REMOVAL OF ZINC (II) FROM AQUEOUS SOLUTION BY ORANGE PEEL AS AN ADSORBENT

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Abstract: The present study was undertaken to develop a cost effective biosorbent and to study the biosorption process for removal of heavy metals. Removal of zinc (II) from aqueous solution was investigated using orange peel as a biosorbent, was observed effects of various process parameters like pH, contact time, adsorbent dosage, and initial concentration was found. The experimental research show for the removal efficiency of zinc from aqueous solution by using orange peel adsorbent 65 %. Optimum condition for removal of zinc (II) was found pH 5, contact time 90 minute with adsorbent dosage 0.5 gm at 10ppm concentration.

Keywords: Zinc (II), Adsorption, Orange peel, Waste water.

1. INTRODUCTION

Water has a leading position in every purpose; one of the main sources of environmental pollution is the industrial wastewater which contains. Various types of heavy metals can be found in many industries such as plating industry, leather, tannery, textile, pigment & dyes, paint, wood processing, petroleum refining industries and photographic film production [1]. Industrial and domestic waste water refuge toxic heavy metal ions have high solubility in the aquatic environments and thus they can be absorbed by living organisms [22]. Industrial wastewater streams contain toxic metal ions, for example, Ni^{2+}, Zn^{2+}, As, Cd, Cr, Hg, Pb, Co, etc. or their oxyanions in up to few hundred mg/dm3, which must be removed before water recycling or discharge directly into surface waters, [1-7]. Zinc metals enters in water from galvanizing, electroplating, automobile, paints, pharmaceutical, and metal refining industries [5,17]. Zinc is biologically essential, but an overdose can lead to dehydration electrolyte imbalance, stomach ache, nausea, dizziness, depression, lethargy, carcinogenesis, reproductvity, disorder, effect on nervous system, mutagenesis and teratogenesis neurologic signs such as seizures and ataxia, increased thirst, and in co-ordination in muscles [5,14,21]. EPA (Environmental Protection Act) has stated that drinking water should contain no more than 5 mg of zinc per litre of water [3] .

Although excessive amount of heavy metal removal from waste water can be achieved by conventional methods, including chemical precipitation, oxidation/reduction, electro-chemical treatment, evaporative recovery, filtration, ion exchange, phyto-extraction, coagulation flocculation, extraction, ultra and membrane technologies, they may be ineffective or cost-expensive, especially when the metal ion concentrations in solution are in the range of 1-100 mg/l[1,11]. In choosing the appropriate method, several factors must be taken into consideration such as effectiveness, operational cost and production of toxic by-products.

In recent decades, adsorption is the most employed and an effective technique for removal of heavy metals from wastewater [4, 12, 6, 7, 8, 14]. Agricultural wastes have emerged as a better choice, there are a quite large number of studies regarding the preparation of agricultural wastes which include nutshells, fruit sheel, bagasse, coirpith, coconut shell,oil palm waste, agricultural residues from sugarcane, rice, peanut, sawdust, canes from some easy-growing wood species, and orange peel, [6,9,13,17,23]. Bio sorbent material presents strong potential due to its high content of cellulose, pectin (galacturonic acid), hemicelluloses and lignins. Biosorbent are available at very low cost. Many researchers have been reported, biosorption for removal of heavy metals from waste water [23]. Orange peel mainly constitutes of hemi-cellulose, cellulose, pectin substances, chlorophyll pigments and other low molecular weight compounds like limonene, etc., [7]. Hydroxyl and carboxyl are the functional groups of cellulose which are active binding sites for metals.

The purpose of this work is to investigate the potential of the orange peel powder as an adsorbent for removal of zinc (II) metals from aqueous solution.

2. MATERIALS AND METHODS

This chapter gives information about preparation of adsorbent, glass ware and apparatus used during experiments. Batch mode adsorption studies had conducted during experiment to analyze various effects of parameters like pH, contact time, initial concentration, adsorbent dose etc.

Reagent

All chemicals used in present work were either of analytical reagent (AR) or laboratory reagent (LR) grade. Zinc Chloride ($Zncl_2$), HCl (98% w/w,), NaOH and Distilled water, was used in all preparations.

