Synthesis, Characterization, Distribution Behaviour And Binary Separation Of A Chelating Sorbent Containing β-Diketo Group Onto Neutral Alumina

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ABSTRACT

A series of chelating sorbents comprising liquid chelating ion exchanger(0.002 to 0.2 M 2,4, Decanedione) and neutral alumina was synthesized by impregnation method. The support and the synthesized chelating sorbent has been characterized by DSC, FTIR, DRS, Particle Size distribution(PSD) and specific surface area(PSD method). The surface morphology of the support and chelating sorbent has been studied by scanning electron microscope(SEM). The above studies confirm the presence of β-diketo group on the surface of the support. Distribution coefficient for several metal ions like Cu, Pb, Co, Cd, Zn, Hg, Ce and Ni has been studied using different loading of chelating ion exchanger onto the support, different concentration of the metal ion solution and different electrolytes. The separation factor was also calculated and based on its values a few binary separations such as Cu(II)-Ni(II) 98-98%, Co(II)-Ni(II) 95-97% , Co(II)-Zn(II) 96-97% and Zn(II)-Cd(II) 96-98% have been proposed.
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KEYWORDS

INTRODUCTION

Recently with fast development of industry, heavy metals are released into the environment. These effect the eco system and also to living organism. Heavy metals are highly toxic and cause serious affects to humans too. These metals are released in the environment in the form of industrial effluents, sewage wastewater, automobile combustion, etc. Various different methods using different solid/liquid ion exchangers[1-11] have been proposed and developed for the removal of the metal ions.

One of the most commonly used method for the preliminary concentration of metals from aqueous solutions is based on utilization of chelating sorbents and many such material containing various groups have been proposed[12-16]. A chelating sorbent essentially consists of two components: the chelate forming functional group and the polymeric matrix or the support. The selectivity of the sorbents is determined mainly

by the nature of the functional groups and/or donor atom(O, N, and S) capable of forming chelate rings.

A number of chelating sorbents have been found interesting popularity[13-22], especially interesting are silica gels modified with various chelating reagents. Recently chelating resins containing β-diketo group has gained importance due to its good analytical use[11,23-25]. A literature survey shows that no work has been carried out on chaleting sorbent comprising β-diketo group and neutral alumina. So it was thought of interest to carry out study for the same.

The present article describes the synthesis, characterization and analytical applications of the chelating sorbent containing a-diketo group onto neutral alumina. Liquid chelating ion-exchanger,2,4, decanedione was supported onto neutral alumina by impregnation method. The synthesized chelating sorbent has been characterized by DSC, FTIR, DRS, PSD, specific surface area(PSD method) and SEM. The distribution behavior of a number of metal ions like Cu, Pb, Co, Cd, Zn, Hg, Ce and Ni was studied by varying different parameters such as different loading of chelating ion exchanger onto the support, different concentration of the metal ion solution and different electrolyte concentrations. The separation factor was also calculated and based on its values a few binary separations such as Cu(II)-Ni(II), Co(II)-Ni(II), Co(II)-Zn(II) and Zn(II)-Cd(II) have also been carried out.

EXPERIMENTAL

Materials

All the chemicals used were of AR grade of E.Merck.

Synthesis of the chelating sorbent

1.1. Synthesis of liquid chelating exchanger

The synthesis of liquid chelating exchanger was carried out in two steps; the first step was the synthesis of the ester. The second step consists of the conversion of the obtained ester into the liquid chelating ion exchanger.

Synthesis of the ester

Heptanoic acid was mixed with excess of absolute alcohol and few drops of the concentrated sul-furic acid. The mixture was refluxed in a round bottom flask provided with a double walled condenser for 24 hours on a heating mentle at 60^0C for 24 hours. The content was cooled, distilled and separated out. The obtained product, ester was designated as E.

