Synthesis, Characterization and removal of heavy metal ions from water bodies using novel hybrid materials based on silica

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Abstract: *A new chelating material was synthesized by modifying the activated silica gel with 4-hydroxy benzyldehyde. The synthesized material was characterized by FTIR and BET surface area measurement techniques. The extraction of metal ions such as Fe^{+2}, Zn^{+2}, Mn^{+3} and Cr^{+3} by chelating materials was found to be higher than that of silica gel alone. The order of metal sorption was found to be $Fe^{+2} > Zn^{+2} > Mn^{+3} > Cr^{+3}$. Experimental evidences for existence of surface silanol and its chemical nature here explored the idea of silica surface modification. Adsorption of trace elements in separation and preconcentration from comples synthetic mixture as well as natural water is presented.*
Keywords: *Silica, 4-hydroxy benzaldehyde, Metal ions, Extractor concentration.*

I. Introduction

Over the past few decades there has been a change in focus from scientific expansion and innovation to the widespread chronic effects of metals. This is due to concern towards worldwide environmental safety. Global growth and industrial development are the mojor factors that cause immense atmospheric depositions of metals. Actually, industrial operations like electroplating, mining and metal processing arc the key contributors to unnatural metal contamination in the surroundings. Voluminous discharge of these metals has dramatically altered the biogeochemical cycles and there is no compartment of the atmosphere that has not been deteriorated by their toxic effects. This uncontrolled release of metals creates toxic or inhibitory effects and other degenerative diseases in living system. For instance, Cd and Zn can lead to severe gastrointestinal and respiratory damage and acute heart, brain and kidney damage. Being persistent in natural ecosystems for an extended period, these metals accumulate in unexcessive levels of the biological chain. The problem is even worse in developing countries owing to accelerated urban growth and lack of efficient control. Unfortunately, water bodies have been subjected to maximum ion and they are severely degraded or polluted. This is due to the fact that the treatment of wastewater generated by is not given the necessary priority it deserves and this wastewater is discharged into water resources without treatment. This water is then used in agricultural and day-to-day practices, posing several threats to mankind. Various rivers, lakes and estuaries have been found to be severely polluted with poisonous elements such as Cr, Cu, Cd and Ni to different degrees. Therefore, extraction and removal of toxic metal ions from various mat rices at trace levels are of paramount importance.

As a solution to this, chelating agents immobilized on a solid support, known as chelating resins, are attracting great interest in environmental applications to remedy the polluted water resources. Solid supports can be mainly categorized as organic ones, which include synthetic as well as other polymeric compounds of natural origin, while inorganic solid supports comprise silica gel, alumina, magnesia, zirconia and other oxide species. Immobilization of organic complexing agents on the surface of an inorganic or organic solid support is usually aimed at modifying the surface with certain target functional groups that can be exploited for specific metal extraction.

Analysis of metal ions at trace levels poses a unique problem to analysts, because it involves the rigorous requirements of versatility, specificity, sensitivity and accuracy in the analysis. A wide variety of analytical techniques has been developed to determine concentrations of trace metals in various samples. However, the results may be erroneous because the metal ions may be present in these samples together with other elements at low levels. Thus, to quantify the desired analytes, the best way is to separate and preconcentrate the metal ions from the matrix constituents and determine them in an isolated state. Various techniques have been employed for this purpose. The most widely used method for the separation and preconcentration of metal ions with suitable complexing agent is solid phase extraction (SPE).

SPE is considered to be a powerful tool for the separation and enrichment of various inorganic as well as organic analytes [1-5]. The basic principle of SPE is the transfer of the analyte from the aqueous phase to the active sites of the solid phase. It has several advantages [6,7] including:
- Stability and reusability of the solid phase.

- High preconcentration factors.
- Ease of separation and enrichment under dynamic conditions.
- No need for toxic and costly organic solvents.
- Minimum costs due to low consumption of reagents.

SPE is mainly based on the utilization of inorganic and organic solid sorbents such as XAD resins [8-10], ion exchange resins [11], silica gel [12,13], cellulosic derivatives[14], polyurethane foam[15], active carbon[16], nanometer silica [17] and rice husks [18]. Extraction and removal of metal ions by these sorbents is well known and mainly based on the possible surface reactivity and adsorptive characteristics incorporated into these solid phases [19]. However, the basic disadvantage these solid sorbents is the lack of metal selectivity, which leads to high interference of other existing species with the target metal ion(s) [20]. To overcome this problem, a chemical or physical modification of the sorbent surface with a metal-selective complexing agent is required.

