Synthesis of Novel Schiff Based Xerogel Silica for Adsorption of Cr(III) and Pb(II)Ions

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Summary: Schiff bases have been successfully doped with sol- gel silica by our group. There are only few previous reports on doping of Schiff bases with sol- gel silica. This study pertains to novel synthesis of *4-(2-(2-hydroxybenzylideneamino) ethyl) benzenesulfonamide* (a Schiff base) doped in xerogel silica, its characterization by FTIR, thermogravimetry, scanning electron micrography and porosimetry studies besides its application in adsorption of chromium (III) and lead (II) ions from aqueous media. The large Schiff base molecules are entrapped by the pores of xerogel. Likewise, metal ions in aqueous solution make complex with Schiff base by either ion exchange or chelation through the pores. Doping of Schiff base in xerogel gives a porous and stable surface working at high temperature. Doping of Schiff base provides a convenient approach of tailoring the surface properties of mesoporous silica by organic functionalization. Both blank and Schiff based xerogels exhibit ordered mesoporous structures and hydrophilic properties responsible for ion exchange or chelation mechanism. Adsorption phenomenon was studied by noting solution pH, contact time and concentration of adsorbate. The equilibration time was as swift as it completed within ten min. Finally, 0.1 *N* HNO₃ was employed for desorption of metal ions followed by regeneration and periodic recycling of synthesized xerogels in this study.

Keywords: Schiff base, Blank xerogel, Schiff based xerogel, Adsorption, Characterization, Desorption.

Introduction

The pollution of water with toxic heavy metals due to industrial operations is a burning issue in the world. The toxic heavy metals are not degraded biologically. As a result they acquire an increasing quantity in living things. Chromium is highly toxic causing asthma in humans. It is a human carcinogen causing cancer of lungs and stomach. Chromium is utilized in manufacturing alloys, dyes, pigments, paints, ceramics, glasses, fungicides and mostly in leather tanning industries. Chromium comes in the body by using these products. WHO limit of Chromium in drinking water is 0.05 *mg/L* [1]. According to U. S. Environmental Protection Agency (EPA) chromium is on the top priority list of toxic pollutants. Pb(II) is toxic for human's body systems such as digestive, nervous and skeleton system. Lead is utilized in manufacturing pigments, paints, coatings, cable coverings, plastics, bullets and shells. Blood Pb(II) concentration above 0.1 *mg/L* causes adverse effects on intellectual functioning [2]. Many researchers applied a variety of adsorbents such as biomaterials, active carbons, clays, zeolites and organic resins for the removal of Chromium and lead in recent years. Many of these materials have problems like low binding strength, less sorption capacity, small selectivity, low resistance to heat, light and chemicals, high cost and poisonous nature. These problems were minimized by the development of many new materials. Out of these materials organically doped porous sol–gel materials have developed as versatile materials. They opened new research areas in bio–medical [3], optical and chemical sensors [4, 5], catalysis [6], drug delivery [7], removal of toxic heavy metals [8] and many other fields. They show no swelling. They show good stability to chemicals, thermal and mechanical stability. They show high selectivity imparted by entrapped ligands and fast attainment of equilibrium in adsorption [9]. Doping is easily handleable, cost effective and can be experimentally performed by various substances (organic, inorganic, biological) as solutions or suspensions in the sol–gel reaction mixture when it is being solidified. Organically doped sol–gel is dried and aged under ambient conditions to produce xerogel. The large sized organic ligand avoids effusion from the pores of the xerogel. A range of biomolecules from enzymes to antibodies and even functional nucleic acids have been doped successfully in sol–gel silica retaining biological properties [10, 11]. The Schiff bases are excellent chelating agents [12, 13]. They have been applied in determination [14, 15] and removal of toxic metals [16]. They are bioactive organic compounds showing important bioactivities such as antibacterial, anticancer, antitubercular, insecticidal etc [17 – 18]. Organically doped sol–gels having entrapped Schiff bases can find use in drug delivery applications. The Schiff base catalysts have been used in different synthetic reactions [19–21]. We have developed methods for doping Schiff bases with sol–gel silica because of their analytical, industrial, biological and catalytic applications. There are only

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few previous reports on doping of Schiff bases with sol–gel silica [22]. We demonstrated here the principle by the entrapment of *4-(2-(2-hydroxybenzylideneamino) ethyl)benzenesulfonamide* in sol – gel silica via chemical doping as model system. The Schiff based xerogel is utilized for the adsorption of Chromium and lead ions from aqueous media.

