# Application Of Graphene Oxide Modified with 8-Hydroxyquinoline for Adsorption of Copper from Leachate

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**ABSRTACT**

In this paper the study is to find out adsorption capacity of copper from leachate by adsorption process using Graphene oxide and 8-hydroxyquinoline in Moshi kachra depot, Pune. As copper is one of the most toxic heavy metal usually found in environment. In leachate concentration of copper was exceeding limit that is discharging limit in natural streams is 3mg/lit by guidelines limit for wastewater effluent set by National Environmental standard and Regulation Enforcement Agency . The adsorbent material will be characterized by FTIR, XRD, XPS. The adsorption isotherms and kinetics of copper (Cu) onto adsorbent and the effect of temperature and ph on the removal efficiency will be thoroughly analyzed. Also breakthrough The maximum adsorption capacity will be 85-95 percent mg/lit. Therefore, these materials can be used as effective adsorbent for Cu-containing wastewaters

**KEYWORDS** — 8-hydroxyquinoline, graphene oxide, isotherm, kinetics, Cu

## 1. INTRODUCTION

Pimpri –Chinchwad, the twin city of Pune has a landfilling and waste dumping site, called PCMP Moshi Kachara Depot, it is spread over 45 acres. Organic and inorganic waste is dumped at this site. Residents from those areas were agitating day in and day out to have the dumping ground remove from its place. Now BVG India Ltd was given responsibility to manage the PCMC Moshi Kachara Depot in 2011 and changed the entire scenario that existed for over 50 years. BVG emptied the entire area and processed the garbage.60 to 70%garbage was organic waste, the remaining 30 to 40% was plastic, metal, and glass. Everyday approximately 800 tons of garbage is collected and brought to dumping ground. Earlier, the entire 800 tons of garbage was sent to landfill. Today only 100 to 125 tons of garbage is processed. The generation of leachate is decomposing solid waste, the percolating water becomes contaminated and flows out of waste material. As liquid moves through the landfill many organic and inorganic compounds, like heavy metals are transported in leachates. This leachates consists of heavy metal such as copper(Cu), nickel(Ni), lead(Pb), mercury(Hg), chromium (Cr) and zinc(Zn), iron(Fe). However copper is a common hazardous pollutant in water and wastewater and it is often released from several sources of industries like metal finishing processes, fertilizer, tannery

  

operation, chemical manufacturing, metal surface treatments as plating refining paints and pigments.

Adsorption process has shown many many advantages like ease of operation, low cost. Graphene is new carbon material with two- dimensional structure and many excellent properties and high specific area with good chemical stability make graphene a good material for adsorption treatment of leachate. Aggregation leads to great reduction in surface area, and is not beneficial for adsorption of heavy metal. Moreover the affinity of material to adsorb molecules is mainly determined H-bonding, van der Waals interaction. Therefore proper chemical modification of graphene is required to make it water soluble and have suitable surface properties to improve its water adsorption capacity. Therefore Graphene oxide is modified with 8-hydroxyquinoline (8-HQ), it is chemically immobilized on different solid supports such as chelating resin, bentonite and silica nanoparticles to form various solid adsorbents, where it has been shown great enhance the removal of heavy metals ions from aqueous solution. 8-HQ is strong bidentate chealating agent that contains an oxygen donor atom and a nitrogen donor atom(as two coordination atoms) which can be used as a modifying agent for various sorbents through the formation of chelating ring.

## 2. REVIEWS FROM LITERATURES

A number of research experiments has been done particularly in recent years to reduce or decompose garbage waste with landfill leachate with many processes like coagulation, biological but adsorption process is used widely with natural adsorbent as well as chemical adsorbent to reduce the concentration of heavy metal from landfill leachate. The use of chemical adsorbent like calcium carbonate, sulfur microparticles, manganese dioxide, mesoporous silica, modified graphene oxide (GO) sheets, pectin-coated iron oxide magnetic nanocomposite (PIOMN) and Chitosan-Fe-S-C, are better, fast adsorbing adsorbent then natural adsorbent like rice husk, saw dust, tea powder etc.These chemicals are carried out with different mix proportion also.

