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Uptake of Heavy Metal Ions by Carbonaceous Material Obtained from Industrial Waste Lignin Using Microwave Irradiation

ARCHANA R. CHAUDHARI†, LAXMAN P. NAGPURKAR‡ and JAYANT D. EKHE*
Department of Applied Chemistry, Visvesvaraya Regional College of Engineering, Nagpur-440 011, India
E-mail: j_dekhe@ahoo.com

Lignin is a major waste material from the pulp and paper industries. Its lesser utilization and disposal problems make it a matter of environmental concern. Therefore, in such a case, greater and better utilization is the key to minimize the waste, that too for the treatment of waste waters. In the present studiy, the microwave irradiation, zinc chloride and subsequent treatment have been utilized. It produced a good yield of carbonaceous solid material having good capacity to uptake the toxic metal ions from aqueous solutions. Uptake studies have been undertaken on toxic metal ions, *viz.*, Cu^{2+}, Ni^{2+}, Cr^{6+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, As^{3+} and Hg^{2+}, etc. Interestingly, the exahausted material may also be used as a solid fuel supplement due to its high calorific value, 5400 kcal/kg.

Key Words: Uptake of heavy metal ions, Carbonaceous material, Microwave irradiation.

INTRODUCTION

Enormous quantity of wood material is utilized by pulp and paper industries. Several pulping processes such as soda process, sulphite process and sulphate process are used for delignification. The lignin thus removed from wood is a major waste product of pulp and paper industries besides suspended solids, phenols, ammonia and other hydrocarbons. It is in the form of black liquor. Hundreds of tonnes of lignin is produced annually. If not disposed of, it may become a matter of environmental concern.

Many vital industries such as non-ferrous metals, pigments, storage batteries, metal processing, finishing and plating discharge heavy metals in their waste streams, some of which are extremely toxic even in traces. Precipitation, ion exchange, adsorption and reverse osmosis are some of the techniques which have been used with considerable success to scavenge heavy metal ions. Interest has

†Department of Applied Chemistry, Priyadarshini College of Engineering and Architecture, Nagpur, India. Tel: (0712) 264193.
‡Department of Chemistry, Manohar Bhai Patel College of ACS, Sakoli-441 802, Dist. Bhandara, India. Tel: (07186) 36140.

arisen recently in the use of agricultural waste products[1] such as onion skin, flour waste, paddy husk, paddy straw for binding heavy metal ions from solution. Many reports have appeared on the development of activated carbon from cheaper and readily available waste material such as rice husk[2], coconut shell[3], cashewnut and rubber seed coat[4], paper waste[5] etc. for uptake of heavy metal ions from solutions.

Lignin is a polymeric natural product arising out of enzyme initiated dehydrogenative polymerization of primary precursors[6], *e.g.*, coniferyl alcohol, sinapyl alcohol and *p*-coumaryl alcohol. Considerable amount of research work has been reported for the utilization of lignin, *e.g.*, hydrogenation[7], alkali fusion[8], pyrolysis[9] etc. However, these methods do not ensure greater utilization of lignin. Therefore, the carbonaceous residue remained after degradation was tested for its uptake capability. The capability was further enhanced by using microwave energy and $ZnCl_2$[10]. The promise of microwave has attracted the chemists, the potential use of microwaves in areas such as organic synthesis, material processing and waste remediation[11] which is friendly to the environment[12]. The results of investigation on the use of carbonaceous materials (coke) obtained from industrial waste lignin for binding toxic metal ions such as Cu^{2+}, Ni^{2+}, Cr^{6+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, Hg^{2+} and As^{3+} etc. are presented in this communication.