Results and Discussion

The ligand *4-(2-(2-hydroxybenzylideneamino) ethyl) benzenesulfonamide* has many active sites for ion exchange or chelation with metal ions as shown in Fig. 1. The ligand is sufficiently bulky to prevent leakage from the solid host matrix of xerogel.
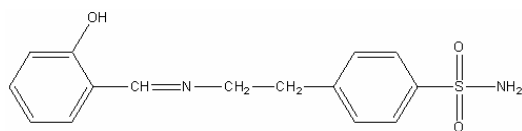

Fig. 1:   *4-(2-(2-hydroxybenzylideneamino)ethyl)benzenesulfonamide*

Characterization

TGA plots of blank xerogel (SG), Schiff based xerogel (SBSG) and free Schiff base ligand (SB) are shown in Fig. 2. By comparing these TGA plots, it is evident that the thermal behaviour of free Schiff base ligand is quite different from doped ligand. The chemical doping has caused enhancement in thermal stability of the ligand, showing entrapment of the ligand in the pores of xerogel. Both blank and Schiff based xerogels show high thermal stability. Blank xerogel showed negligible weight loss while Schiff based xerogel show some weight loss showing doping of Schiff base with xerogel. Amount of entrapped Schiff base can be calculated by comparing weight loss data of blank and Schiff based xerogel.
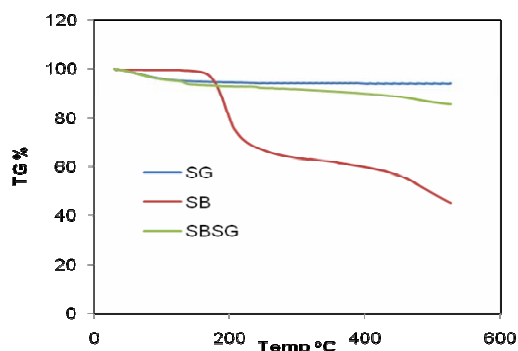

Fig. 2:   TGA curves of the xerogels; SG (Blank Xerogel), SB (Schiff base), SBSG (Schiff based Xerogel).

Porosimetry data show decrease in surface area, pore diameter and volume after doping as shown in Fig. 3.

Blank Xerogel to Schiff based Xerogel:

Surface area decreased from 280 m^2/g to 230 m^2/g
Pore volume decreased from 0.65 cm^3/g to *0.55* cm^3/g
Pore diameter decreased from 19.45 *nm* to 9.3 *nm*
The decrease in pore diameter and pore volume after doping is showing encapsulation of the ligand in the pores of gel. Both blank and Schiff based xerogel are mesoporous as evident from the hysteresis loop in both gels in adsorption/desorption isotherms (Fig. 3). The shape of the hysteresis loop in both gels show compacts of spheroidal particles of uniform size and array in both. The shape of hysteresis loop in both xerogels is similar in both gels. The difference of particle sizes in both gels can be seen in their SEM pictures in Fig. 4. SEM shows increase in particle sizes from blank to Schiff based xerogel. It also shows homogeneous nature of both xerogels and porosity in them.

FTIR spectra of blank xerogel (SG), Schiff base (SB) and Schiff based xerogel (SBSG) are presented in Fig. 5. There are no remarkable differences in the spectra of blank and Schiff based xerogels. Both show absorptions at;

3000 – 3600 cm^{-1} – corresponding to hydrogen bonded water and silanol groups;
1637 cm^{-1} – showing the presence of water in the samples;
1075 – 1200 cm^{-1} – correlated with asymmetric stretching vibrations of siloxane groups;
750 – 1000 cm^{-1} – correlated with symmetric stretching vibrations of siloxane groups.