Glassware and Apparatus Used

All glass ware and instrument (conical flask, pipette, burette, measuring, cylinder, petri dish, and taste tubes etc.

Analytical instrument for experiments (data observation) presented

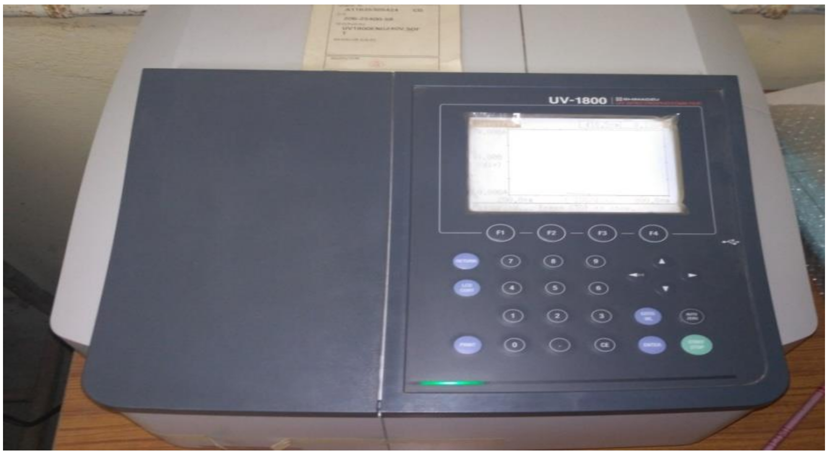

Figure 2.1 UV-1800, spectrophotometer shimazdu japan.

List of Instrument

Table 2.1 Lab Instruments

S. No.	**Instrument**	**Name of Company**
1.	UV-visible spectrophotometer	Uv-1800 Shimadzu, UV Spectrophotometer
2.	Digital Weight Balance	Shimadzu, Japan
3.	What man filter paper no.41	Whatman
4.	Orbital incubator shaker	Remi Instrument,
5.	pH meter	Analab Digital ph meter AN ISO 9001 : 2008
6	Hot air oven 142	Remi instrument, Mumbai
7	Magnetic stirrer	Remi equipments
8	Natural draft dryer	Nutronics

METHODOLOGY:

Adsorbents:

Orange peel was used as the low cost natural bio-adsorbents, which obtained from local market Ujjain, Nanakheda, M.P. (India).

Preparation of orange peel:

Orange peel was first washed with tab water 1-2 times, and thereafter washed with distilled water 5-6 time, dried in sun light for 6 days in summer season and then in an dryer for 4 hours at 60 ^{0}C. The final product was dried in hot air oven at 100 ^{0}C for 5 hours, after drying the product was cooled at room temperature in desiccators and stored in air tight polythene bags shown in figure (2.2). After drying the biosorbent was used in experiment. Unreacted citric acid and other soluble substance was removed by washing procedure.

