\) and \(Ce\) are the initial and final concentrations of heavy metal ion in the solution phase (mg l\(^{-1}\))

**Result and Discussion**

In the present study, zinc oxide was used for toxic metals removal from aqueous solution of E waste sample. The effect of various important parameters such as pH, initial concentration, adsorbent dosage and contact time are investigated.

![Figure 1: Adsorption of metals on nano adsorbent ZnO of different pH at 298 K.](image)

**Optimum Conditions for removal of heavy metals**

Adsorption dose for cadmium: 0.3 mg/l, initial concentration Cd-20 mg/l

Adsorption doses for lead: 0.3 mg/l, initial concentration Pb-30mg/l

Adsorption doses for mercury; 0.25 mg/l, initial concentration Hg-30 mg/l

<table>
<thead>
<tr>
<th>pH</th>
<th>% Removal of Cd (II)</th>
<th>% Removal of Pb (II)</th>
<th>% Removal of Cd (II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>93.4</td>
<td>92.1</td>
<td>88.6</td>
</tr>
<tr>
<td>4</td>
<td>98.8</td>
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<tr>
<td>8</td>
<td>86.2</td>
<td>86.8</td>
<td>94.4</td>
</tr>
<tr>
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<td>85.6</td>
<td>84.3</td>
<td>84.1</td>
</tr>
<tr>
<td>12</td>
<td>85.4</td>
<td>83.1</td>
<td>83.6</td>
</tr>
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</table>

**Table1:** Effect of pH and maximum percentage removal of metals by adsorbent ZnO at 298.

**Explanation**

Figure 1 shows that the percentage adsorption is higher at lower pH reaching maximum at the pH range 4 -6 but it decreases with increase in pH and become constant at pH>10 because of metal hydrolysis and co precipitation of ions.
Effect of initial concentration on adsorption

Figure 2: Adsorption of metals on nano adsorbent ZnO of different concentration at 298 K.

<table>
<thead>
<tr>
<th>Initial Concentration</th>
<th>% Removal of Pb (II)</th>
<th>% Removal of Cd (II)</th>
<th>% Removal of Hg (II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>88</td>
<td>82</td>
<td>74</td>
</tr>
<tr>
<td>20</td>
<td>90</td>
<td>88</td>
<td>79</td>
</tr>
<tr>
<td>30</td>
<td>97</td>
<td>92</td>
<td>98</td>
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<td>90</td>
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</tr>
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<td>50</td>
<td>84</td>
<td>86</td>
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<td>80</td>
<td>80</td>
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</tr>
<tr>
<td>70</td>
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<td>79</td>
<td>79.6</td>
</tr>
<tr>
<td>80</td>
<td>77.5</td>
<td>77</td>
<td>76</td>
</tr>
</tbody>
</table>

Table 2: Effect of initial concentration of removal of toxic metals on ZnO at 298K.

Explanation

The variation of percentage adsorption with initial concentration shown in Fig 2 and Table 2, exhibits that the percentage adsorption decreases with increase in initial concentration of adsorbate. However, the uptake capacity increases with increase in initial concentration. Which the presence of larger number of toxic metal ions in solution for sorption may be the likely cause of this observation. The higher initial concentration of adsorbate provides impetus to overcome the mass transfer resistance of the metal ions from the samples to the solid phase. This results in greater chance of collision between metal ions and the active sites. Effectively, a higher acceptance of toxic ions for the given amount of treated adsorbent ZnO [11].

Effect of Adsorbent dosage on adsorption

Figure 3: Effect of adsorption dose on adsorption of toxic metals on ZnO.
Optimum Conditions with dose of adsorbent [ZnO]

Contact time for cadmium; 30 min, initial concentration Cd; 20mg/l at 4 pH and temperature 298 K

Contact time for lead – 1h, initial concentration Pb -30mg/l at 4 pH and temperature 298 K

Contact time for mercury 30 min, initial concentration Hg; 30 mg/l at 6 pH and temperature 298

<table>
<thead>
<tr>
<th>Adsorbent doses</th>
<th>% Removal of Pb (II)</th>
<th>% Removal of Cd (II)</th>
<th>% Removal of Hg (II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>73.4</td>
<td>81.1</td>
<td>78.6</td>
</tr>
<tr>
<td>0.15</td>
<td>78.8</td>
<td>84.6</td>
<td>86.6</td>
</tr>
<tr>
<td>0.2</td>
<td>88.2</td>
<td>90.8</td>
<td>96.2</td>
</tr>
<tr>
<td>0.25</td>
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<td>96.8</td>
<td>97.4</td>
</tr>
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<td>0.3</td>
<td>98.6</td>
<td>99.6</td>
<td>94.1</td>
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<tr>
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<td>93.1</td>
<td>93.6</td>
</tr>
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</tr>
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<td>0.45</td>
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<td>89.4</td>
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<tr>
<td>0.5</td>
<td>87.2</td>
<td>85.2</td>
<td>87.6</td>
</tr>
</tbody>
</table>

Explanation

Effect of adsorbent dosage of the percent removal of toxic metals shown in fig 3. It clearly indicates that the removal of toxic ions increased with increase of adsorbent dosage. However it is observed that adsorption capacity of metal ions decreasing trend with increasing ZnO dosage. The adsorption capacity increased 73.4 to 98.6% (adsorbent dose 0.3mg/l) for cadmium, 81.1% to 99.6% (Adsorbent dose 0.3 mg/l) for lead ions and 78.6% to 97.4% (adsorbent dose .25 mg/l) for mercury. By increasing the adsorbent dose from 0.1 mg/l to 0.5 mg/l, a drop in adsorption capacity is observed which is basically due to sites remaining unsaturated during the adsorption reaction. Similar trend has also been reported by other investigators in toxic ions sorption (12).