In FTIR spectrum of Schiff based xerogel, the broad absorptions of gel have covered up the sharp absorptions of the ligand in 450 – 500 cm^{-1} and 750 – 1200 cm^{-1} regions and by broad absorptions of water molecules in 1550 – 1700 cm^{-1} region. Though the intensities of bands of Schiff base in other regions of spectrum have also been lowered by the intense bands of xerogel, the bands of Schiff base can be clearly seen on very sensitive instruments. The results of FTIR studies also show the entrapment of Schiff base molecules in the pores of xerogel.
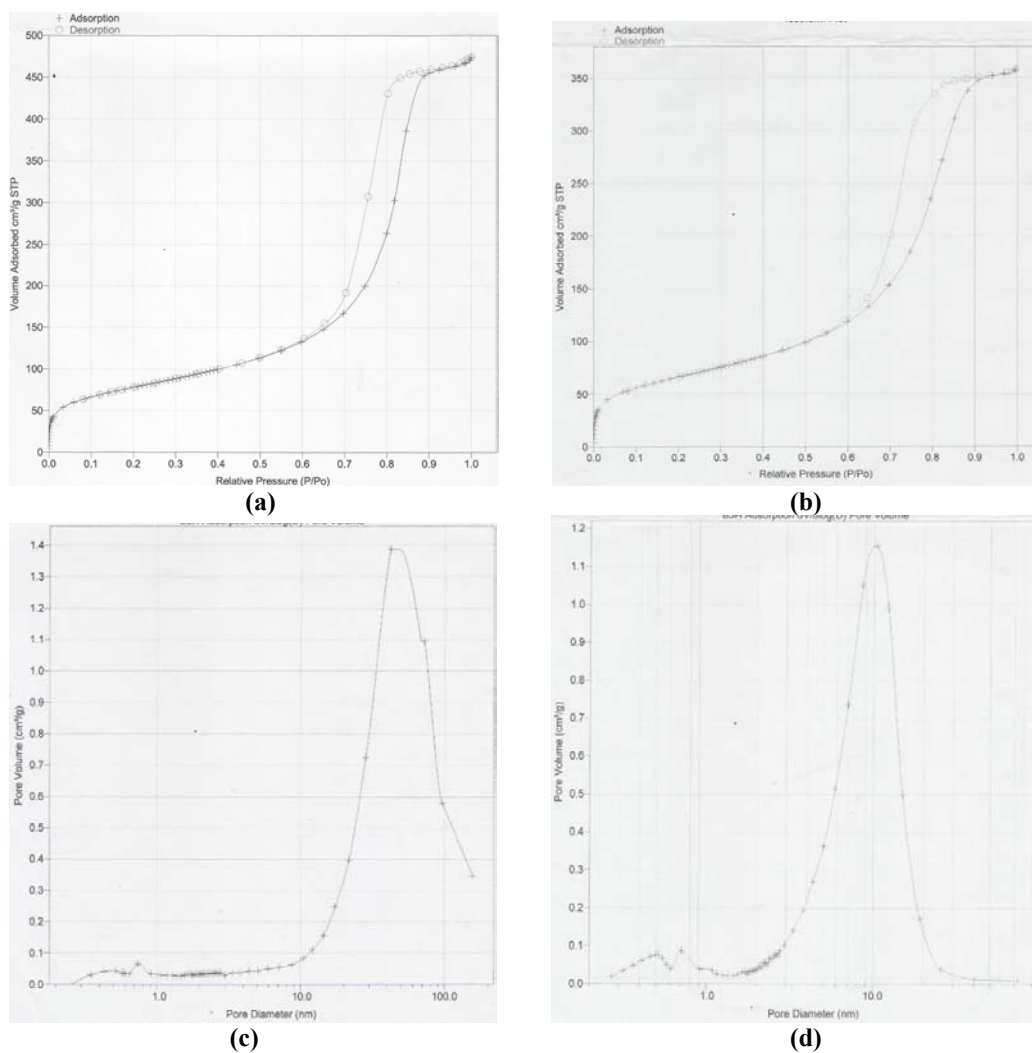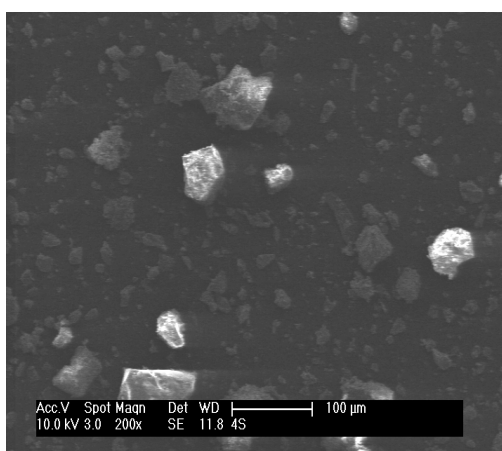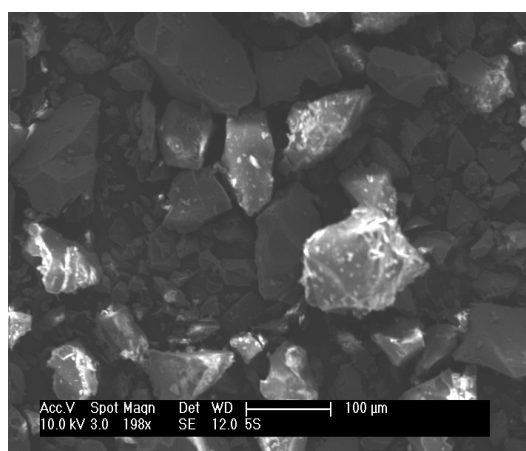
Fig. 3: (a) Adsorption/desorption isotherms of blank xerogel (b) Adsorption/desorption isotherms of Schiff based xerogel (c) BJH adsorption pore volume of blank xerogel (d) BJH adsorption pore volume of Schiff based xerogel.