Figure 2.2 Orange peel powder

PROCESS FLOW DIAGRM

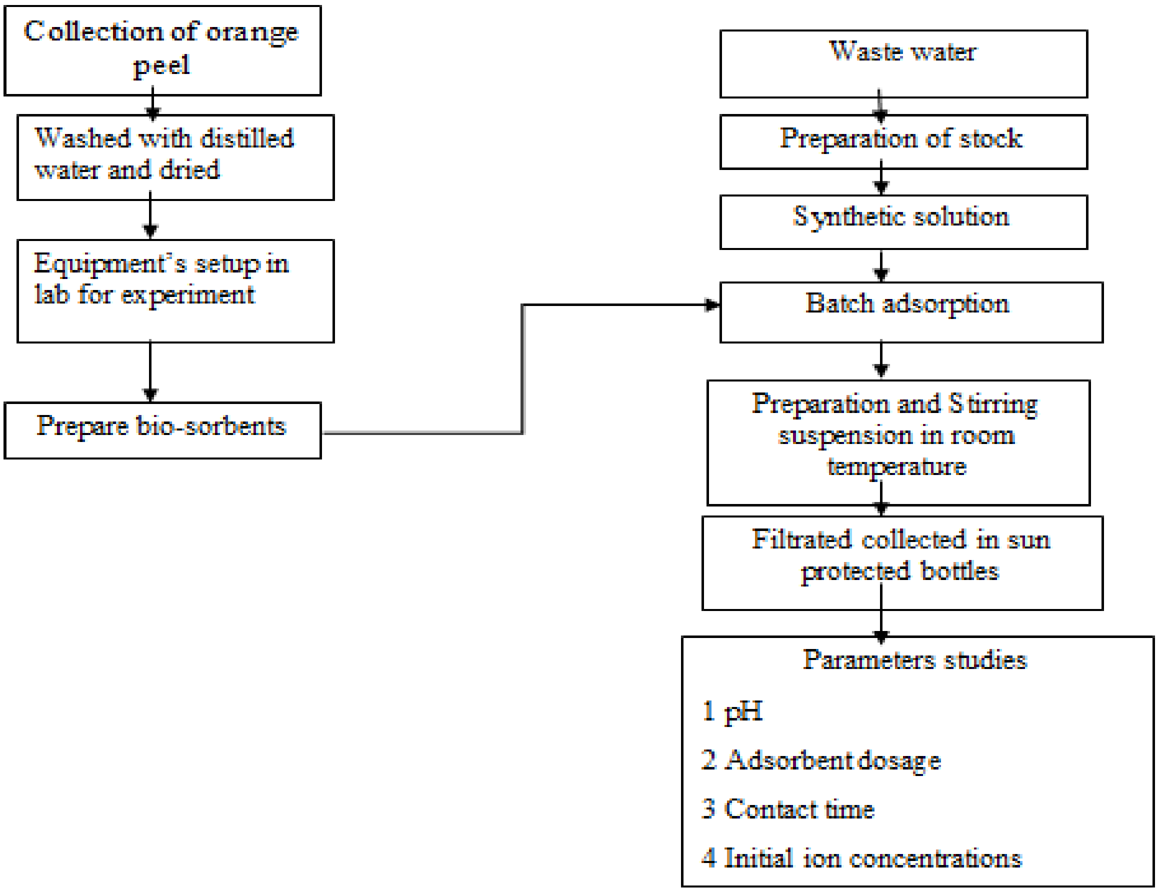

Figure 2.3 Experiment working steps

Preparation of Zinc Metal Solution:

The stock solution containing 1g/L of standard Zn (II) was prepared dissolving 2.08g of AR grade $ZnCl_2$, HCl was added in $ZnCl_2$ solution to prevent the precipitation of metals. All experiment conducted by using the stock solution.

Figure 2.4 Stock of solution

Batch adsorption studies

Experiment carried out at the various pH value, contact time, adsorption dosage, and various initial zn concentration. pH of the solution was maintained by adding 0.1M HCl and 0.1M NaOH solution. A known weight of Orange peel adsorbent was added in 100ml of (Zn) solution with varying concentration (10, 20, 50,100 ppm) in borosil glass flask at a room temperature (30^0C) in a magnetic stirrer for 3 hours. After the completion of adsorption on various parameter, the sample was filtered, using whatman No. 41 filter paper. The filtrate was analysed by UV spectrophotometer (systronic 1800)

Figure 2.5 Batch process

3 Experimental procedure and Data analysis

3.1 Methods for Zinc removal at various pH

Aqueous solution of Zinc (II) was prepared from stock solution. The study conducted at an initial metal ions concentration of 10, 20, 50, and 100ppm, and constant adsorbent dose 0.5g/100ml solution, at different pH 2, 3, 4, 5, 6, and 7 pH. The pH of the solution was adjusted using 0.1 M HCl and 0.1 M NaOH solution. Thereafter, these 100 ml plastic bottles were agitated for 3 hours in magnetic stirrer at room temperature. After 180 minutes of agitation, the suspension were filtered through filter paper (Whatman No.41). The filtrate was analysed by (UV Spectrophotometer), data obtained by UV spectrophotometer fitted in graph.