1.1 Benefits of Chelating Sorbents
Extraction of metal ions using chelating sorbents has the following advantages over more conventional methods [21].
- Selective determination of metal ions is possible using a chelating sorbent having a ligand possessing high selectivity to the targeted metal ion.
- It is free from difficult phase separations, which are caused by the mutual solubility between water and organic solvent layers.
- The chelating sorbent method is economical since it uses only a small amount of ligand and can be reused a number of times.
- Trace metal ions at concentrations as low as parts per billion (ppb) can be determined.
- The adsorption of metal ions can be visibly estimated from the color in tensity of the solid phase if the metal complex formed possesses adsorption in the visible wavelength region.
- Use of carcinogenic organic solvents is avoided and thus the technique is eco-friendly.

The chelators based on functionalized silica gel are preferred over conventional ion-exchange-based resins because of their high selectivity and capability of binding metals through multiple coordinating groups attached to the support [22]. The multiple coordination of metal ions on the chelating resin makes it particularly suitable for the collection, of metal ions.

1.2 Silica Gel: An Ideal Support Material
Silica gel is a granular, porous form of silica and is made synthetically from sodium silicate or silicon tetrachioride or substituted chlorosilanc/orthosilicate solution. Stober et al. [23] have reported the synthesis of spherical silica particles from tetraethoxysilane using NH_3 as catalyst.

Silica gel is commonly used as a rigid matrix for ligand immobilization. The chemical modification of silica gel surfaces with donor atoms such as N, S, O and P is primarily aimed at improving the adsorption and exchange pre of the silica gel along with properties incorporation of the particular selective characteristics into the modified silica gel phases towards certain metal ions. The immobilization of chelating materials containing donor atoms on the silica gel surface can occur via chemical bond formation between organic modifiers like the amino- or chioro-modified silica gel phases or through simple physical adsorption processes [24]. Such a process often incorporates selectivity in the synthesized materials. Several new chemically modified silica gels have been synthesized and applied as normal or selective solid phase extractors for metal ions. The advantages of silica gel over other support materials are [25,26]:
- The polymeric support in the form of silica gel offers high chemical stability and a compact structure, so that during the synthesis of function alized silica the functional structure of the chelating agents is not changed.
- Unlike organic polymers, which are flexible and can swell up to varying degrees depending on the solvent, temperature and pressure, silica gel has a rigid structure and hence during the synthesis of functionalized silica the functional structure of the chelating agent is not changed.
- Silica is less susceptible than organic polymers to chemical or thermal degradation, so functionalized silica gels can be used over a wide range of temperatures and under strongly acidic or alkaline conditions.

1.3 Functionalization of Silica Gel
A brief description of the various functional groups present on the silica surface followed by the methods employed in the synthesis of function alized silica gels now follows.

1.4 Surface Chemistry of Silica Gel

The silica surface consists of two types of functional groups: siloxane (Si—O—Si) and silanol (Si—OH). Thus, silica gel modification can occur *via* the reaction of a particular molecule with either the siloxane (nucleophilic substitution at the Si) or silanol (direct reaction with the hydroxyl group) group, although it is gene rally accepted that the reaction with the silanol group constitutes the main modification pathway. The silanols can be divided into isolated groups (or free silanols), where the surface silicon atom has three bonds into the bulk structure and the fourth bond attached to a single OH group, and vicinal silanols (or bridged silanols), where two isolated silanol groups are bridged by a hydrogen bond. A third type of silanol, called geminal silanols, consists of two hydroxyl groups attached to one silicon atom.