(a)   (b)

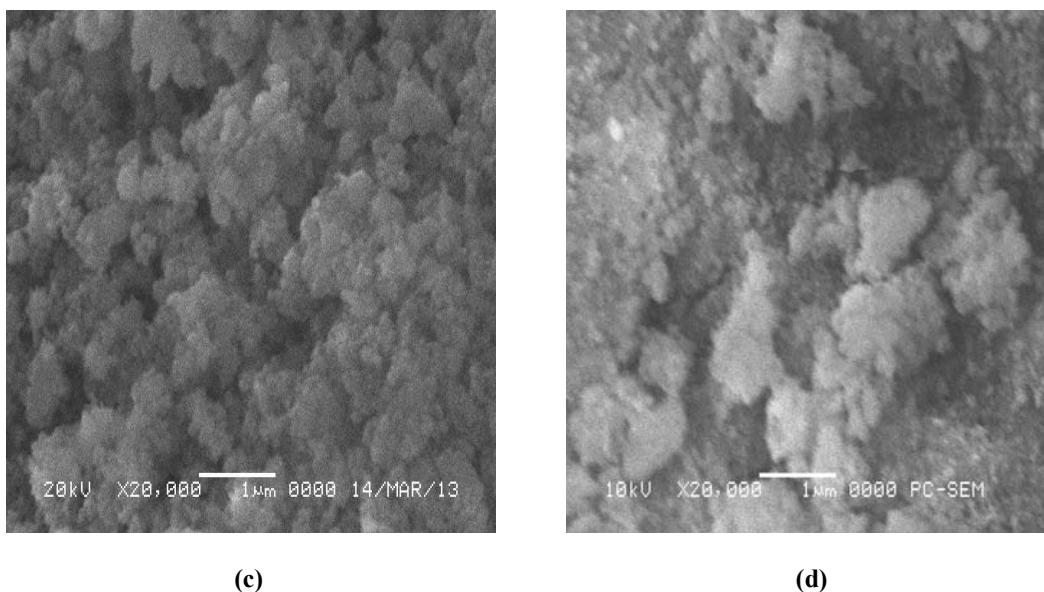**(c)**   **(d)**

Fig 4:   (a) SEM of blank xerogel (b) SEM of Schiff based xerogel (c) SEM of blank xerogel showing porosity (d) SEM of Schiff based xerogel showing lack of porosity.
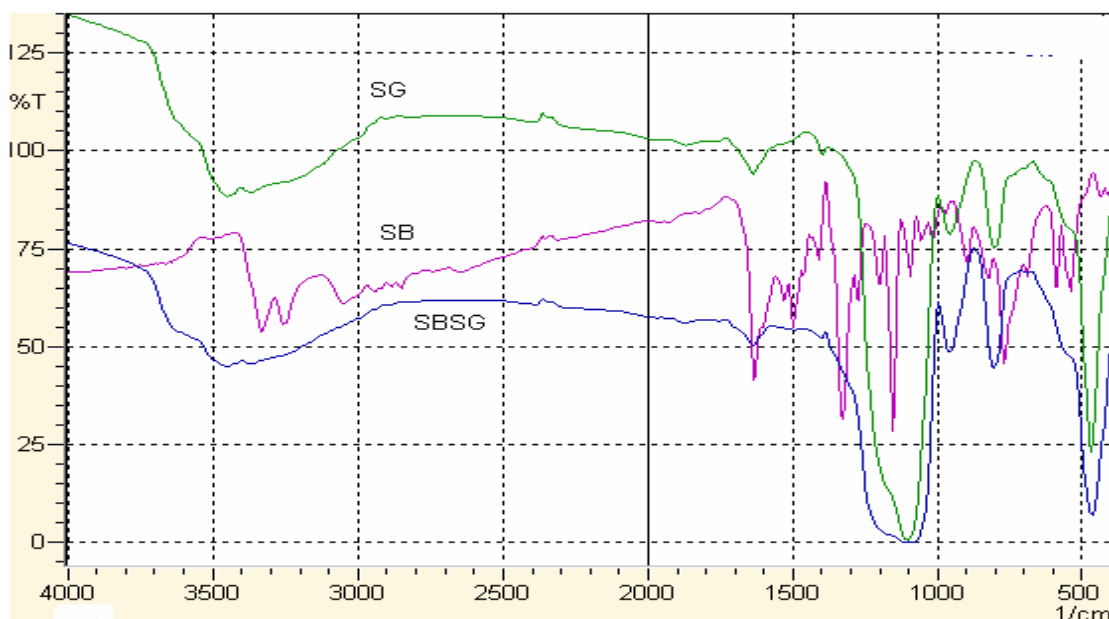