## 3. MATERIAL AND METHODS

A. Material for experimental work. (preparation of graphene oxide)

1. Graphite powder
2. Potassium Permanganate
3. Sulphuric Acid
4. Hydrogen Peroxide
5. Distilled Water.
6. 8-hydroxyquinoline

**Procedure for preparation of graphene oxide**

Graphene oxide was synthesized from natural graphite powder by an improved hummer method. 3g of graphite and 18 g of potassium permanganate were slowly added into a 500 ml flask containing 360ml of concentrated sulfuric acid and 40 ml of phosphoric acid maintaining the reaction temperature at 35-40 degree Celsius with subsequent mixing for 12 hours at 50 degree Celsius. After cooling to the room temperature, the mixture was gradually dropped into 400 ml ice water, and 15 ml of 30 wt% hydrogen peroxide were slowly added to it under vigorous stirring changing the color of the mixture from black to light yellow. The obtained mixtures were washed with 30% sulphuric acid, ethanol and deonized water until pH 7.0 then separated the solid by centrifugal separation method. The resulting sample was freezed –dried under vacuum for 48hours. After that to modify the graphene oxide. Addition of 0.0004 ml 8hydroxyquinoline to the graphene oxide and analysis was done for FTIR (Fourier transform infrared spectroscopy), XRD (X-ray diffraction), and XPS (X-ray photoelectron spectroscopy). After analysis the adsorbent will be applied by number of dosages and varying contact time to sample for getting actual result with high efficiency of adsorption of copper from sample in less time.

B. Adsorption Isotherm

In adsorption isotherm graphene oxide(GO) and 8-hydroxyquinoline (8-HQ)was added with different mix proportion to 200ml distilled water and shacked for 8hours on shaking machine then the samples were filtered with filter paper. The filtrate was checked under spectrophotometer for absorbance of graphene oxide on 8-HQ. The filtrate powder form was dried and used as adsorbent for reducing copper from leachate sample.

C. Adsorption Kinetics

In adsorption kinetics the peak point sample was collected that is maximum point at which copper was adsorbed by adsorbent.

  

In this procedure the 500ml of copper sulfate stock solution was prepared by standard lab procedure and peak point sample adsorbent was added to it and shacked continuously and after every 5minutes the 5ml of sample was removed and checked under spectrophotometer for concentration of copper.

D. Variations of 8-HQ on leachate

In this process the 8-HQ was added with 10 different proportion to leachate sample for adsorption of copper from sample. This sample was shacked for 6hours and filtered by filter paper and checked under spectrophotometer for concentration of copper.

E. pH variations on leachate

The 3 samples were taken with same proportion of adsorbent and checked pH at 3 different points that is pH 3, pH 5 and pH 9 and checked concentration of copper.

F. Temperature variation on leachate

The 3 samples were taken with same proportion of adsorbent and checked temperature at 3 different temperatures in degree Celsius at 15 degree Celsius, 25 degree Celsius, 50 degree Celsius and checked variation of temperature on concentration of copper.

G Breakthrough Model Curve

In these 2 columns were taken and cotton plug was induced in it. Columns with different diameter were varied for bed height and purification of sample. 20 samples were removed after every 45mintues and checked concentration under spectrophotometer for leacahte sample. Also better column was checked.

## 4. METHODOLOGY

The steps involved in optimization of process parameters using adsorbent and spectrophometer are as follow.

Step1 – Selection of site and survey of site.

Step2 – Collection of leachate sample from site.

Step3 – Sample analysis by spectrophotometer and characterization of parameter.

Step4 – Identification of highly concentrated heavy metal.

Step5 –Selection of method for removal of heavy metal.

Step6 – Selection of adsorbent for treating sample

Step7 –Analysis and testing of adsorbent by FTIR, XRD, XPS.

Step8 –Treatment of sample by different dosage of adsorbent and contact time, pH variation, temperature variation, speed agitation.

Step9 – Analyzing accurate result for treating sample for extraction of copper.

Step10 –Test the treated sample under spectrophotometer for removal efficiency of copper.

## 5. RESULTS AND DISCUSSION

A. Characteristics of leachate

Important physicochemical characteristic of leachate sample collected from Moshi kachraa depot are presented below table 1. The leachate contained 7.8 pH, Biological oxygen demand was 1100mg/lit, chemical oxygen demand was 3688.52mg/lit, total suspended solids was 981.0mg/lit. Other elements such as lead, cadmium, chromium, copper, zinc, nickel was analyzed by spectrophotometer. Results presented in tables1 and table2.

