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Synthesis and Application of p-Phenylene Diamine derivative of wood flour in removal of Zinc (II)

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ABSTRACT

p-Phenylene Diamine derivative of wood flour (PPDWF) has been used for the removal of Zn (II) ions from polluted water samples prepared in laboratory. By chelation Zn (II) ions are chelated on the newly synthesised chelating resin and get removed from water sample. The chelation process was studied as a function of pH (3.0 to 6.5), contact time (≃60 min.), initial concentration (10 ppm) and temperature (30°±1°C) keeping constant amount of wood flour (0.1 g). The concentration of Zn (II) ions in the filtrate was determined using corresponding calibration curve. It was observed that the pH has marked effect on removal of Zn (II). Result shows that about 71 % removal of Zn (II) takes place at pH at 6.04. At this pH chelation of Zn (II) ion was studied with varying amounts of resin having same initial concentration, temperature and contact time. It was observed that with increasing amount of PPDWF resin the distribution coefficient (K_d) and percentage removal values increase and at 0.5 g amount of resin, these reach to maximum 1712 and 77 % respectively and remains constant at higher amounts of resin.

Key Words: Heavy metals, Calibration curve, Zn (II), Chelation, Absorbance, Polluted water, p-Phenylene Diamine derivative of wood flour (PPDWF).

INTRODUCTION

Water is an essential natural resource for sustaining life and environment but over the last few decades the water quality has been deteriorated due to mixing of chemicals, washed down drains and discharged from factories. The Largest source of water Pollution in India is untreated sewage and toxic substances released through industrial effluents. Industrial effluent contains many types of toxic trace metal ions like Zn (II), Ni (II),Cr(VI), Cd (II), Cu

(II) and Hg(II). Excess dose of heavy metals in to natural environment results various problems in both animals and plants. The main sources of Zinc pollution are galvanizing, paint, rubber, plastic and cosmetic industries. Zinc is a trace element that is essential for human health. When people absorb too little zinc they can feel loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores. Large concentration of Zinc can cause stomach cramps, skin irritation, vomiting and anemia. Water is polluted with zinc, near zinc industries, which accelerates the acidity of water. When zinc enters in the bodies of fish, it is able to bio-magnify up the food chain. EPA has stated that drinking water should contain no more than 5 mg of zinc per liter of water (5 mg/L or 5 ppm) because of taste. Furthermore, any release of more than 1,000 pounds (or in some cases 5,000 pounds) of zinc or its compounds into the environment (i.e., water, soil, or air) must be reported to EPA[1-3].

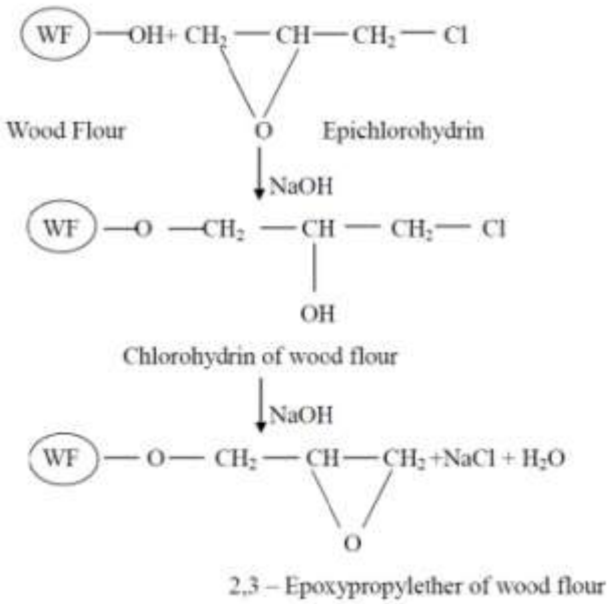
Many methods are used for removal of Zn (II) ions from solutions orpolluted water such as electrolytic, ion exchange, precipitation, flocculation, complexation, biological treatment and adsorption methods[4-10]. In present work we selected chelation method for removal of Zn (II) due to its high efficiency, easy mechanism and low cost[11-16]. We synthesised p-Phenylene Diamine derivative of wood flour and used it to remove Zn (II) from polluted water/solution. The naturally occurring polysaccharides are fibrous in nature, which imparts the ease of accessibility of functional groups even the macro molecules in the surrounding solutions. The effective capacities of the chelating resins based on polysaccharides are higher than those of other chelating resins based on synthetic polymers. The wood flour which is easily available and can be easily processed was used as matrix to form chelating resin for metal removal from polluted water. Wood flour resins may be economically viable substance for water treatment if used in place of commercially high cost resins.

MATERIAL AND METHODS

(A) Synthesis of cross linked wood flour

486g wood flour (corresponding to three anhydrousglucose unit)was taken in a round bottom flask and it was slurred withdioxane. 15ml of 40%(w/v) sodium hydroxide was added to it, tomake it alkaline till pH reached 8.5. The contents of the flask were slurred magnetically at 45°C. Then92.53g (1 mole) epichlorohydrin was added with constant stirring. The stirringwas further continued for four hours at 45°C.