Fig 5:   FTIR Spectra of the xerogels; SG (Blank Xerogel), SB (Schiff base), SBSG (Schiff based Xerogel).

It is evident from the SEM images of blank and Schiff based xerogels that porosity has been decreased after doping.

Effect of pH

pH is one of the most important factors affecting adsorption of metal ions. The adsorption of chromium and lead ions on blank and Schiff based xerogel was studied at different pH values from 1–7 as shown in Fig. 6. The adsorption increased with increasing solution pH. No adsorption was observed at low pH values due to opposition of hydronium ions with the metal ions. 100 % adsorption was observed at pH 4. Therefore pH 4 was selected as optimum pH for further work. After this pH a slight decrease in

adsorption was observed. Therefore further studies were conducted at pH 4. Negligible adsorption was observed by Blank xerogel. So the entrapped Schiff base molecules are responsible for the higher adsorption of metal ions by Schiff based xerogel.
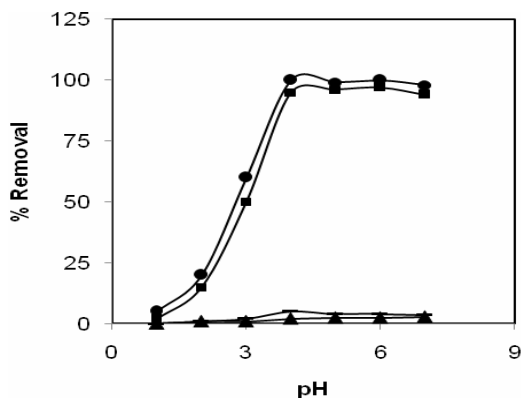

Fig 6: Effect of pH; ●: Adsorption of Cr(III) by Schiff based xerogel; ■: Adsorption of Pb(II) by Schiff based xerogel; — : Adsorption of Cr(III) by blank xerogel; ▲: Adsorption of Pb(II) by blank xerogel (contact time = 15 min, solution vol = 10 mL, adsorbent dose = 50 mg, metal conc = 70 mg/L).
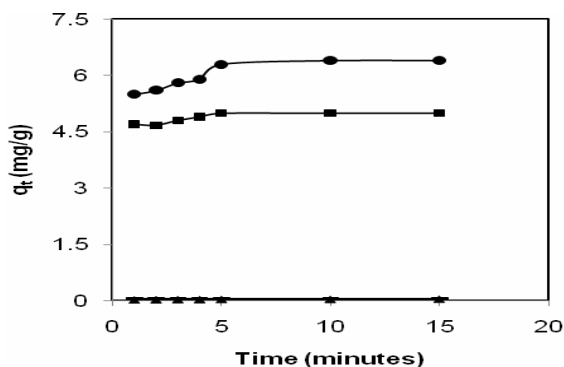

Fig. 7: Effect of contact time; ●: Adsorption of Cr(III) by Schiff based xerogel; ■: Adsorption of Pb(II) by Schiff based xerogel; — : Adsorption of Cr(III) by blank xerogel; ▲: Adsorption of Pb(II) by blank xerogel (pH = 4, solution vol = 10 mL, adsorbent amount = 50 mg, metal conc = 70 mg/L).

Contact Time

The adsorption of metal ions on the blank and Schiff based xerogel was studied by varying the contact time from 1 to 15 min. The adsorption increased with increasing contact time from 1 to 10 min under optimized conditions and then became constant. On safer sides contact time of 15 min was selected as optimum for more work. The observed low equilibration time shows powerful correlation of the Schiff based xerogel with metal ions.