EXPERIMENTAL

Industrial waste lignin was obtained from Simplex Paper Mills, Gondia, Maharashtra state, India. All the chemicals used during the experiment were of analytical grades which were purchased from E. Merck India Ltd. and S.D. Fine Chemicals Ltd. and were used without further purification. The chemical compounds were weighed on electronic balance, type AX 200 Shimadzu Corporation, Japan. The degradation of industrial waste lignin was carried out in a domestic microwave oven, a commercially available Kenstar model no. OM-9918C, 900 watts which was modified (Fig. 1) so as to perform the reactions at normal pressure. The quantitative measurement of the metal ions uptaken were performed on atomic absorption spectrophotometer, GBC 932, Australia. Study of As^{3+} uptake was performed on inductive coupled plasma analyzer (ICPA), model 180 and study of Hg^{2+} uptake was performed on mercury analyzer, 5800E.

Methodology

Thermal degradation of lignin: Industrial waste lignin was subjected to thermal degradation using a round-bottomed flask (Borosil) for 5–6 h. The carbonaceous residue obtained was ground and sieved to get a particle size of 300 micron (Indian standard sieves). Then it was treated with 10% NaOH solution followed by washing with distilled water and concentrated HNO_3 for overnight. It was again washed with excess distilled water and dried at 110°C.

Microwave degradation of lignin in presence of $ZnCl_2$: The same lignin was degraded in a modified microwave oven[13, 14] in presence of $ZnCl_2$ in the ratio 1 : 2 for 35 min using reflux condenser. The residue obtained was ground to fine powder and sieved to get particle size of 300 microns. It was treated with dilute

HCl to remove all Zn^{2+} ions present, washed with distilled water and treated with 10% NaOH solution followed by washing with excess water and further treated with conc. HNO_3 for overnight. It was again washed with excess distilled water and dried at 110°C.

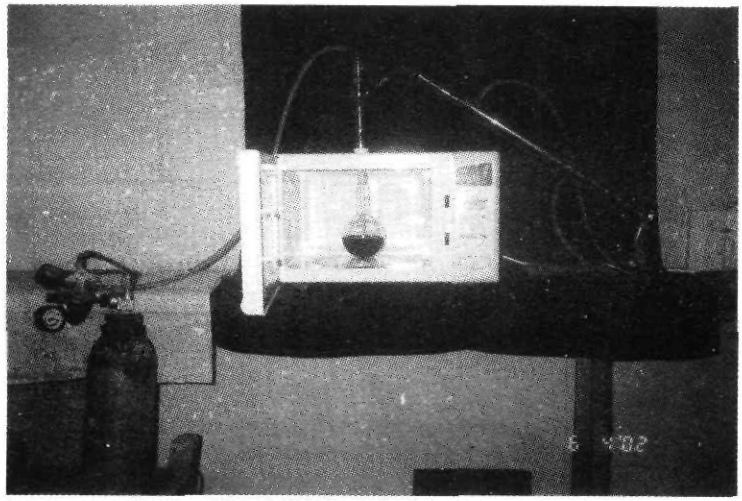

Fig. 1. Modified microwave oven

1 g of the carbonaceous residue was agitated with 50 mL of the metal ion solution for 60 min. The mixture was filtered and analyzed for the amount of metal ions uptaken which was quantitatively calculated by the difference between the initial and final concentrations of metal ion solutions.

To select the coke having better uptake capacity, studies were carried out for Cu^{2+} ions under similar experimental conditions for both the cokes, *viz.*, obtained from thermal degradation and microwave degradation in presence of $ZnCl_2$. The effect of pH of the solution on the uptake of Cu^{2+} ions was also studied. Further, uptake of Ni^{2+}, Cr^{6+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, As^{3+} and Hg^{2+} was determined by using coke residue obtained from microwave irradiation in presence of $ZnCl_2$.

RESULTS AND DISCUSSION

Tables 1 and 2 and Fig. 2 represent the results obtained by using the carbonaceous materials, *viz.*, obtained from thermal degradation **(C)** and from microwave degradation in presence of $ZnCl_2$ **(Cz).** It is observed that **Cz** shows better uptake of heavy metal ions than **C.**

In case of **Cz** microwave energy is used for degradation. Microwave technique is found to be simpler, faster and more effective as far as overall efficiency is concerned. Theremal degradation requires 5–6 h whereas microwave degradation can be accomplished within 30–35 min at full power.

