SOLID PHASE EXTRACTION FOR THE REMOVAL, PRECONCENTRATION VIA RECOVERY AND SEPARATION OF Cu(II) AND Ni(II) USING MODIFIED SILICA GEL

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Abstract— Metal ion toxicity and pollution of water is a real cause of concern to the environmentalist due to the non biodegradable character and long persistence of metals in the ecosystem. Metals in trace level are sometimes play crucial role governing the enzymatic character of biomaterial and behavior of complex matrix.

Trace level determination and separation of copper and nickel from bisolute composition is studied in the present case using salicylaldoxime immobilized silica gel. The process is optimized for initial metal concentration, dose of adsorbent, pH, temperature, shaking time and speed. The pH dependent behavior of Cu(II) and Ni(II) can be utilized for mutual separation in batch mode. Column study reveals that retention of Cu(II) is independent of flow rate up to 10 ml/min while for Ni(II) the tolerable flow rate is found to 6.5 ml/min. HNO_3 or $HClO_4$ is found to have excellent potential for elution of Cu(II) and Ni(II). The distinct elution pattern of Cu(II) and Ni(II) can be utilized for separation of Cu(II) and Ni(II) using gradient elution. A good preconcentration factor 66 and 50 respectively for Cu(II) and Ni(II) makes the operation a promising one for removal and recovery of Cu(II) and Ni(II) from aqueous solution.

Index Terms—Salicylaldoxime, immobilized silica gel, batch experiment, column experiment, preconcentration, solid phase extraction

I. INTRODUCTION

With the advent of material civilization the use of metals has been increased tremendously which
inevitably has resulted in an increased flux of metallic pollutants in the aquatic environment. The toxicity generated may disturb the ecological balance [1]. Again in trace level some metals play important roles in enzymatic metabolism in biological system. The removal as well as trace level determination of metals via preconcentration and separation from complex matrix becomes a challenging task from the environmental, ecological and analytical chemistry view point.

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Chemical precipitation, complexation, coagulation, and flocculation [2] are although widely used techniques for metal ion removal has limitation of secondary pollutant/ sludge generation. Liquid liquid extraction is a very popular technique for trace level metal determination, preconcentration and separation. However, use of large volume of toxic organic solvents, large through output led the scientists in search of alternative techniques. Recently extraction of heavy metal ions by ionic liquid has reported [3] Solid phase extraction method using some solid extractants, as have some advantages over liquid-liquid extraction, is now gaining the popularity. The solid extractants range from the natural [4-6] to synthetic materials as well as the biomaterials [7-9]. Ion exchange materials [10], activated carbon [11] and activated slag [12] are used for the purpose of metal ion separation and recovery. Chelate impregnated over solid substances like cellulose [13] and hybrid polymer [14] show their marked potential. In our laboratory ligand immobilized over silica gel was successfully used for the enrichment of metal ions from water [15, 16]. Silica gel, as a solid support for ligand immobilization, has some special advantages like less swelling property, high resistance towards heat and acid treatment. For the synthesis of solid phase extractant silica gel surface can be modified following different routes [17-23]. The present communication deals with solid phase extraction of Cu(II) and Ni(II) for the removal, recovery, preconcentration vis-à-vis separation from bisolute composition following adsorption using salicylaldoxime immobilized silica gel (SISG) as the adsorbent.

II. II.EXPERIMENTAL

A. Apparatus

Batch experiment was performed in a glass container. A glass column (160 x 6mm i.d) with a coarse sintered glass disc and a tap at the bottom was used for the column study. The absorbance spectra of the solution were recorded using a UV-VIS Spectrophotometer (Shimadzu PC 1401). The IR spectrum of the solid as thin film between KBr windows was taken in an IR spectrophotometer (Perkin Elmer L 120-000A). A systronics pH meter (Model 324) with glass electrode was used for pH measurements. Atomic absorption measurement was recorded on an atomic absorption spectrophotometer (AAS; Perkin Elmer AA 1407) equipped with a standard burner with an air-acetylene flame. Standard hollow cathode lamp was used as a line source. The operating

characteristics of the instrument for the metal ion estimation are as follows:

Metal ion	Lamp current (mA)	Wavelength (nm)	Slit width (mm)
Cu(II)	4.0	324.8	0.5
Ni(II)	4.0	232.0	0.2

B. Materials

All chemicals were of analytical reagent grade. Silica gel H 4267 of particle size 60μm, specific surface area 420 m^2/g and pore size 120^0A was obtained from Sigma. Stock solutions of copper and nickel (200 mg/l) were prepared by dissolving respective metal chloride in doubly distilled water. pH of the experimental solution in the range 3.5-6.0 was maintained by acetate buffer by mixing the required volumes of 0.2 mol/l acetic acid and sodium acetate. pH below 3.5 was maintained by HCl while pH above 6.0 was maintained by NaOH solution. Salicylaldoxime (GR) was obtained from Merck, India.