3.2 Procedure for Zinc removals at various dose.

The study was conducted at an initial metal ions concentration of 10, 20, 50, and 100ppm. Experiments were conducted at various adsorbent dose (concentration) 0.2, 0.4, 0.6, 0.8, and 1g /100 ml aqueous solution. Thereafter, these bottles were agitated for 180 minutes in magnetic stirrer at room temperature (approximate 30^0C). After the compilation of 3 hours of agitation, the suspensions were filtered through filter paper (Whatman No. 41). sample analysed by UV spectrophotometer.

3.3 Procedure for Zinc removal at various contact time.

Experimental procedure conducted by batch adsorption process to study the effects of contact time on the removal of zinc. 100 ml of the synthetic solution take in different concentration 10, 20, 50, and 100 ppm. There after plastic bottles at different concentration were agitated in magnetic stirrer at room temperature (approximate 30^0C). and sample was collected at different time intervals for different concentration. The suspensions were filtered through filter paper (Whatman No. 41). The collected sample was analysed by UV spectrophotometer.

3.4 Procedure for initial Zinc metal concentration.

For each adsorbent dose four set of experiment was conducted at different initial Zinc (II) concentration. The effect of initial concentration at 0.5g/ 100ml adsorbent dosage 90 minutes contact time. The percent removal was calculated using Eq.

Metal ion removal (%) = [(Co – Ce) /Co] × 100 [8,1]

Where Co: initial metal ion concentration of test solution, mg/l

Ce: final equilibrium concentration of test solution, mg/l

4. RESULTS AND DISCUSSION

Effect of various parameters like adsorbent dose, contact time, pH and initial concentration were graphically represented. **Effect of Various Parameters on Adsorption of Zinc (II):** Various parameters like adsorbent dose, contact time, pH and initial concentration were used to determine percentage removal of Zinc (II) which are describe below:

Effect of Contact Time: Fig 4.1 Shows percentage removal of Zinc (II) ion with contact time and different concentration of Zinc II). It shows that increase in contact time, percentage removal also increases, After 90 min it reaches to equilibrium. Maximum removal 63% has been observed for 10 ppm concentration at 90 min. At the begning of the experiment the number of available active sites of adsorbents as well as the concentration of Zinc (II) in the solution is maximum. The driving force for adsorption of Zinc (II) on adsorbent surface is maximum. Further, agitation provides the energy required to bring the Zinc (II) from the bulk of the solution to the active sites of the adsorbent by reducing the resistance to mass transfer between bulk phase and adsorbent. In fact all the above three effects promote adsorption. Removal percentages of Zinc (II) increase very fast in initial stage and also increase with agitation period [13]. It indicates that the rate of removal of Zinc (II) occurs due to the vacant adsorption sites and high solute concentration gradient. Zinc (II) adsorption by adsorbent decreases significantly, due to the decrease in number of adsorption sites. A decreased removal rate, particularly towards the end of experiment, indicated the possible monolayer of Zinc(II) ions on the outer surface, pores of both the adsorbents and pore diffusion onto surface of adsorbent through the film due to continuous shaking maintained during the experiment[7][13].

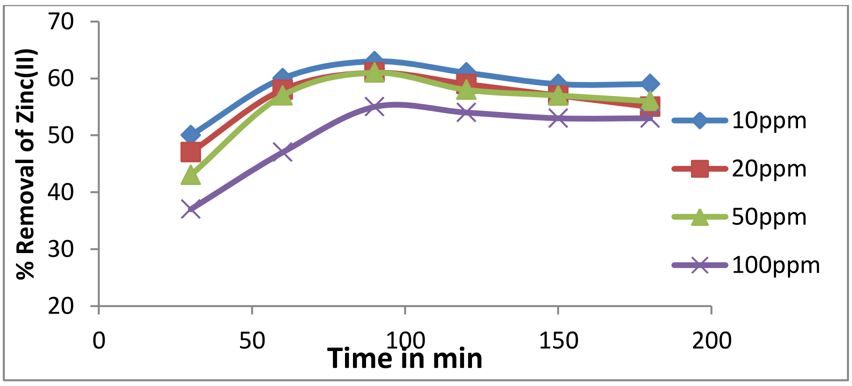

Figure 4.1 Effect of contact time on percentage removal of Zinc (II) byOrange Peel (Parameter- 0.5 g adsorbent dose, 5pH)