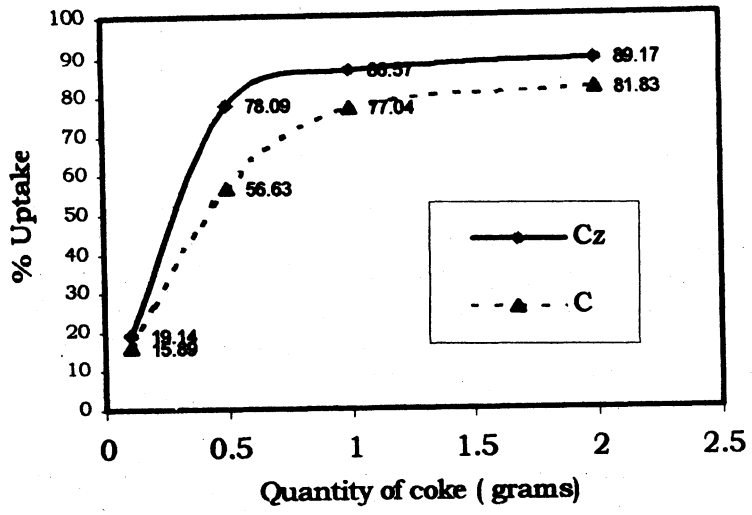

Fig. 2. Relative comparison between capacity of C and Cz coke for the uptake of Cu^{2+}

TABLE-1
UPTAKE OF Cu^{2+} IONS ON CARBONACEOUS MATERIAL OBTAINED FROM THERMAL DEGRADATION OF LIGNIN

S. No.	Quantity of coke (g)	Initial conc. of Cu^{2+} (ppm)	Residual conc. of Cu^{2+} after uptake (ppm)	Reduction in the conc. of Cu^{2+} (ppm)	Uptake (%)
1.	0.1	38.81	32.64	6.17	15.89
2.	0.5	38.81	16.83	21.98	56.63
3.	1	38.81	8.91	29.9	77.04
4.	2	38.81	7.05	31.76	81.83

TABLE-2
UPTAKE OF Cu^{2+} IONS ON CARBONACEOUS MATERIAL OBTAINED FROM MICROWAVE DEGRADATION OF LIGNIN IN PRESENCE OF $ZnCl_2$.

Sr. No.	Quantity of coke (g)	Initial conc. of Cu^{2+} (ppm)	Residual conc. of Cu^{2+} after uptake (ppm)	Reduction in the conc. of Cu^{2+} (ppm)	Uptake (%)
1.	0.1	38.81	31.38	7.43	19.14
2.	0.5	38.81	8.50	30.30	78.09
3.	1	38.81	5.21	33.6	86.57
4.	2	38.81	4.20	34.61	89.17

It is known that the nature of substituent groups affects adsorptibility. Treatment of carbonaceous residue with nitric acid increases the surface acidity and hence high uptake is expected. Acidic sites seems to be the adsorption centres on which metal ions are uptaken.

To remove 80% Cu^{2+} ions from 38.81 ppm of solution 40 g/L of **C** is required whereas 20 g/L of **Cz** is required to remove 86% Cu^{2+} ions from the same solution. This indicates that the microwave irradiation is more effective. Microwave might have been more efficient to cause the structural changes on the surface and also in the core where thermal energy would be less effective due to insulation effect. From Fig. 2 it can be noted that the maximum difference in the uptake capacities of both the cokes, *viz.*, **C** and **Cz**, is 21.96%. It is evident from these observations that $ZnCl_2$ activation is accompanied by increase in surface area and total pore volume (thus the quality coke is better in case where degradation was carried out in presence of $ZnCl_2$). The softening or partial fusion, which lignin undergoes at relatively low temperature (*ca.* 180–280°C) may favour $ZnCl_2$ diffusion throughout the matrix of precursor. Also when resolidification takes place at temperature above the melting point of $ZnCl_2$, a microporous structure has already developed through devolatilisation allowing melt of $ZnCl_2$ to migrate through this microporous net. Thus $ZnCl_2$ activation increases microporosity of carbon residue and subsequently shows greater uptake of heavy metal ions. Thus for further studies of uptake of Ni^{2+}, Cr^{6+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, As^{3+} and Hg^{2+} etc. **Cz** residue was used.