C. Synthesis of salicylaldoxime loaded silica gel (SISG)

The present adsorbent salicylaldoxime loaded silica gel (SISG) was synthesized by first refluxing the silica gel with 6.0 mol/l HCl for about 3 hours to free any contaminating metal such as iron. It was then washed with deionised water and dried under reduced pressure at 150^0C. The dried silica gel was refluxed with salicylaldoxime (SALD) in ethanol (10% w/w) at $70-80^0C$ for 4 hours. The solid thus obtained was filtered and dried under vacuum.

D. Retention procedure

a) Batch Experiment:

Batch experiments were performed to obtain optimum adsorption condition and equilibrium data. The flask containing 20 ml of metal solution (20-200 mg/l) maintained at definite pH was shaken with 1.0 g of SISG in a mechanical shaker for the attainment of the equilibrium. The remaining metal ion in the solution was determined by atomic absorption spectroscopy. The amount of metal ion retained by SISG was determined by the equation,

$M_f = (X-Y)/W$

where, X is the initial amount of metal ion added (μg), Y the equilibrium amount of metal ion remained in solution (μg), W the mass of SISG (g) and M_f the equilibrium amount of metal ion (μg) retained per gram of SISG.

b) Column Experiment:

Column experiment was performed for retention as well as elution of respective metal ion. A funnel type glass chromatographic column, plugged with cotton at the end and uniformly packed with SISG was used. Respective metal ion solution at a definite pH was percolated at a definite flow rate of 5.0 ml/min. After washing the column with about 20 ml of deionsed water, an eluting solution of definite composition (HNO_3 or $HClO_4$) was passed through at a flow rate of 3.0 ml/min. The metal ion concentration in the eluate, after diluting to the desired volume, was determined by atomic absorption spectrophotometer (AAS).

III. RESULTS AND DISCUSSION

A. Characterization of SISG

The IR spectrum (Fig.1) of SISG show characteristic peaks of SALD [24] suggesting that the ligand was immobilized as such without any structural change on the silica gel. In another experiment ethanol was passed through the column packed with a weighed quantity of SISG to remove all the SALD immobilized with silica gel. The eluate gave identical absorption band of SALD (Fig.2). Quantitative determination showed that the amount of SALD in SISG was 27 ± 2 mg/g of silica gel.
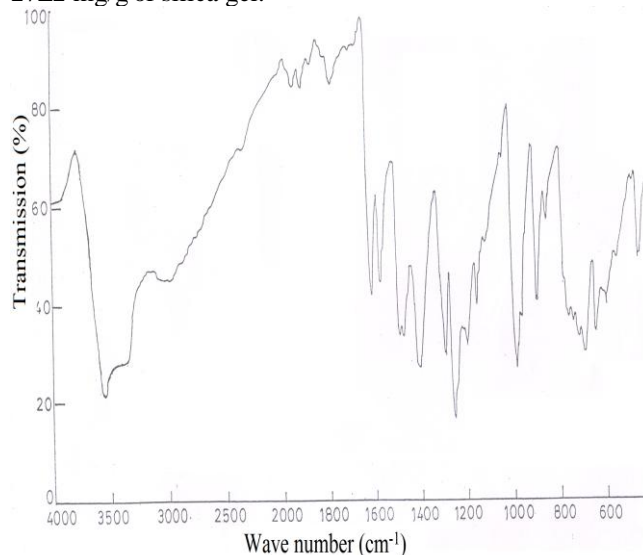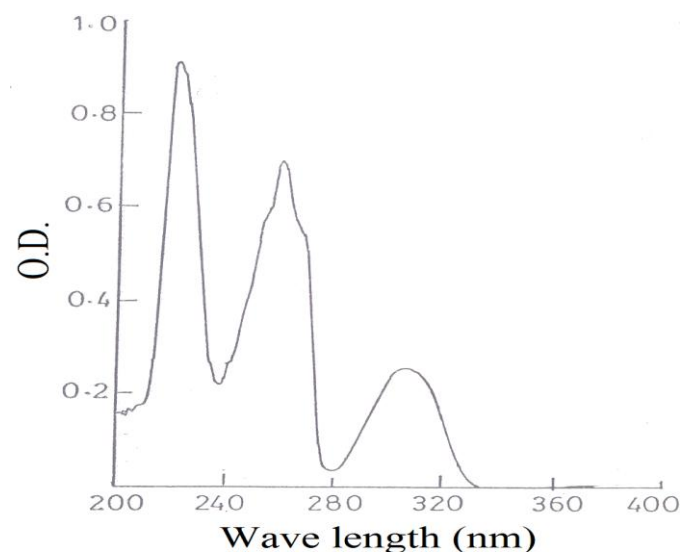