Metal Concentration

The effect of metal concentration on the adsorption was studied by varying metal concentration from 30 – 80 mg/L as shown in Fig. 8. Higher adsorption is observed at higher concentration of metal ions. In case of Cr(III) adsorption increased sharply from 50 to 70 mg/L while Pb(II) ions showed increased adsorption from 40 to 60 mg/L, after these concentration ranges adsorption became constant. Again negligible adsorption was observed by blank xerogel. So the entrapped Schiff base molecules are responsible for the higher adsorption of metal ions by Schiff based xerogel.
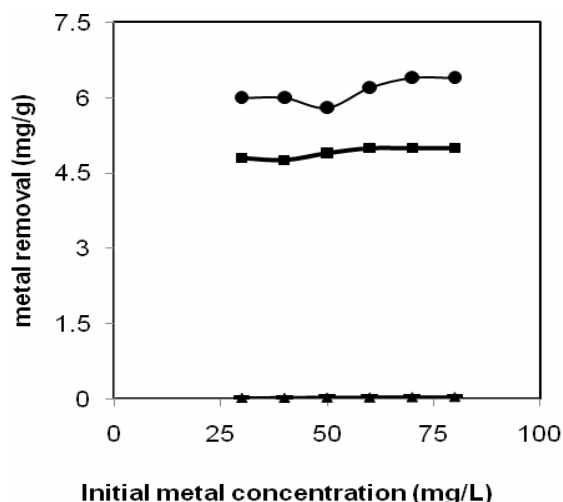

Fig 8: Effect of metal concentration; ●: Adsorption of Cr(III) by Schiff based xerogel; ■: Adsorption of Pb(II) by Schiff based xerogel; — : Adsorption of Cr(III) by blank xerogel; ▲: Adsorption of Pb(II) by blank xerogel (pH = 4, contact time = 15 min, solution vol = 10 mL, adsorbent amount = 50 mg).

Adsorption Kinetics

Kinetic studies are necessary to explain an adsorption process. Chemical kinetics explain the reaction rate, factors affecting the reaction rate and also give an idea about reaction mechanism. Efficiency of an adsorbent is evaluated from the

values of rate constants. The influence of shaking time on metal adsorption was examined from 1 to 15 min. Most of adsorption occurs within first five min. The adsorption achieves highest value in 15 min. The low equilibration time shows powerful correlation of the Schiff based xerogel with the metal ions. To study the adsorption kinetics the following kinetic models were practised:

Pseudo–1ˢᵗ Order Kinetic Model

The pseudo–1ˢᵗ order equation is:

$$\log(q_e - q_t) = \log q_e - \frac{k_f t}{2.303}$$

Following this equation *(log q_e–q_t)* is plotted against *t*. The plot is not linear with low correlation coefficient R^2 values for both Cr(III) and Pb(II) adsorption. The equilibrium adsorption capacity q_e values are calculated. These values are quite different from the experimental values for both Cr(III) and Pb(II) adsorption by Schiff based xerogel. The values of equilibrium adsorption capacity q_e and adsorption rate constant k_f are presented in Fig. 9 (a)

(a)

(b)
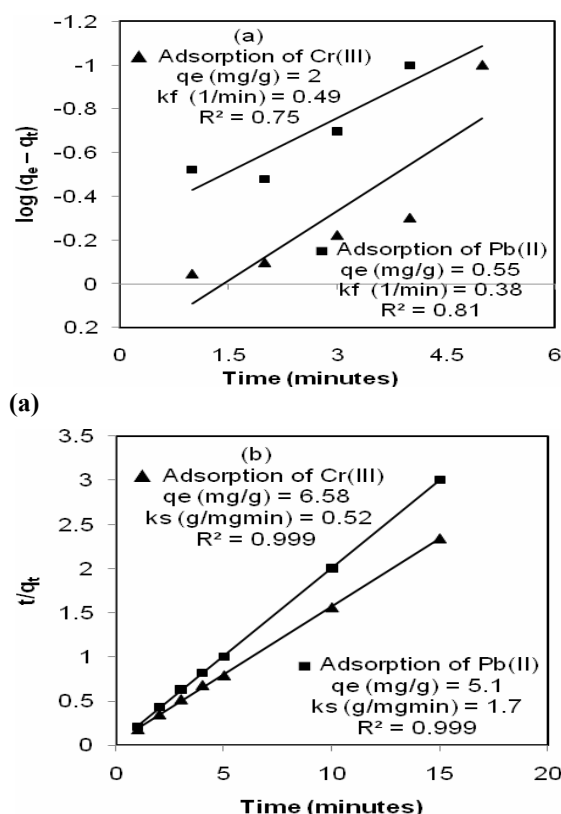
Fig 9: (a) Pseudo–1ˢᵗ order plot, (b) Pseudo–2ⁿᵈ order plot for the adsorption of metals by the Schiff based xerogel.