The uptake rate of metal ions has been studied using carbonaceous residue obtained from microwave degradation of lignin in presence of $ZnCl_2$. It was found that maximum uptake of ions could be achieved within 1 h duration.

Fig. 3 and Table-3 represent the effects of pH on the uptake of Cu^{2+} ions from solution. pH range 5 to 6 was found to be most suitable for maximum uptake. Table-4 represents the uptake of heavy metal ions including Cu^{2+}, Ni^{2+}, Cr^{6+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, Hg^{2+} and As^{3+} by **Cz** coke. About 20 g of **Cz** coke was found to be capable to remove 80–90% of various metal ions from their one litre solution (pH 5–6) with 40–50 ppm concentrations. It may be concluded that 1 g of **Cz** coke can remove 1.95 mg of Cu^{2+}, 1.93 mg of Ni^{2+}, 1.98 mg of Cr^{6+}, 2.12 mg of Pb^{2+}, 1.69 mg of Cd^{2+}, 1.21 mg of Zn^{2+}, 0.53 mg of As^{3+} and 0.30 mg of Hg^{2+} (Fig. 4). Maximum uptake was noticed in case of Pb^{2+}, Cr^{6+} and Cu^{2+}

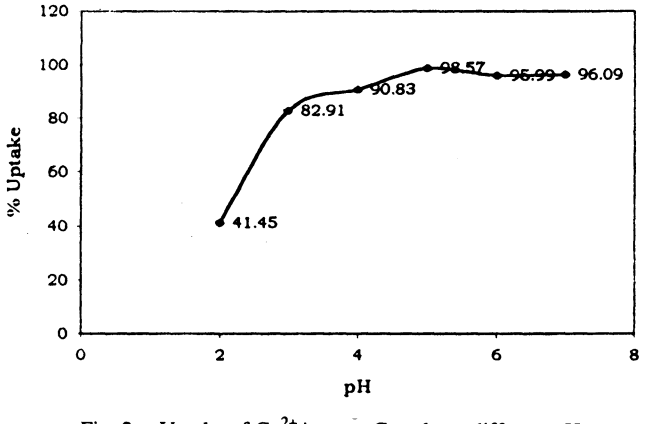

Fig. 3. Uptake of Cu^{2+} ions on Cz coke at different pH

TABLE-3
UPTAKE OF Cu^{2+} IONS ON CARBONACEOUS MATERIAL OBTAINED FROM MICROWAVE DEGRADATION OF LIGNIN IN PRESENCE OF $ZnCl_2$ AT DIFFERENT pH VALUES

Sr. No.	pH	Quantity (g) of coke per 50 mL of solution	Initial conc. (ppm) of Cu^{2+}	Residual conc. (ppm) of Cu^{2+} after uptake	Reduction in the conc. (ppm) of Cu^{2+}	Uptake (%)
1.	2	1	40.69	23.82	16.87	41.45
2.	3	1	40.69	6.95	33.74	82.91
3.	4	1	40.69	3.73	36.96	90.83
4.	5	1	40.69	0.58	40.11	98.57
5.	6	1	40.69	1.63	39.06	95.99
6.	7	1	40.69	1.59	39.10	96.09