1.5 Chemical Modification of the Silica Surface

Silica gel can be used as a very successful adsorbing agent, as it does not swell or strain, has good mechanical strength and can undergo heat treatment. In addition, chelating agents can be easily loaded on silica gel with high stability, or be bound chemically to the support, affording a higher stability. The surface of silica gel is characterized by the presence of silanol groups, which are known to be weak ion-exchangers, causing low interaction, binding and extraction of various metal ions such as Cu. Ni. Co, Zn and Fe [27,28]. In addition, silica gel as a sorbent has a very low selectivity to extract a particular metal ion over background matrices. Consequently, modification of the silica gel surface has been performed to obtain solid sorbents with greater selectivity. In most of the methods for the preparation of immobilized silica gel, a two-step procedure has been used for loading the surface with specific organic compounds: physical adsorption and chemical functionalization. In the first case, the organic compound is directly adsorbed on the silanol group of the silica gel surface (impregnated or loaded sorbent), either by passing the reagent solution through a column packed with the adsorbent or by shaking the adsorbent in the reagent solutiort. In the second approach, a covalent bond is formed between the silica gel surface groups and those of the organic compound (functionalized sorbent). Chemisorption of chelating molecules on the silica surface provides immobility, mechanical stability and water insolubility, thereby increasing the efficiency, sensitivity and selectivity of the analytical applications [29]. Chemical modific ation of the silica surface by organic chelating groups acts as an ion exchanger, which provides greater selectivity for the analyte than that offered by a traditional ion exchanger. The most convenient way to develop a chemically modified surface is by simple immobilization (or fixing) of the group on the surface by adsorption, electrostatic interaction, hydrogen bond formation or other types of interaction [30,31]. Simple impregnation of the modifier solution [32] or covalent binding, socalled covalent grafting of the chelating molecule to the silica matrix *via* silanization, is the common practice for synthesizing a metal. specific functionalized silica gel.

Silica gel is an amorphous inorganic polymer containing an internal siloxane group (Si-O-Si) with silanol groups (Si-OH) distributed on the surface). It is commonly used as a rigid matrix for ligand immobilization. The chemical modification of silica gel surfaces with donor atoms such as N, S, 0 and P is primarily aimed at improving the adsorption and exchange properties of the silica gel along with incorporation of the particular selective characteristics into the modified silica gel phases towards certain metal ions. The immobilization of chelating materials containing donor atoms on the silica gel surface can occur via chemical bond formation between organic modifiers like amino or chloro modified silica gel phases or through simple physical adsorption processes. Such a process often incorporates selectivity in synthesized materials. Several new chemically modified silica gels were synthesized and applied as normal or selective solid phase extractor for many toxic and other metal ions. They were found to be superior to the conventional ion exchange resins in their ability to extract and selectively pre-concentrate the heavy metal ions from solutions containing high concentrations of alkali and alkaline earth metal ions. Advantages of the modified solid phase extractors compared with the classical liquid extractor's were reported.

Schiff bases, having multi dentate coordination sites, are known to form complexes with transition metal ions readily. The Schiff bases derived from Salicylaldehyde (Salens) as polydentate ligands are known to form stable complexes with transition metal ions.

1.6 Objective of study:
- The chemical modification of silica gel surfaces with donor atoms such as N, S, O and p is primarily aimed at improving the adsorption and exchange properties of the Silica gel.
- Due to the presence of many reactive sites on silica gel large number of organic molecule could be immobilized on its surface to improve its sorption behavior by chemical bonding due to simple condensation.
- Analytical applications of the hybrid mesoporous organic – inorganic materials has been increased due to characteristics or large specific surface areas, pore sizes, thermal and chemical resistance, high adsorption capacity and easiness of functionalization.

- Recent works have shown increasing utility or hybrid mesoporous materials to produce sorbent for trace metal enrichment.
- In proposed work, we shall prepare new adsorbent materials by modification of silica using both commercial as well as newly synthesized silence based.
- To compare the metal binding, extraction and selective abilities using batch techniques.

II. Experimental

2.1 Apparatus

The specific surface areas of the dry silica and loaded silica were determined by BET method on NOVA 1000, High Speed Gas Sorption Analyzer. Quantachrome Corporation, USA. A Shimadzu atomic absorption spectrophotometer (Model AA- 680) equipped with a single element hollow cathode lamp and an air acetylene burner was used for the estimation of metal ions. The instrument parameters were those recommenced by the manufacturer. The wave lengths (nm) selected for the analytes were as follows: Mn (279.5 nm), Cr (357.9 nm), and Zn (213.9 nm). The FTIR spectra were recorded in a Perkin Elmer 1800 Model. The pH values of sample solutions were determined by a Systronic digital pH meter Model 335 equipped with a combined glass calomel electrode for pH adjustment.