Pseudo–2ⁿᵈ Order Kinetic Model

The pseudo–2ⁿᵈ order equation is:

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t$$

Following this equation t/q_t is plotted against *t*. Straight line with slope $1/q_e$ and intercept $1/k_s q_e^2$ is obtained, correlation coefficient R^2 values are as high as 0.999 for both Cr(III) and Pb(II) adsorption. The equilibrium adsorption capacity q_e values are calculated. These values are very close to the experimental values for both Cr(III) and Pb(II) adsorption by Schiff based xerogel. The values of equilibrium adsorption capacity q_e and adsorption rate constant k_s are presented in Fig. 9 (b).

Adsorption Isotherms

The Langmuir and Freundlich isotherms are oftenly applied on adsorption systems. We found that the adsorption of metal ions on Schiff based xerogel follow Langmuir isotherm.

Langmuir Isotherms

The Langmuir equation is:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$$

Following this equation C_e/q_e is plotted against C_e. Straight line is obtained, correlation coefficient R^2 values are high for both Cr(III) and Pb(II) adsorption by Schiff based xerogel. The equilibrium adsorption capacity q_e values are calculated. These values are very close to the experimental values for both Cr(III) and Pb(II) adsorption by Schiff based xerogel showing applicability of this model to the adsorption process. The values of maximum adsorption capacity q_m (monolayer capacity) and energy of adsorption K_L are presented in Fig. 10 (a).

Freundlich Isotherms

Heterogeneous adsorption systems follow this isotherm. The Freundlich equation is:

$$ln\,q_e = \frac{1}{n}ln\,C_e + ln\,K_F$$

Following this equation $ln\,qe$ is plotted against $ln\,Ce$, correlation coefficient R^2 values are low for both Cr(III) and Pb(II) adsorption by Schiff based xerogel. The adsorption capacity K_F values are calculated. These values are different from the experimental values for both Cr(III) and Pb(II) adsorption by Schiff based xerogel showing that this model is not applicable on the adsorption process. The values of adsorption capacity K_F and favourability of adsorption process n are presented in Fig. 10 (b).
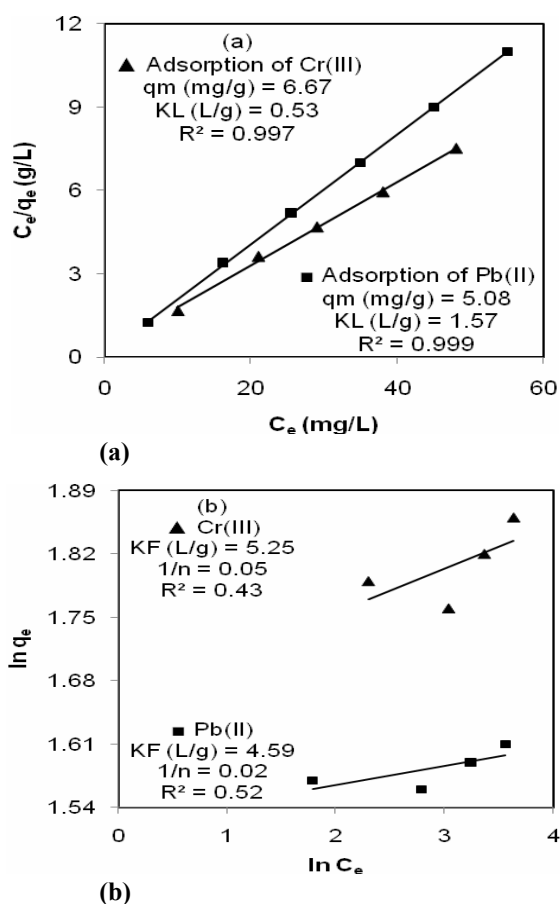

(a)

(b)

Fig 10: Adsorption isotherms (a) Langmuir isotherms, (b) Freundlich isotherms for the adsorption of metals by Schiff based xerogel.

Desorption of Metals from Schiff based Xerogel

Desorption of metal ions was successfully accomplished with 0.1 N HNO$_3$. The doped gel having noted quantity of adsorbed metal was washed with optimum pH solution. Then it was dried at 50^oC till constant weight. Then it was stirred with 10 mL of 0.1 N HNO$_3$ for fifteen min. The amount of eluted metal was measured by spectrophotometer. When the Schiff based xerogel was absolutely retrieved from metal ions, it was washed with abundant water. Then it was neutralized with sodium bicarbonate solution and again washed with water for another use. 99 – 100 % desorption of metal ions was attained. After elution the adsorbent was recycled 3 to 5 times without showing decrease in adsorption capacity.