Effect of contact time on adsorption

![Graph](image)

**Figure 4a:** Effect of different initial concentration of mercury on the % removal of Hg(II) at pH 6 as a function of contact time, using 0.25 mg/l dose of adsorbent ZnO.
Figure 4b: Effect of different initial concentration of mercury on the % removal of Cd(II) at pH 4 as a function of contact time, using 0.30 mg/l dose of adsorbent ZnO.

Figure 4c: Effect of different initial concentration of mercury on the % removal of Pd(II) at pH 4 as a function of contact time, using 0.30 mg/l dose of adsorbent ZnO.

From the figure 4a, 4b and 4c it is evident that the percentage removal of toxic metals increases with contact time, attains a maximum value and then tends to attain an equilibrium value. The results of the adsorption experiments are summarized by Maximum % removal of Hg (II), 97.4 % at contact time of 30 min at adsorbent dose of 0.25 mg/l at pH 6. The maximum percentage removal of Cd (II) showed 98.6 % at contact time of 30 min at adsorbent dose of 0.30 mg/l at pH 4, and 99.6 % at contact time of 40 min at adsorbent dose of 0.30 mg/l at pH 4 for Pb (II). Adsorption study indicated that the greatest increase in the rate of adsorption of Pb(II) ions on nano adsorbent ZnO was observed at the pH = 4, adsorbent dosage 0.3 mg/l of solution and equilibrium time one hour.

Adsorption isotherm modeling

The linear form of Freundlich adsorption isotherm is expressed as

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$
Where $K_F$ (L/g) is the Freundlich constant and $n$ (g/L) is the Freundlich exponent. Therefore, a plot of log $q_e$ versus log $C_e$ enables the constant and exponent $n$ to be determined.

**Figure 6[a]**: Freundlich isotherm for adsorption of Cd(II)

**Figure 6[b]**: Freundlich isotherm for adsorption of Pb (II)

**Figure 6[c]**: Freundlich isotherm for adsorption of Hg (II)

Adsorption data has been subjected to Freundlich models as they are the most common isotherms describing solid-liquid adsorption system. The adsorption studies were observed at conditions of initial metal ion concentration 20 mg/L contact time 30 min and pH of solution 4 for adsorption of Cd(II) ions and 30 mg/L initial concentration, 30 min contact time and pH of solution 4 for adsorption of Pb(II) ions while for Hg(II), the optimum condition found with 30 mg/l initial concentration and contact time 30 min at 6 pH on zinc oxide nanoparticles.

**Conclusion**

ZnO nanoparticles have been prepared using wet chemical synthesis method and were characterized by XRD and SEM. XRD and SEM studies confirmed the nanostructures for the prepared ZnO nanoparticles. Zinc Oxide has a good Nano adsorbent capacity for the removal of toxic ions. The removal of some toxic metals such as Cd (II), Pb (II) and Hg (II) from aqueous solutions at different concentrations, pH and temperatures by Nano adsorbent zinc oxide has been studied. The adsorption studies of toxic metals on the
ZnO nanoparticles show that per cent adsorptions of Cd (II), Pb (II) and Hg (II) onto the adsorbate decreases from 98.6 to 73.4, 99.6 to 81.1 and 97.4 to 78.6 respectively, when their concentrations in solutions are increased from 10 to 50 mg/l at pH 4, and 6, at 298 K respectively. An equilibrium time of 30 minutes was required for the adsorption of ions Cd (II), Hg(II) onto adsorbent zinc oxide and an equilibrium time 60 min was required for the adsorption of Pb(II) ions. Adsorption parameters were determined using Freundlich isotherms. Results revealed that adsorption rate initially increased rapidly and the optimal removal efficiency was reached within 30 min to 60min. The equilibrium time for the adsorption of cadmium and mercury on zinc oxide from aqueous solution of E-waste samples is estimated 30 min., while for lead is 60 min. The adsorption process of toxic ions can be described by Freundlich isotherm model. The results showed that nanoadsorbent has potential to remove cationic toxic metal from E-waste water in the order of Pb (II) > Cd (II), > Hg (II) The maximum adsorption of lead took place at the pH 4.

Acknowledgement

The author would like to thank Dr Sanjay Dhoble, Prof., RTM University, Nagpur for his motivation and for providing the instruments used for the research work. The authors wish to thank Dr.Vinit Nayar, Asstt. Prof. C.M.D. P.G College, Bilaspur [C.G] for his constant encouragement and valuable suggestions.

References