2.2 Preparation of hybrid mesoporous materials for removal of heavy metal ions

Analytical applications of the hybrid mesoporous materials have been increased due to the main characteristics such as: availability of large surface area, thermal and chemical resistance, high adsorption capacity, easiness of functionalization. Recent works have shown increasing utility of hybrid mesoporous materials for the pre-concentration of trace elements [33].

2.3 Chemical modification of silica gel:
Dried silica gel (120 mesh size) was activated using hydrochloric acid (1 N). The activated silica gel was taken in methanol and first chemically modified with a silane compound. Then it is again modified with 4-hydroxy benzaldehyde/N-vinyl pyrrolidone to produce two new materials. The reaction scheme with benzaldehyde is given below:
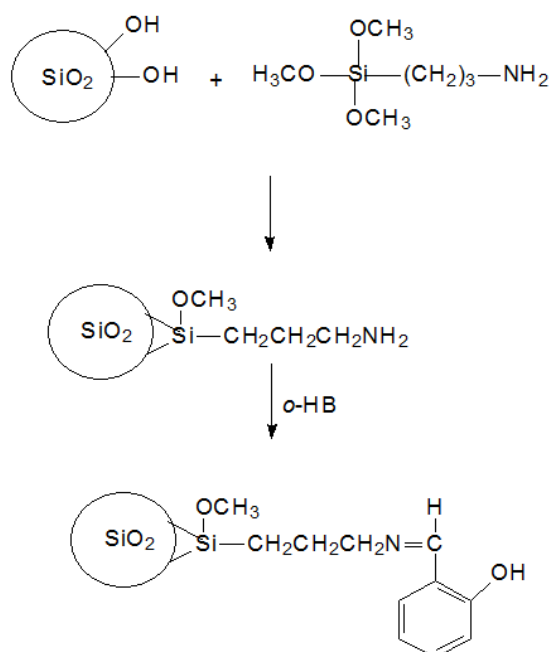
2.4 Study of Adsorption Models:
1. Adsorption is a process in which soluble chemical (adsorbate) is removed from a fluid by contact with solid surface (the adsorbate).
2. Adsorption can be classified as either physical or chemical.
3. Langmuir Model: $C_e/q_e = 1 / K_L + (a_L/K_L).C_e$; ($K_L$ and a_L are the Langmuir isotherm constants; C_e and q_e are the liquid phase concentration and solid phase concentration of adsorbate at equilibrium.
4. Freundlich Model: $\ln q_e = \ln K_f + b_f \ln C_e$; ($K_F$ and b_f are the Freundlich constants.
5. Dubinin-Radushkevich (D-R) isotherm: $\ln q_e = \ln q_m - k\varepsilon^2$; ($\varepsilon$ (Polanyi potential)

2.5 Analytical Studies

The metal ion uptake studies were carried out by both batch and column techniques. The adsorption capacity (Q, mmol g^{-1}), the distribution ratio (D, cm^3 g^{-1}), and the selectivity factor (α) was calculated according to the following equations:

$Q = (Co – Ce) V/m$

$D = Q/Ce$

$\alpha = D1/D2$

Here, Co, and Ce are the initial concentration and final concentration of metal ions (mmol dm^{-3}) at equilibrium, respectively. V is the volume of the solution in dm3, and m is the mass of the chelating materials, $D1$ and $D2$ refer to the distribution ratios of metal ion 1 and metal ion 2, respectively.

III. Results and Discussion

3.1 Characterization by FTIR

Analysis of the FTIR spectra (Fig. 1) of the activated silica gel and the organofunctionalized silica gel shows the presence of Si-O-Si at around 1050 cm–1 and a band at 3200 – 3400 cm–1 corresponding to the silanol group and adsorbed water molecules. Peaks around 1440, 1410, and 1356 cm–1 are assigned to deformation modes of the –CH2-group generated from an organofunctionalized compound. The peak that appeared at about 1560 cm–1 was assigned to deformation mode $\delta(NH)$ of –CNH-moiety from organofunctionalized silica gel material. The peak that appeared at 1660 cm–1 was assigned to the $\delta(OH)$ of the matrix. The presence of N–H stretch (H bonded) at 3372 and 3290 cm–1 and the C–N stretch at around 1071 cm–1 characterizes the presence of amine groups in the chelating material. These spectral changes confirmed that the organic group is bound to the silica surface. The effect of contact time upon the sorption of the metal ions from aqueous solution was investigated in batch experiments. The amount of the metal ions sorbed per unit mass of the chelating materials was increased with the increase in contact time period (Fig. 2). The saturation (plateau value) in each curve was obtained within a period of 30 min for Zn^{2+} and Mn^{2+}. However, the sorption of Cr^{3+} required nearly 3 h. For both the chelating materials, the order of sorption of the metal ions was found to be $Zn^{2+} > Mn^{2+} > Cr^{3+}$. This, in turn, decreases the electron density upon the phenolic oxygen atom and consequently the metal coordination capability. However, the metal chelating nature of the chelating materials also depends on the nature of the ligand groups present and their accessibility towards the metal ions. The steric hindrance of the matrix as well as hydrophobic nature of the ligands may also limit the metal complexation process.