Fig. 1 IR spectrum of SISG

Fig. 2 Absorption spectrum of SALD

B. Retention behavior of metal ions on SISG

1) Batch experiment:

a) Effect of initial metal ion concentration and shaking time:

The adsorption of each metal ion on SISG is found to depend on both initial metal concentration and the shaking period. The time at which equilibrium is attained is considered as the equilibrium time and the corresponding concentration in the solution is the equilibrium concentration.

It is found that the uptake of metal increases with lapse of time and reaches a maximum in 30 minutes for Cu(II) and in 85 minutes for Ni(II). The maximum retention of 98% for Cu(II) and 93% for Ni(II) was observed corresponding to an initial concentration of 20 mg/l.With increase of metal ion to 200 mg/l, the percent adsorption was found to be 46.7 and 53.6% for Cu(II) and Ni(II) ion respectively. It may be thought that with increase in metal ion concentration, the ratio of the initial number of moles of metal ions to the available retention sites becomes fewer. A comparison of adsorption behavior indicates that both the equilibrium time and the extent of metal retention follow the order Cu(II)> Ni(II).

b) Effect of agitation speed:

The agitation speed was varied from 100 to 400 rpm keeping each initial metal concentration at 20 mg/l. It is found that adsorption increases from 61 to 98% for Cu(II) and from 53.6 to 93.0%. for Ni(II). It may be thought that the resistance to mass transfer in the bulk solution decreases resulting in the increased driving force and hence the increased adsorption on SISG.

c) Effect of the dose of SISG.

It is found that as the dose of SLSG increases the adsorption increases both for Cu(II) and NI(II). The optimum dose for Cu(II) and Ni(II) was found to be 0.65 and 0.80 g for Cu(II) and Ni(II) respectively corresponding to even the highest concentration studied of 200 mg/l. However, all subsequent experiments were performed using 1.0g of SISG.

d) Effect of pH:

The metal ion adsorption is found to be pH dependent where both the pattern and extent of adsorption vary with change of pH for each metal ion. A maximum adsorption of 98% occurred at pH 2.2 for Cu(II) while for Ni(II) a maximum adsorption of 93% occurred at pH 3.5. The pH dependent adsorption behavior as illustrated in Fig.3 can be utilized for separation of Cu(II) and Ni(II) from their mixture in batch mode. However, the extent of adsorption corresponding to each pH for Cu(II) and Ni(II) is presented in Fig.4.
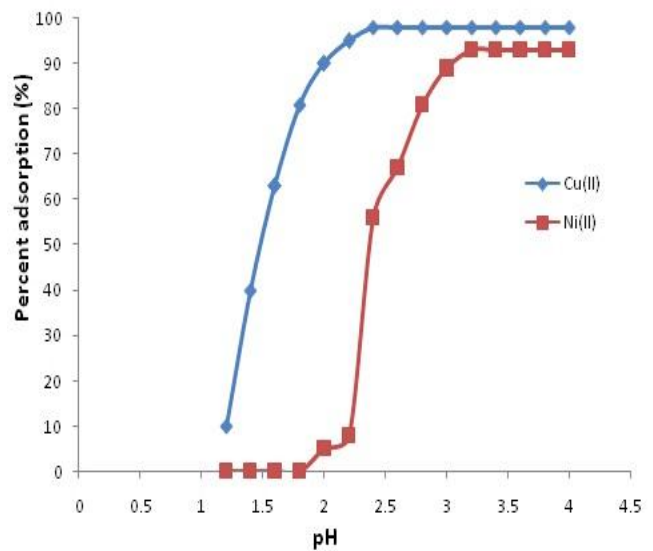