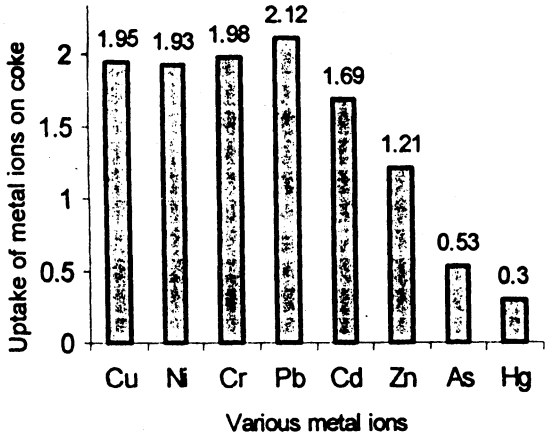

Fig. 4. Uptake of different metal ions on coke (Cz) in mg/g at pH 6

TABLE-4
UPTAKE OF Cu^{2+}, Ni^{2+}, Cr^{6+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, As^{3+} and Hg^{2+} ON CARBONACEOUS MATERIAL OBTAINED FROM MICROWAVE DEGRADATION OF LIGNIN IN PRESENCE OF $ZnCl_2$

Sr. No.	Metal ion	Quantity of coke (g) per 50 mL of solution	Initial conc. (ppm)	Redidual conc. (ppm) after uptake	Reduction in conc. (ppm) of metal ion	Uptake (%)	Cation sorbed on coke (mg/g)
1.	Cu^{2+}	1	40.69	1.63	39.06	95.99	1.95
2.	Ni^{2+}	1	49.27	10.52	38.75	78.64	1.93
3.	Cr^{6+}	1	50.21	10.42	39.79	79.24	1.98
4.	Pb^{2+}	1	44.16	1.74	42.42	96.05	2.12
5.	Cd^{2+}	1	40.60	6.65	33.95	83.62	1.69
6.	Zn^{2+}	1	41.30	17.01	24.29	58.81	1.21
7.	As^{3+}	1	24.50	13.90	10.60	43.26	0.53
8.	Hg^{2+}	1	27.44	21.39	06.05	22.04	0.30

Table-5 represents the uptake of metal ions from the mixture of Cu^{2+}, Ni^{2+} and Cr^{6+}. Here it was observed that Cr^{6+} showed preferential uptake over Cu^{2+} and Ni^{2+}. This may be due to the effect of pH, as pH of this mixture was 4. It is also reported earlier[5] that Cr^{6+} shows better uptake at pH range 3 to 4.

TABLE-5
UPTAKE OF METAL IONS FROM MIXTURE OF Ni^{2+}, Cu^{2+} AND Cr^{6+} BY CARBONACEOUS MATERIAL OBTAINED FROM MICROWAVE DEGRADATION OF LIGNIN IN PRESENCE OF $ZnCl_2$

Sr. No.	Mixture containing metal ions	Initial conc. (ppm)	Residual conc. (ppm) after uptake	Reduction in conc. (ppm)	Uptake (%)
1.	Ni^{2+}	18.72	2.47	16.25	86.80
2.	Cu^{2+}	17.55	1.07	16.48	90.90
3.	Cr^{6+}	23.71	1.08	22.63	95.44

To select the coke having better uptake capacity, studies were carried out for Cu^{2+} ions under similar experimental conditions for both the cokes, *viz.*, obtained from thermal degradation and microwave degradation in presence of $ZnCl_2$. The effect of pH of the solution on the uptakes of Cu^{2+} ions was also studied. Further, uptake of Ni^{2+}, Cr^{6+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, As^{3+} and Hg^{2+} were determined using coke residue obtained using microwave irradiation in presence of $ZnCl_2$.

Conclusion

These studies indicate that a better quality, low cost adsorbent can be obtained from the industrial waste, lignin after appropriate treatments, paricularly using zinc chloride, HNO_3 and careful application of microwave energy for substantial time reduction. This microwave induced approach also ensures the greater utilization of industrial waste lignin particularly for the uptake of toxic metal ions which could be useful in waste water treatment and also for the removal of various toxic organic species. Finally it provides a good quality of fuel as a supplement (calorific value over 5400 kcal/kg). Thus utilization of the lignin in this way is promising and minimizes the disposal problems and converts the waste into useful raw materials and finally ends up as an energy source.

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