Table - 1 Preliminary experimental work

| **Sr. no** | **Parameter** | **Result** | **Permissible Limit/max discharge limit** |
|---|---|---|---|
| 1. | pH | 7.8 | 6-8 |
| 2. | BOD | 1100mg/lit | 50mg/lit |
| 3. | COD | 3688.52mg/lit | 100mg/lit |
| 4 | Total suspended solids | 981.0mg/lit | 1200mg/limit |

Table 1. shows actual results of sample leachate and permissible limit/max discharge limit of pH, BOD, COD, Total suspended solids.

B. Leachate sample analysis by spectrophotometer

Table – 2 Leachate sample analysis by spectrophotometer

| **Sr. no** | **Metals** | **Result** | **Permissible limit** |
|---|---|---|---|
| 1 | Lead (pb) | 0.55mg/lit | 0.1mg/lit |
| 2 | Cadmium (Cd) | 0.05 mg/lit | 0.1 mg/lit |
| 3 | Chromium (Cr) | 2.05 mg/lit | 1.0 mg/lit |
| 4 | Copper (Cu) | 9.81 mg/lit | 3.0 mg/lit |
| 5 | Zinc (Zn) | 2.13 mg/lit | 2.0 mg/lit |
| 6 | Nickel (Ni) | 0.59 mg/lit | 1.0 mg/lit |

C. Adsorption Isotherms

  

Fig1. Shows effect of adsorbent that is adsorption capacity of copper in leachate at different dosage of adsorbent for ten different points. From analyzation it is predicted that sample 6 has maximum adsorption capacity that is 3mg graphene oxide modified with 8-HQ OF 0.0004M which was added to sample of 200ml of leachate has maximum adsorption capacity.

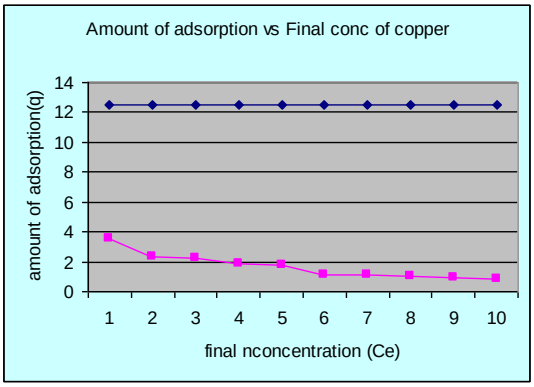


Fig 1.Amount of adsorption and Final concentration of copper

D. Adsorption Kinetics

Fig 2. shows Adsorption kinetics peak point that is final concentration decreases suddenly that amount of GO/8-HQ is taken that is (3gm of GO and 0.0004M 8-HQ) into flask with 500ml of copper solution and is stirred continuously and after every 5 minutes 5ml of solution is withdrawn and measured concentration of copper solution upto ten different samples vs. time.

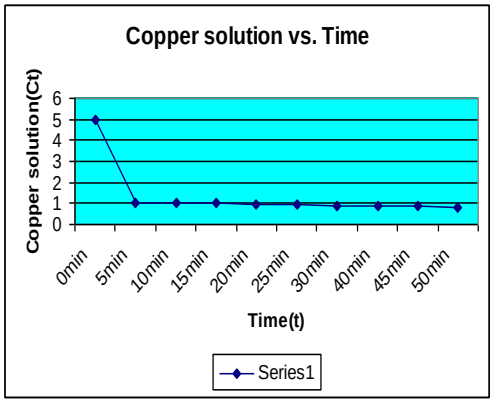


Fig 2.Copper solution varied with Time

Fig.2 Time (t) vs. Concentration of Copper solution (Ct) shows that at 0 mintue conc. Is higher as compared to 50mintute conc. That is as time increases conc. decreases of copper.

E. Varation of 8-hydroxyquinoline with concentration copper.

Fig 3 shows the adsorption of 8-HQ with respect to concentration of copper in leachate. The copper is adsorbed 85 to 95% of copper from leachate.