1.2. Synthesis of liquid chelating ion exchanger

So formed ester(E) was mixed with freshly prepared sodium ethoxide and with excess of pure acetone. The mixture was refluxed in a round bottom flask provided with a double walled condenser for 24 hours. Then it is cooled, distilled and separated out. The resulting product(2,4,decanedione) was designated as LCE.
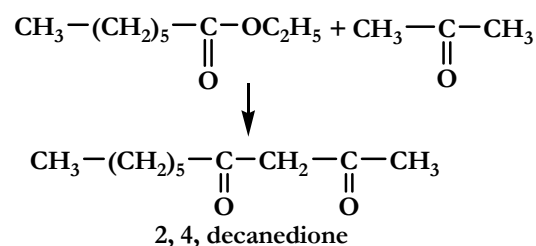
2. Synthesis of chelating sorbent(Impregnation of the 2, 4, decanedione onto neutral alumina)

A series of chelating sorbents were synthesized by impregnating 50mL of 0.02 M LCE with chloroform as a solvent on to 1g of neutral Al_2O_3. The mixture was stirred for 35 hrs on a magnetic stirrer. The solvent was evaporated and the solid was dried at room temperature and designated as AlCE. The obtained AlCE was heated at 100^0C for 5, 10 and 20 h and designated as $AlCE_5$, $AlCE_{10}$ and $AlCE_{20}$ respectively.

CHARACTERIZATION

The chemical stability of the synthesized chelating sorbent was checked in different acids, bases and organic solvents.

The DSC was carried out in air at a rate of 10^0C/min on TA Instruments DSC-2010. The FTIR spectra and the reflectance spectra were recorded on Perkin Elmer RX-1 using KBr as reference and on Perkin-elmer Lambda 15 UV/VIS spectrophotometer using $BaSO_4$ respectively. Scanning electron microscope(SEM) was recorded on a Jeol SEM in-

$$CH_3-(CH_2)_5-\underset{\underset{O}{\|}}{C}-OC_2H_5 + CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

$$\downarrow$$

$$CH_3-(CH_2)_5-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$$

2, 4, decanedione

Full Paper

strument(model JSM-560L0) with scanning electron electrode at 15KV. The study on the particle size distribution was carried out on Malvern particle size analyzer, Maltersizer 2000.

Distribution studies

The distribution coefficient(K_d) is a measure of the functional uptake of a metal ion in a solution. It can be determined by batch method experiments in which a small amount of the resin/ion exchanger is shaken with a solution containing a known concentration of the solute, followed by analysis of the two phases after equilibrium has been attained. The filtrate is then titrated against EDTA of the known concentration.

In the present work, the distribution behavior for different metal ions such as Cu, Pb, Co, Cd, Zn, Hg, Ce and Ni were studied.

Cu(II) ion was taken as an example for optimization of different parameters such as concentration of the loading of the liquid chelating exchanger onto the supports, concentration of the metal ion solution, volume of the metal ion solution and electrolytes. The results are shown in TABLE 1 and 2.

Binary separations

The rate at which two constituents separate in a column is determined by the ratio of the two corresponding distribution coefficient. The separation factor α is given by the equation $\alpha = K_{d1}/K_{d2}$

K_{d1} =Distribution co oefficient of constituent 1
K_{d2} =Distribution co oefficient of sonstituent 2

The greater the deviation of the 'α" from unity, the easier it will be the separation of the metal ions.

For binary separations, 1g of the ion exchanger is taken in its H^+ form in a glass column (30cm+1cm diameter). First the column is washed thoroughly with the conductivity water and then loaded with the chelating sorbent. Then we mentain the flow rate of 0.5ml/min. In all the binary separations, the concentration of the metal ions was maintained at 0.01M. the amount of the metal ions taken was 5 ml. the separation was achieved by passing an appropriate solvent through the column as an eluant and the metal ion of the effluents were determined. The metal ion pairs selected for binary separations are:

TABLE 1: Effect of loading of LCE, different concentration of metal ion and different volume of metal ion solution