Experimental

Reagents and Materials

The chemicals used in this work were of high purity obtained from sealed bottles. Ethyl alcohol (EtOH) and tetraethyl orthosilicate (TEOS) were obtained from E. Merck, Germany, ammonium fluoride (NH$_4$F) and 4(2-aminoethyl) benzene sulfonamide were obtained from Aldrich, USA). Deionized water (DW) of electrical Conductivity 0.2 $\mu S/cm$ and neutral pH was used.

Apparatus and Instruments

For metal estimations flame atomic absorption spectrophotometer (FAAS, model, A–1800, Hitachi, Japan) was used. Shaker (model HAAKE SWB–20) was used in all adsorption studies. The shaking speed was kept constant at 150 cycles/min. Thermogravimetric analyses (TGA) were performed on a Netzsch STA 409 under nitrogen environment. Porosimetry data of previously degassed solids at 100^oC was obtained on Micromeritics ASAP 2010 Porosimeter. SEM studies were accomplished on Oxford EDS 7573 attached with Scanning Electron Microscope and Fourier transform infrared spectroscopy analyses (FTIR) were done using a Shimadzu FTIR spectrophotometer with pellets of potassium bromide (KBr).

Preparation of Schiff Base doped sol–gel Silica

The Schiff base ligand was prepared as reported in the literature [23]. 20 mL TEOS was stirred with 20 mL deionized water. In the above mixture 50 mL EtOH solution of 0.005 M ligand was introduced along with solution of 0.005 M NH$_4$F as nucleophilic catalyst. It was found necessary to use ethanol to avoid non–homogeneous gelation and to increase the gel aging time. For seven days the reaction mixture was retained at room temperature to evaporate solvents and complete the gelation. The obtained gel was kept in oven at 48^oC up to constant weight. The obtained hard gel pieces were pressed

and sieved. The obtained gel powder was immersed in water for two days to leak the unbound ligand. The complete removal of undoped ligand was checked spectrophotometrically. The obtained gel was kept at 48^oC up till constant weight. Blank gel was also prepared using the mentioned method without introducing organic ligand in the reaction mixture.

Adsorption of Metal Ions

Adsorption of chromium and lead ions was studied at room temperature using batch method. To explain the adsorption process, factors affecting adsorption were optimized. The adsorption was studied at different pH values from 1–7 as shown in Fig. 6. HNO_3 was used to prepare solutions of pH 1–6. The adsorption percentage was calculated using the following relation:

$$\% \; adsorption = \frac{C - C_e}{C_e} \times 100$$

where *C (mg/L)* is initial concentration of metal ions and C_e *(mg/L)* is equilibrium concentration of metal ions.

The kinetic information of adsorption was obtained by letting Schiff based xerogel (50 *mg*) in contact with 10 *mL* of metal solutions of pH 4 for 1–15 min in labelled flasks. After specified time intervals the flasks were removed and centrifuged one by one. The concentration of metal ions was analysed on FAAS and adsorption percentage was calculated. The obtained data is used to study adsorption kinetics.

To study the effect of metal concentration, Schiff based xeorgel was weighed (50 *mg*) and put into each of 25 *mL* flasks. Cr(III) and Pb(II) solutions of 30–80 *mg/L* having pH 4 were prepared and 10 *mL* of each solution was taken in the test bottles having pre-weighed adsorbent. The suspensions were shaken for 15 min, centrifuged and analyzed for final metal concentrations on FAAS. q_e, the equilibrium adsorption capacity (*mg/g*) is calculated using the following equation:

$$q_e = C - C_e \times \frac{V}{m}$$

Where *m* is the mass of adsorbent in *g* and *V* is the solution volume in *L*. The obtained data is used to study adsorption isotherms. The above experiments were repeated using blank xerogel as well.

Conclusions

It is concluded from the adsorption data that the prepared Schiff based xerogel is a promising material for the adsorption of Chromium and lead ions. Its synthesis is very simple and economic. The doping of Schiff base with xerogel is confirmed by both characterization techniques, for example; TGA, porosimetry, FTIR, SEM and adsorption studies. Our synthesized material has been proved as a good adsorbent because of the following features:

1. Easy preparation
2. Ordered mesoporous structure
3. High stability towards temperature and medium used.
4. Rapid attainment of equilibrium
5. Quick elution of adsorbed metal ions, regeneration and recycling.

Thus it has been established experimentally in this study that Schiff bases could be entrapped into sol – gel silica for analytical, industrial, biological and catalytic applications. Schiff bases may retain their biological and catalytic properties as encapsulated in the solid cages of xerogel.

Acknowledgements

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