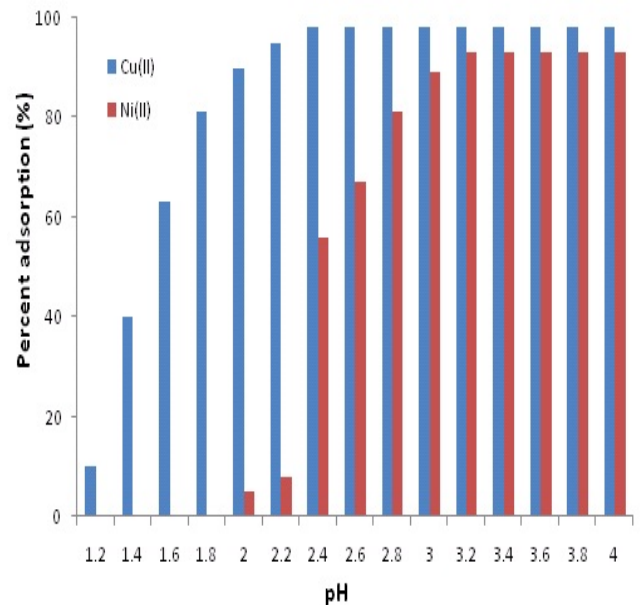Fig. 3 Dependent adsorption pattern of Cu(II) & Ni(II)

Fig. 4 Comparison of adsorption extent of Cu(II) & Ni(II)

e) Effect of temperature:

The temperature has an influence on the metal adsorption. It is found that for both Cu(II) and Ni(II) the adsorption increases with increase of temperature. This is probably because the equilibrium constant of the process that is expected to increase with increased temperature. The adsorption is found to increase from 46.7 to 56.1% for Cu(II) and 53.6 to 67.0% for Ni(II) for an increase of temperature from 298 to 318K corresponding to each metal concentration of 200 mg/l.

f) Tolerance level of electrolytes, foreign ions:

Different electrolytes such as sodium chloride, potassium nitrate and potassium chloride possess higher tolerance during metal adsorption. Other ions and salts show different level of tolerance (Table 1).

Table.1. Tolerance level of added salts on metal adsorption

Salt added	Tolerance level		Effect on adsorption
	Cu(II)	Ni(II)	
KCl, KNO$_3$, NaCl, NaNO$_3$,	1 g	1g	unchanged
CH$_3$COONa, NH$_4$Cl	1 g	1g	unchanged
KH$_2$PO$_4$, NaClO$_4$	500 mg	500 mg	unchanged
NH$_4$F	100 µg	150 µg	decrease
KI	100 µg	200 µg	decrease
KCNS	100 µg	200 µg	decrease
NaCN	5 µg	10 µg	decrease
EDTA	5 µg	5 µg	decrease
CaCl$_2$, MgCl$_2$, AlCl$_3$, MnCl$_2$	1 g	1 g	unchanged

Metal ion: 20 cm^3 (20 mg/l) at the optimum condition

2) *Column experiment:*

a) *Retention behavior*

The effect of flow rate of the solution through the column on the retention behavior of each metal ion solution was studied over the range 1.0-10.0 ml/min. The extent of metal retention was found to remain unchanged up to a flow rate of 10.0 ml/min for Cu(II) and 6.5 ml/min for Ni(II). In the present study a flow rate for metal ion retention was maintained at 5.0 ml/min. Again when the volume of the sample solution was varied no change in the extent of metal retention was observed up to a volume of 1000 ml.

b) *Elution behavior*

In an aim to recover, preconcentrate or separate metal ions from aqueous sample elution of the retained metals from SISG was studied. SISG after metal adsorption was subjected to interaction with a varying concentration of HNO$_3$ or HClO$_4$ for elution. The flow rate during elution was maintained at 3.0 ml/min. About 98.0% of retained Cu(II) was recovered when treated with either 1.4 mol/l HNO$_3$ or 0.4 mol/l HClO$_4$ within a small volume of 15 ml. The elution was found effective with either HNO$_3$ (0.4 mol/l) or HClO$_4$ (0.01mol/l) and about 95.0% of the added Ni(II) was recovered within 25 ml of the eluent. The preconcentration factor for Cu(II) and Ni(II) were evaluated as 66 and 40 respectively.