Effect of pH: The pH of the aqueous solution is a controlling factor in the adsorption process and it significantly affects the zinc (II) removal efficiency. Experiments were conducted at an initial Zinc(II) concentration of 10, 20, 50,100ppm, in 100ml solution, and constant adsorbent dose 0.5g /100ml solution for Zinc(II) ions at varying pH from 2 to 7. It is show from figure (4.2) that the percentage removal of Zinc (II) 2 to 5 and thereafter drops slowly. pH 5 was found optimum for removal of Zinc (II) from synthetic waste water, if the solution is very acidic (2 to 4 pH) hence the net positive charge on the biomass cells, which results in higher electrostatic repulsion between the metal ions and H^+ ions during the uptake of metal ion [1,7,14,23]. Net negative charge on the biomass, at higher pH hence, decrease in the electrostatic repulsion and thus increase the biosorption the maximum removal of zinc(II) 65 percentage, occurs at 5 pH and 10 ppm concentration for Zinc(II) and there after it decreases with further increase in pH. In acidic medium, the lower Zinc (II) removal is due to the formation of weakly ionized hydrofluoric acid,[7] which reduces the availability of free Zinc(II) for adsorption and in alkaline medium, lower adsorption may be due to competition of OH^- ions with Zinc(II) ions for absorption because of similarity in charge these carry and in their ionic radius [2,13]. The maximum removal was found at 5 pH, for all the initial concentration.

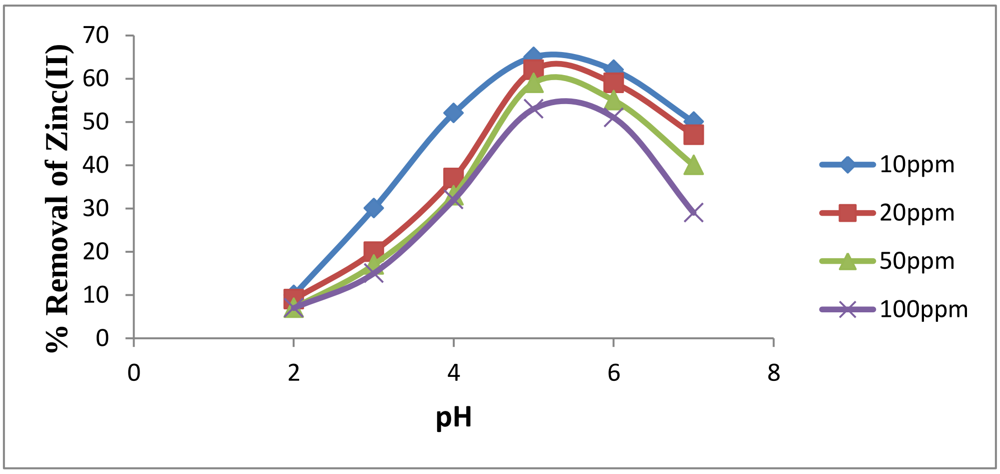

Figure 4.2 Effect of pH on percentage removal of Zinc(II) by Orange Peel (Parameters- 0.5g adsorbent dose, 90 min. contact time)

Effect of adsorbent dose: Studies (fig. 4.3) on effect of adsorbent doses were conducted by varying adsorbent doses between 0.2g to 1 g/100 ml. The pH is maintained at 5. Fig 4.3 shows effect of adsorbent dose on percentage removal for various Zinc (II) concentrations. The increase in the removal efficiency with simultaneous increase in adsorbent dose is due to the increase in surface area, and hence more active sites are available for the adsorption of zinc (II), but after certain amount of adsorbent dosage the removal efficiency found decrease [23]. Binding force increase because surface area of adsorbent increase [13]. Thus more surface area is available for adsorption, thereby increasing the zinc percentage removal from the solution, maximum removal of zinc (II) 65 percentage at 0.6gm/100ml adsorbent dosage.