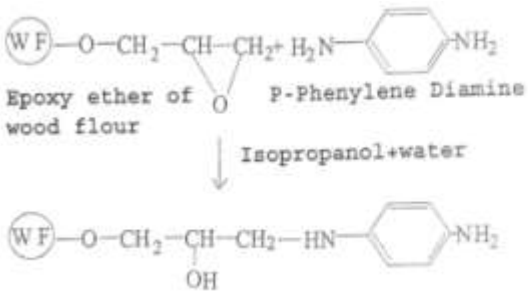
The reaction mixture was allowed to settle down. The supernatant liquid was decanted off and the product was filtered under vacuum and washed with 80% aqueous methanol containing few drops of nitric acid, to remove inorganic impurities and excess alkali in the contents. Washing was done till the filtrate was free from chloride ions and was no more alkaline. The washed product was dried in an oven at 40°C. Obtained cross linked wood flour was further used for derivatization.



Scheme 1 : synthesis of cross linked wood flour

(B) Synthesis of p- Phenylene Diamine derivative of wood flour(PPDWF)

In a round bottom flask 0.01 mole of cross linked wood flour i.e. Epoxy ether of wood flour was taken and slurred with 70% aqueous isopropanol.10 ml of 50% (w/v) aqueous sodium hydroxide was added to it gradually with continuous stirring at 45°C. 0.02 mole of p-Phenylene was dissolved in 70% aqueous isopropanol and then added to reaction mixture. Heating and magnetic stirring at constant speed was continued for 5 hours. The product thus formed was washed with 80% methanol to remove excess p-Phenylene diamine, alkali and other inorganic impurities. The washed product was airdried and successively treated with 0.1 N NaOH and 0.1 N HCl . The supernatant liquid was decanted and resin was washed till the supernatant liquid was free from the acid and any suspended impurity. The product was finally washed with absolute ethanol and dried in a vacuumdesiccator. The product was yellowish powder.



Scheme 2 :synthesis of p- Phenylene Diamine derivative of wood flour (PPDWF)

REAGENTS

All the chemicals used were of analytical grade obtained from E. Merck. Stock solutions of 2000 mg/L each of the Zn (II) were prepared separately by dissolving required amounts in distilled water. Working solutions of required concentrations were prepared by diluting the stock solutions. The pH of solutions was adjusted using 0.2M sodium acetate and 0.2M acetic acid.

INSTRUMENTATION

AGRONIC-511 digital pH meter was used to determine pH of the solutions. Spectrophotometric observations were obtained on an AIMIL-MAKE 'spectrochem' spectrophotometer. Magnetic stirrers manufactured by metrex scientific Pvt. Ltd. were used for stirring.

EXPERIMENTAL METHODS

Measurement of absorbance for standard Zn (II) solutions and CalibrationCurve

To 10 ml of Zinc solution in a separatory funnel, 5.0 ml of buffer solution (pH 4.75) and 1.0 ml of sodium thiosulphate solution was added. Then 5.0 ml of 0.001% of dithizone in CCl_4 was mixed with the contents of separatory funnel and shaken vigorously for 2 minutes. Pour the clear CCl_4 extract into a covered cell to obtain the transmittance of the solution of mixed colour with a light beam of 620 nm wave length, avoiding exposure of extract to strong light. Similarly using Zinc(II) solutions of different concentration calibration curve was plotted.With help of this calibration curve,concentration of unknown Zinc(II) solutions can be determined.

Absorbance for standard Zn (II) Solutions

Table - 1

S.No.	Concentration (ppm)	Absorbance
1	2	0.06
2	4	0.12
3	6	0.18
4	8	0.23
5	10	0.29

The Calibration Curve is given in fig. 1

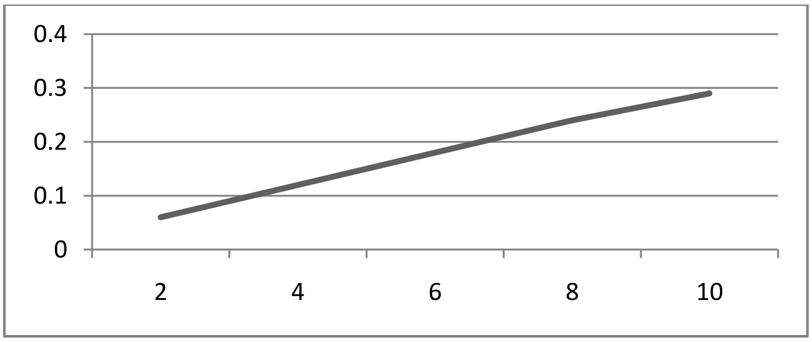


Figure 1 : Calibration Curve for Zn (II) Solutions

RESULT AND DISCUSSION

A. Chelation of Zn (II) on constant amount of PPDWF resin with varying pH

0.1 g of dry resin and 25ml of 20ppm solution of Zn (II) were taken. Appropriate amounts of 0.2M acetic acid and 0.2M sodium acetate were added to each set to obtain desired pH. The total volume of sodium acetate-acetic acid buffer was kept 25ml in each set. The contents were stirred magnetically. The filtrates were analysed for Zn (II) concentration spectrophotometrically. The results are given in Table 2.