In order to separate Cu(II) and Ni(II) from the bisolute composition the difference in the elution character was utilized and the gradient elution either with HNO$_3$ or HClO$_4$ was tested. Initially HNO$_3$ at a concentration of 0.4 mol/l was passed through the column and Ni(II) was recovered. Next a higher concentration of HNO$_3$ (1.4 mol/l) was passed and Cu(II) is eluted. The recovery of Cu(II) and Ni(II) with HNO$_3$ was shown in Fig.5. The resolution is found to be > 18.0

volume unit while band width is found to be < 6.0 volume unit. Similarly separation of Cu(II) and Ni(II) can be made by gradient elution with HClO$_4$. The retention and elution parameters for Cu(II) and Ni(II) in the column mode is described in Table 2.
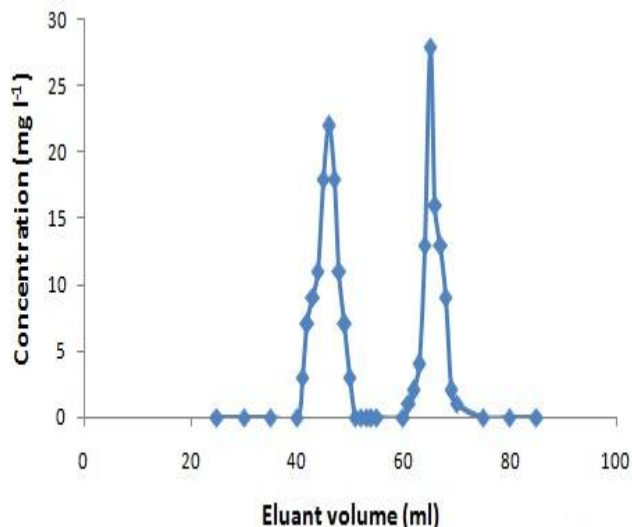

Fig. 5 Gradient elution characteristic of Cu(II) & Ni(II)

Table 2: Column parameters for metal ions

Metal ion	Maximum tolerable flow rate (ml/min)	Eluent strength (mol/l)		Elution volume (ml)	Recovery (%)	P. F	LOD (µg/l)
		HNO$_3$	HClO$_4$				
Cu(II)	10.0	1.4	0.4	15	98	66	1.0
Ni(II)	6.5	1.0	0.1	20	92	50	1.5

Influent sample volume: 1000ml; P.F: Preconcentration factor; LOD: limit of detection

In order to find the effectiveness of the process the recovery of Cu(II) and Ni(II) was determined from spiked samples. The results (Table 3) showing high recovery recommend SISG as a promising adsorbent for Cu(II) and Ni(II).

Table 3: Recovery of metal ions from synthetic and spiked samples

Sl No.	Metal added		Cu(II)		Ni(II)	
	Mean (µg/ml)	Spiked (µg/ml)	Found (µg/ml)	Recovery (%)	Found (µg/ml)	Recovery (%)
1	1.0	0.0	0.98±0.04	98.0	0.92±0.04	92.0
2	1.0	0.5	1.47±0.06	98.0	1.38±0.04	92.0
3	1.0	1.0	1.97±0.05	98.5	1.84±0.05	92.5
4	1.0	5.0	5.89±0.04	98.2	5.53±0.06	92.2
5	1.0	10.0	10.82±0.04	98.4	10.16±0.05	92.4
6	1.0	20.0	2.58±0.04	98.0	19.32±0.04	92.0

(n = 5; Standard deviation < 0.06; 95% confidence level)

IV. CONCLUSION

The present communication shows that salicylaldoxime immobilized silica gel as a solid phase extractant can be employed for the removal, recovery, preconcentration vis-à-vis separation of Cu(II) and Ni(II) from bisolute composition. The removal was found to depend on time of contact, initial metal concentration, agitation speed, temperature and pH of the medium. At the optimum condition 98% of Cu(II) can be adsorbed at pH 2.2 and 93% of Ni(II) at pH 3.5.

In column mode the quantitative elution of the retained Cu(II) and Ni(II) (98 and 92%) makes the process comparable with other known methods viz., solvent extraction and ion exchange . The lower detection limit calculated as the concentration of metal with a signal to noise ratio equal to 2 makes the process much effective. Considering the enrichment factor of 66 and 50 corresponding to Cu(II) and Ni(II) at least 1.0 and 1.5 l of Cu(II) and Ni(II) respectively can be detected by the proposed method. Moreover the separation of Cu(II) and Ni(II) from the mixture with high resolution makes the process viable for analytical work.

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