Changes in pH of the medium are one of the most important parameters affecting the preconcentration procedure, which is related to the formation of soluble metal complexes and subsequently their stabilities in aqueous solution [19]. A series of metal ions, Cr^{3+}, Mn^{2+}, and Zn^{2+}, were examined in various buffer solutions of pH 1.0 to 8.0 (Fig. 3). In acidic pH (within pH 1–4), the chelating materials showed low metal ion uptake properties due to the protonation of chelating sites in the ligands that inhibit their binding to metal ions.20 With increase in pH of the medium, the metal sorption of the chelating materials increased due to the increase in coordination ability for the formation of phenoxide ion upon phenolic OH-group and due to the increase in basicity of the imine nitrogen atom. The order of metal ion sorption by both the chelating materials was found to be $Zn^{2+} > Mn^{2+} > Cr^{3+}$, indicating that the highest affinity is towards Zn^{2+} extraction, and the lowest is exhibited for Cr^{3+}. We did not attempt to go beyond pH 8.0 due to the observation of precipitation in the medium.

3.2 Sorption kinetics

The effect of metal ion concentration on the uptake behavior of the chelating materials was studied in the concentration range 10 to 100 μg cm–3. A leveling effect was noticed at higher concentrations because of saturation of available coordination sites.21 The sorption isotherms were evaluated for Langmuir equation and Freundlich adsorption equations.22,23 The equation is Ce/Qe = 1/Qo·b + Ce/Qo, where Ce is the equilibrium concentration (μg cm–3), Qe is the amount adsorbed at equilibrium, and Qo and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The linear plot of Ce/Qe versus Ce shows that the adsorption obeys the Langmuir adsorption model (Fig. 4). The correlation coefficient for the linear regression fitting the Langmuir plot was found to be 0.9657. Qo and b determined from the Langmuir plot were found to be 270.27 μg g–1 of the chelating material and 0.01 μg–1. The equilibrium parameter RL is defined by RL = 1/(1 + bCo), where b is a Langmuir constant, and Co is the initial concentration of Zn2+. At two different initial concentration of Zn^{2+}, i.e., 10 and 100 mg dm–3, the RL values were found to be 0.5 and 0.09, respectively. The values obtained at two different concentrations lie between 0 and 1, which indicated a favorable adsorption of Zn^{2+} onto the chelating material surface (Si-DDE-o-HB). Plotting the Freundlich equation: log(x/m) = log kad + 1/nlog Ce, where, Ce is the equilibrium concentration of the metal ions in μg cm–3, m is the weight of the chelating materials, x is the quantity of metal ion sorbed by the chelating material in μg and n is the constant. A plot of log(x/m) versus log Ce (Fig. 5) is linear and the constants kad and n are

found to be 3.446 and 1.227, respectively. The value, $1 < n < 10$, indicates the favorable sorption of Zn^{2+} onto the chelating material. The correlation coefficient for the isotherm found to be 0.9831, indicating a better fit for the experimental data than the Langmuir plot.

Selective extraction or separation of a given metal ion in the presence of other metal ions is controlled mainly by the following factors: (i) the nature of the donating sites in the ligand that are capable of selective bonding to the central metal ion; (ii) the nature of the metal ion to be selectively extracted; and (iii) the hydrogen ion concentration. The chelating material (Si-DDE-o-HB) was utilized to study the competitive sorption of Zn^{2+}/Mn^{2+}, Zn^{2+}/Cr^{3+} from dilute aqueous solution at different pH values of the medium. The higher affinity towards Zn^{2+} ions in a competitive environment could be due to the preferentially binding with the positionally active (non-sterically hindered) oxygen atom present in the salicylaldehyde Schiff base ligand.