Chelating sorbent	K_d values with different LCE concentration		K_d values with different Metal ion concentration		K_d values with different volume of metal ion	
	0.2M LCE	0.02M LCE	Cu=0.01 N	Cu=0.05 N	Cu=20ml	Cu=25ml
AlCE$_{RT}$	23	41	41	38	39	41
AlCE$_5$	35	46	46	42	41	46
AlCE$_{10}$	49	48	48	45	44	48
AlCE$_{20}$	20	20	20	40	39	20

*=average of 3 readings; Volume of Cu ion=25ml, LCE=0.02M; Volume of Cu ion=25ml; Concentration of Cu=0.01M; LCE=0.02M; Cu=0.01 N

TABLE 2 : Distribution coefficient of all the metal ions with different electrolytes

Metal ions	K_d values			
	Distilled Water	0.01M HNO$_3$	0.1 M HNO$_3$	0.01M NH$_4$NO$_3$
Cu(II)	48 (22)	46 (12)	51 (22)	163 (37)
Pb(II)	82 (22)	90 (44)	53 (12)	72 (25)
Co(II)	125 (30)	86 (23)	46 (6)	108 (66)
Cd(II)	54 (19)	48 (12)	NS (NS)	105 (37)
Zn(II)	NS (NS)	NS (NS)	57 (20)	NS (NS)
Hg(II)	70 (30)	88 (24)	NS (NS)	NS (NS)
Ni(II)	101 (24)	136 (52)	NS (NS)	NS (NS)
Ce(IV)	131 (31)	100 (49)	NS (NS)	NS (NS)

Chelating sorbent=AlCE$_{10}$, NS=No sorption, The number in the parenthesis indicate the result for alumina alone

TABLE 3 : % Separation of the metal ions in binary system

Metal ion pair	Amount loaded (mg)	Amount eluted(mg)	% efficiency
Cu(II)-Ni(II)	0.3175-0.2935	0.3111-0.2876	98-98%
Co(II)-Ni(II)	0.294-0.2935	0.2793-0.2846	95-97%
Co(II)-Zn(II)	0.294-0.327	0.2822-0.3171	96-97%
Zn(II)-Cd(II)	0.327-0.562	0.3139-0.5507	96-98%

Cu(II)-Ni(II), Co(II)-Ni(II), Co(II)-Zn(II) and Zn(II)-Cd(II). The results are summarized in TABLE 3.

RESULT AND DISCUSSION

There was no change in colour, nature and weight of the chelating sorbent which indicating stability of synthesized chelating sorbent into various acids, bases and organic solvents.

DSC of ALCE shows an endothermic peak at 80^0C due to the removal of adsorbed water. After that there is no appreciable change till 350^0C which indicates that the synthesized materials are stable upto 350^0C.
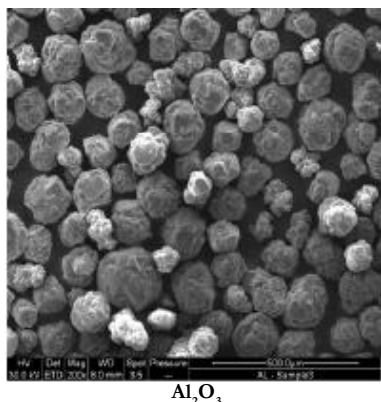
Al$_2$O$_3$

Figure 1(a) : SEM of neutral alumina

ALCE

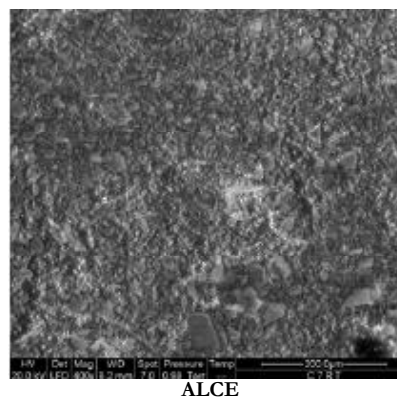**Figure 1(b) : SEM of ALCE**

FT-IR spectra of LCE shows sharp bands at 1445cm^{-1} corresponding to bending of methyl group. It also shows bands at 1715cm^{-1} and 1620cm^{-1} attributed to the presence of ketone group and β-diketone group respectively. The FTIR spectra of ALCE shows a band at 1632-1642cm^{-1} indicating the presence of the β-diketo group in the synthesized chelating sorbents.