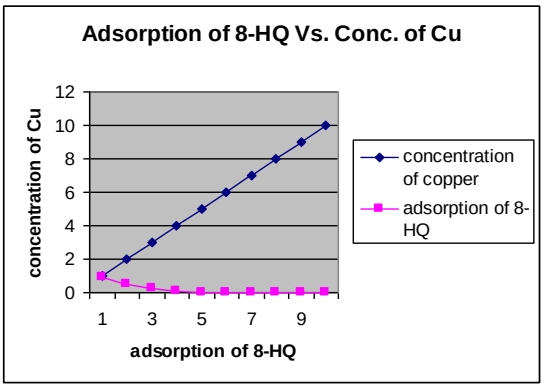


Fig .3 Adsorption of 8-HQ Vs.Conc of Cu

F. Variation of pH on concentration of copper in leachate.

Fig 4. shows the maximum adsorption of Cu was observed at pH 5.0 At lower pH, adsorbent is positively charged due to protonation and Cu ions exists as anion leading to electrostatic attraction between them. A sharp decrease in adsorption above pH 5 may be due to occupation adsorption sites by anion. Maximum adsorption of Cu was observed at pH 5 and significantly decreases by increasing the pH

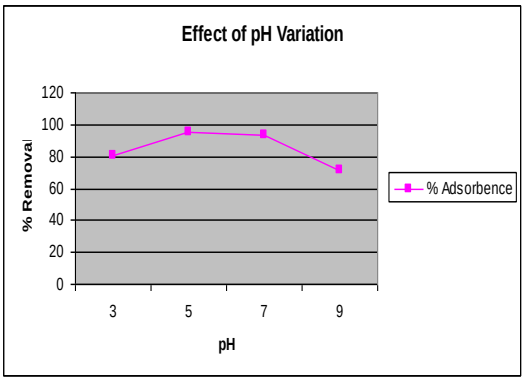


Fig. 4 pH varation Vs. Conc. Of Cu.

G. Varation of temperature for concentration of copper in leachate.

Fig5. shows that there is no change in concentration of copper in leachate if temperature increases or decreases that are temperature at 15, 27 and 50 degree celcius are almost same.

  

There is no effect of temperature on concentration of copper in leachate.

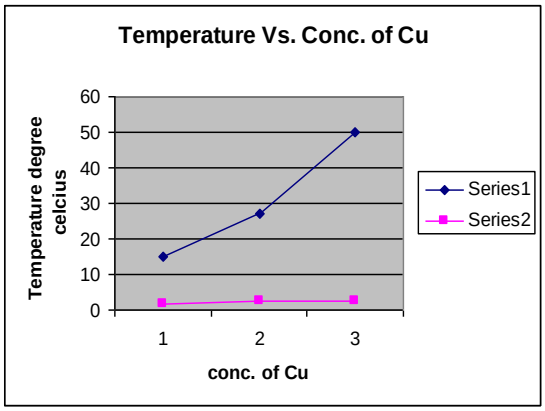


Fig. 5 Temperature vs. Conc of Cu.

H. Breakthrough Model Curve.

In this model operation has fixed – bed adsorption which is representative one as continous adsorption is applied in practical water treatment. The model has three zones saturated zone, adsorption zone and non-work zone. The adsorption zone moves downward gradually with time increases. The height of non work zone decreases as the solute in leachate would break through as adsorption zone reaches the bottom of column. When adsorption zone reaches bottom, the effluent concentration begins to rise rapidly. The breakthrough point i.e sample 4(a) occurs when leachate concentration reaches the desired conc.*( Ca).* The point when leachate concentration reaches 90-95% of influent one that is sample 15, 16*(Cb)* is adsorption exhaustion point (b). The adsorption ability is totally used at adsorption exhausted point is reached. Fig 6 shows breakthrough column curve.

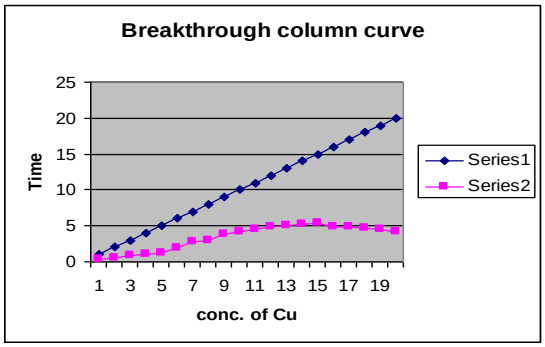


Fig 6. Breakthrough Model Curve

## 6. CONCLUSION

In this paper, adsorption process was studied for removal of heavy metal that is copper from leachate by adsorbent process using graphene oxide modified by 8-hydroxyquinoline. The results of this study indicate that upto 95% of copper is adsorbed by graphene oxide modified by 8-hydroxyquinoline by dosage of 3mg/L for leachate sample that is concentration of copper is reduced which is heavy metal and toxic for environment. Therefore, adsorption method can be considered as appropriate alternative for copper reduction and are widely used in waste water treatment plants.

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