IV. Conclusion

Functionalization of the surface of these mesoporous materials with organic or inorganic functional groups leads to new physical and chemical properties. These modified materials can be used in a variety of applications such as catalysis, adsorption, and separation as chromatographic column packing.

Introduction of organic groups in the mesoporous materials permits the tuning of surface properties, alteration of the surface reactivity, protection of the surface from chemical attack, hydrophobization of the surface by silylation to preclude water attack, and modification of the bulk properties of the materials while at the same time stabilizing the materials towards hydrolysis. Separation of transition metals, heavy metal ions or radioactive materials from aqueous streams is currently one of the most significant and fascinating problems to be challenged, severely hampered by the presence of a large excess of competing ionic species. Therefore, materials to be used for the adsorption and separation of these toxic substances are required to be specific enough to differentiate between transition metals, heavy metal ions and radioactive compounds on the one hand and on the other benign metal cations. A key issue for the applicability of these mesoporous materials is associated with the thermal, and more importantly the hydrothermal and mechanical stabilities.

Acknowledgement

References

[1]. D. Bilba, D. Bejan and L. Tofan, Croat. Chem. Acta., 71 (1998) 155.
[2]. M. E. Mahmoud, M. M. Osman and M. E. Airier, Anal. Chim. Ada., 415(2000) 33.
[3]. M. E. Mahmoud, Anal. Chim. Ada., 398 (1999) 297.
[4]. K. S. Abou-El-Sherbini, I. M. M. Kenawy, M. A. Ahmed, R. M. Issa and R. Elmorsi, Talanta, 2002, 58, 289.
[5]. A. R. Ghiasvand, R. Ghaderi and A. Kakanejadifard, Talanta., 62(2004) 287.
[6]. R. K. Sharma and P. Pant, J. Hazard. Mater., 163 (2009) 163, 295.
[7]. R. K. Sharma and P. Pant, ml. J. Environ. Anal. Chern., 87 (2009) 503.
[8]. U. Pyell and G. Stork, Fresenius J. Anal. Chem., 342 (1992) 376.
[9]. Y. Guo, B. Din, Y. Liu, X. Chang, S. Meng and J. Liu, Talanta, 62 (2004) 209.
[10]. Y. S. Kim, G. In, C. W. Han and 3. M. Choi, Microchem. J., 80 (2005) 151.
[11]. V. A. Lemos, D. G. da Silva, A. L. de Carvaiho, D. A. Santana, G. S. Novaes and A. S. Passos, Micro chem. J., 84 (2006) 14.