It is well known that in α- diketones the absorption is related to the presence of α, β-unsaturated carbonyl system. According to the woor-board rules, the calculated value of λ max is ~252nm. In the presence of intramolecular H-bonding and impregnation on to the support, a shift in λ max(~252nm) is expected. The synthesized chelating sorbent shows λ max of 270nm as expected.

The figure 1a and 1b shows the scanning electron microphotograph of neutral alumina and the chelating sorbent respectively. It is seen from SEM that the surface is distinctly altered and there are some bright spots which may be due to the impregnation of the liquid chelating ion exchanger on to the surface of the support.

The values for average particle size obtained from the particle size distribution(PSD) study for neutral alumina and ALCE are 114.018μm and 17.829μm respectively(figure 1b). The decrease in the average particle size of ALCE(17.829μm) as compared to that of neutral alumina(114.018μm) may be due to the supporting as well as uniform dispersion of the liquid chelating ion exchanger onto the surface of the support. The specific area of ALCE is 1.02m^2/g and that for neutral alumina is 0.0555m^2/g. The in-

crease in the value of the specific surface area may also be due to the supporting of the liquid chelating ion exchangers onto the surface of the support. The particle size decreases, specific surface area increases. In the present case the obtained results are, order of average particle size as Al>ALCE, order of specific surface area is ALCE>Al. The obtained results are in good agreement with each other.

TABLE 1 shows better K$_d$ values when chelating sorbents are loaded with 0.02 M LCE, concentration of Cu is 0.01 N and volume of Cu ion =0.01 N, 25mL.

Thus, the optimum conditions for Cu(II) metal ion are: Metal ion concentration=0.01 N, Volume of metal ion=25ml, Concentration of loading chelating ion exchanger=0.02M, Chelating sorbent= ALCE$_{10}$.

K$_d$ shows the rate at which two constituents can separate on the column and is determined by ratio of two corresponding K$_d$ values of the two metal ions. K$_d$ is an important factor for determining analytical potential of an ion exchanger/chelating sorbent.

K$_d$ values depends on the ion exchange capacity of the material, ionic radii, atomic number and ionic charge of the metal ion being exchanged/sorbed. Sundandammma has very well explained the correlation of K$_d$ value with the above mentioned properties. In general, as the ionic radii increases, a regular increase in K$_d$ value is observed and vice versa. K$_d$ value also increases with the increase in the charge of the metal ion.

The order for the K$_d$ values for Cu, Ni, Zn, Cd, Co, Pb, Hg and Ce metal ion is as follows
Co> Ni > Cu > Zn

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In a period the ionic radii decreases from left to right. So accordingly, K_d values are also expected to decrease. It is seen from the TABLE that the K_d value of Co is maximum and Zn is nil (i.e. metal doesn't sorbed/exchanged). Further, the order of K_d values for Zn, Cd and Hg is

Hg > Cd > Zn

As ionic radii increases, K_d values also increases. In a group, ionic radii increases from top to bottom and so the highest K_d values for Hg is expected. The obtained results are in good agreement with the observations.

The highest K_d value for Ce (IV) may be due to the higher charge. It is also known that the K_d values increases with increase the charge of the ion.

TABLE 3 shows that the separation processes using chelating sorbents is simple, rapid and quantitative.

CONCLUSION

DRS and FTIR confirms the presence of the diketone group in the synthesized LCE.

PSD and SEM studies show that uniform dispersion of liquid chelating ion exchanger onto the surface of the support. The data shows that very less amount of chelating sorbent is required for maximum extraction of the metal ions. Further, the method is very rapid and efficient, requires very simple equipment as well as involves low cost reagents.

From the above studies it could be concluded that the synthesized chelating sorbent can be successfully used for the separation of metal ions. They offer new opportunities in the area of separation science and technology.

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