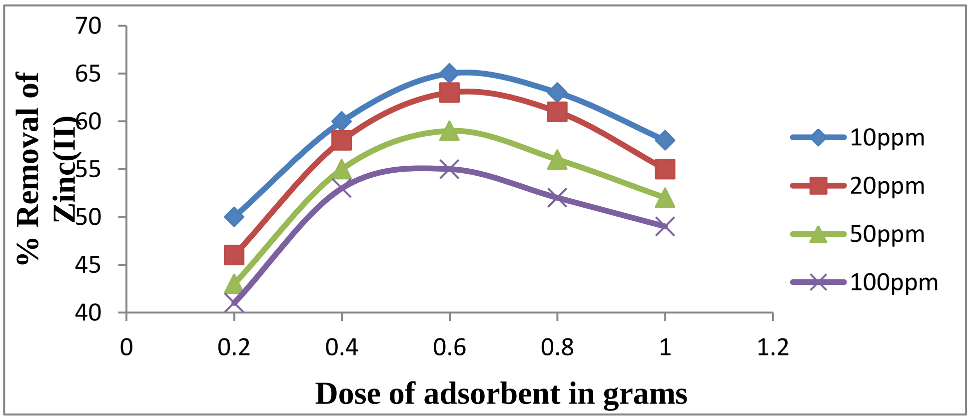

Figure 4.3 Effect of adsorbent dose on percentage removal of Zinc(II) by Orange Peel (Parameter- 5 pH, 90 min. contact time).

Effect of initial concentration variation : The effect of initial concentration on percentage removal of Zinc(II) by Orange Peel at 0.5g/100ml adsorbent dose, 5 pH and 90 min contact time show in fig (4.4) shows the percentage removal decreases with the increase in initial Zinc (II) concentration [23].

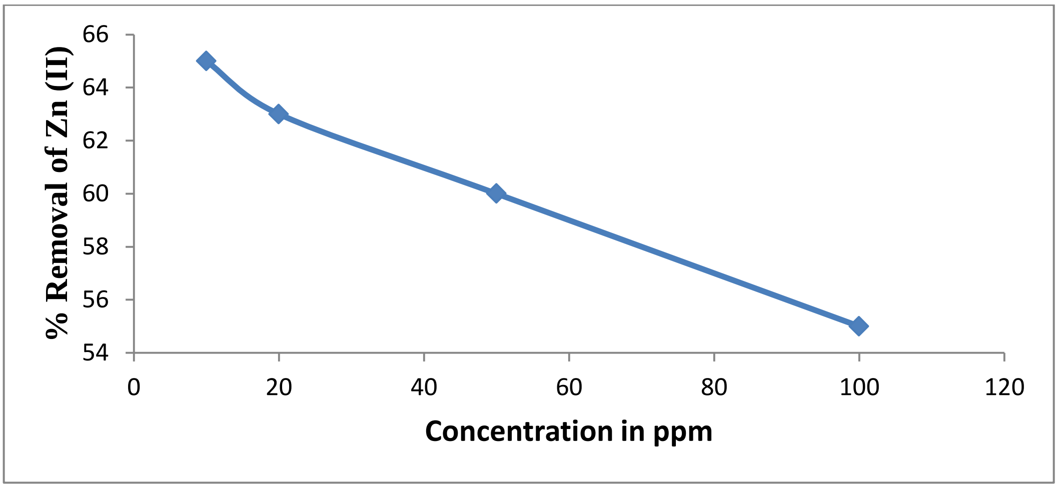

Figure 4.4 : Effect of concentration on % removal of metal ions by orange peel adsorbent

The percentage removal of the metal ion from solution decrease because at higher concentration metal ion diffused on the surface of the adsorbents [13]. Maximum 65 percentage removal has been observed for 10 ppm concentration of Zinc (II). It shows that reduction in immediate solute adsorption owing to the lack of available active sites on the adsorbent surface, compared with the relatively large number of active sites required for the high initial concentration of Zinc (II).

CONCLUSIONS

The present study shows that orange peel is low cost and effective adsorbents for the removal of Zn (II) from synthetic waste water under particular parameter and suitable experimental conditions.

a) The maximum removal of Zinc (II) occurs at an adsorbent dosage 0.5gm/100ml at pH 5 at 10 ppm concentration.
b) The maximum removal of Zinc was found at contact time 90 minute.

These experimental investigation by using low cost adsorbents would be quite useful in developing an appropriate technology for the removal of zn from industrial effluents.

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