The distribution coefficient (K_d) and percentage removal of Zn (II) are calculated by applying following formulae -

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$$K_d = \frac{\text{Amount of Zn (II) in wood flour derivate (PPDWF) Phase /g of dry wood flour derivative}}{\text{Amount of Zn (II) in Solution /ml of solution}}$$

%Removal of Zn (II)

$$= \frac{\text{(Initial concentration of Zn (II)sol.} - \text{Concentration of Zn (II) solution after treatment with wood flour derivate)}}{\text{Initial concentration of Zn (II)solution}} \times 100$$

Table - 2

Chelation of Zn (II) on constant amount of PPDWF resin with varying pH

Amount of PPDWF added = 0.1 g
Volume of Zn (II) of 20 ppm =25 ml
Total volume = 50 ml.

Initial concentration = 10 ppm
Temperature = 30°± 1° C

S.No	Vol. of 0.2 M acetic acid (ml)	Vol. of 0.2 M sodium acetate (ml)	pH	O.D. of filtrate	Conc. Of Zn (II) in filtrate (ppm)	Amount of Zn (II) in sol. (mg)	Amount of Zn (II) in PPDWF (mg)	K_d	% Removal
1	23	2	3.51	0.23	8.5	0.420	0.080	95	16
2	19	6	4.01	0.20	7.4	0.365	0.135	184	27
3	15	10	4.50	0.18	6.7	0.330	0.170	257	34
4	7	18	5.02	0.16	5.9	0.290	0.210	362	42
5	3	22	5.03	0.12	4.4	0.215	0.285	663	57
6	1	24	6.04	0.08	3.0	0.145	0.355	1224	71

Inference

It is observed that with the increase of pH the K_d values for Zn (II) on PPDWF increases. At pH 6.04 the distribution coefficient value is maximum (1224) and removal percentage is 71%. On pH more than 6.04 the K_d value and removal percentage decreases.

B.Chelation of Zn (II) on varying amount of PPDWF resin at constant pH

Different amounts of PPDWF resin were taken in each flask and 1 ml of 0.2M acetic acid 24 ml of & 0.2M sodium acetate were added to get the pH 6.04. Now 25ml (20 ppm) solution of Zn (II) was then added to each set. The contents were stirred magnetically and equilibrated over night. The contents were filtered and analysed. The results are given in Table 3.

Table-3

Chelation of Zn (II) on varying amounts of PPDWF resin at constant pH

Volume of Buffer = 25 ml
(1 ml Acetic acid + 24 ml Na-Ac)
Volume of Zn (II) of 20 ppm =25 ml
Total volume = 50 ml.

Initial concentration = 10 ppm
Temperature = 30°± 1° C
pH = 6.04

S.No.	Amount of PPDWF added (mg)	O.D. of Filtrate	Conc. Of Zn (II) in Filtrate (ppm)	Amount of Zn (II) in solution (mg)	Amount of Zn (II) in PPDWF (mg)	k_d	% Removal
1	100	0.12	4.4	0.222	0.278	626	56
2	200	0.10	3.7	0.187	0.313	837	63
3	300	0.09	3.3	0.167	0.333	997	67
4	400	0.08	3.0	0.152	0.348	1145	70
5	500	0.06	2.2	0.113	0.387	1712	77
6	600	0.06	2.2	0.113	0.387	1712	77

Inference

It is observed that at constant pH 6.04, the K_d value and percentage removal of Zn (II) increases with amount of PPDWF. These reach to maximum at 500 mg amount of PPDWF. At this amount K_d is 1712 and percentage removal is 77%. These remain constant on further increase of amounts of resin.

CONCLUSION

The wood flour gives hydrophilic base for preparation of chelating resins. The polysaccharide based resins are more effective and compatiblein metal ion separation from solution. The Naturally occurring polysaccharides are fibrous in nature, which imparts the case of accessibility of functional groups even to macro molecules in the surrounding solutions. With this aim in view, we have synthesized p-Phenylene Diamine derivative of wood flour (PPDWF), resin for removal of Zn (II) from standard solutions and also their applications in removal of some toxic metal ions from waste water and effluents. It is clearly seen from Table-2 that 71% of Zn (II) is removed at pH 6.04and its distribution coefficient (1224) is also maximum at this pH. Results in Table-3 show that percentage removal of Zn (II) is increased with increase of amount of PPDWF resin at constant pH 6.04. At 500 mg amount of resin the percentage removal is maximum (77%) and K_d is also maximum (1712). These remain constant on further increase of amounts of resin. Finally we concludethat p-Phenylene Diamine derivative of wood flour is a good and economical resin for removal of toxic metals from solution and waste water.

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