[12]. 0. Abollino, M. Aceto, C. Sarzanini and E. Mentasti, Anal. Chi,n. Ada, 411 (2000) 223.
[13]. P. K. Jal, S. Patel and B. K. Mishra, Talanta, 62 (2004) 1005.
[14]. A. R. Khorrami, T. Hashempur, A. Mahmoudi and A. R. Karimi, Micro chein. J., 84 (2006)75.
[15]. V. Gurnani, A. K. Singh and B. Venkataramani, Talanta., 61 (2003) 889.
[16]. P. PohI and B. Prusisz, Anal. Chim. Acta., 502 (2004) 83.
[17]. I. Narin, M. Soylak, L. Elci and M. Dogan, Talanla, 52 (2000) 1041.
[18]. Y. Cui, X. Chang, Y. Zhai, X. Zhu, H. Zheng and N. Lian, Microchein. J., 83 (2006) 35.
[19]. C. R. T. Tarley. S. L. C. Ferreira and M. A. Z. Arruda, Microchern. J., 77 (2004) 163.
[20]. P. Liu, Q. Pu, Z. Hu and Z. Su, Analyst., 125 (2000) 1205.
[21]. R. K. Sharma, B. S. Garg, N. Bhojak and S. Mittal, Microchem. J., 61 (1999) 94.
[22]. G. Schmuckler, Talanta., 12 (1965) 281.
[23]. M. Feldman and P. Desrochers, md. Innovation, 10 (2003) 5.
[24]. R. K. Sharma, S. Mittal and M. Koel, Crit. Rev. Anal. Chem., 33 (2003) 183.
[25]. R. K. Sharma and S. Dhingra, Designing and Synthesis of Functionalized Silica Gels and their Applications as Metal Scavengers, Sensors, and Catalysts: A Green Chemistry Approach, LAP Lambert, Saarbrücken, Germany, 2011.
[26]. R. K. Sharma, S. Mittal, S. Azmi and A. Adholeya, Surf Eng., 21 (2005) 232.
[27]. R. J. Kvitek, J. F. Evans and P. W. Carr, Anal. Chim. Acta, 144 (1982) 144.
[28]. A. R. Saricar, P. K. Datta and M. Sarkar, Talanta., 43 (1996) 1857.
[29]. P.K. Jal, R.K. Dutta, M. Sudershan, A. Saha, S.N. Bhattacharya, S. N. Chintalapudi and B. K. Mishra, Talanta., 55 (2001) 233.
[30]. S. B. Savvin and A. V. Milchailova, Zh. Anal. Khim., 51 (1996) 49.
[31]. V.V. Sukhan, 0.A. Zaporozhets, N.A. Lipkovskaya, L.B. Pogasi and A. A. Chuiko, Zh. Anal. Khim., 49 (1994) 700.
[32]. V. M. Ostrovskaya, Zh. Anal. Khim., 32 (1977) 1820.
[33]. Manuela L. Kim, Jorge D. Stripeikis, Mabel B. Tudino, Talanta., 77 (2009) 1068–1074
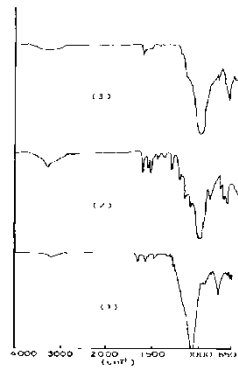
Fig.1: FTIR spectra of Silica, Si-amine, Si-o-HB
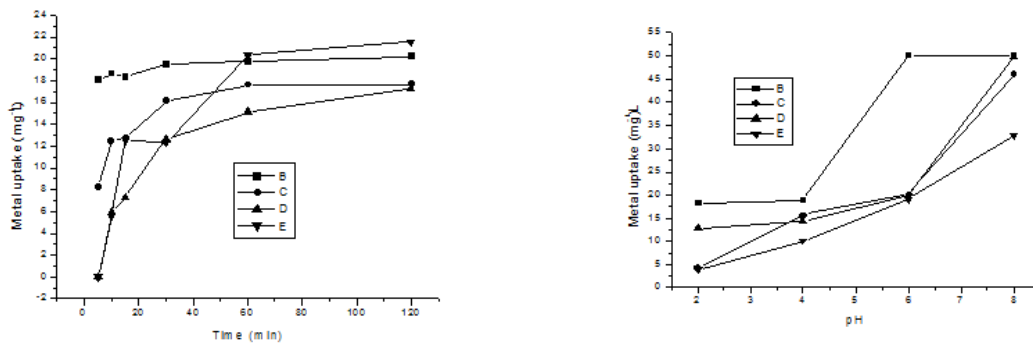
Fig.2: Variation of contact time and pH indicated maximum removal of Fe(III) is possible with respect to Mn, Cr and Zn from dilute aqueous solution
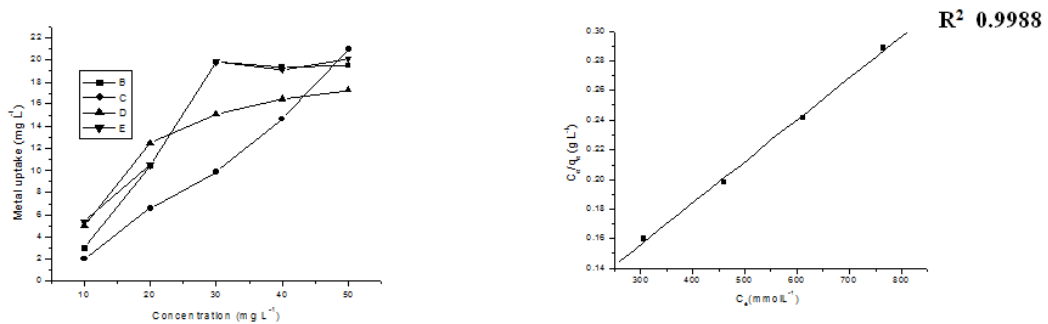
Fig.3: Variation of concentration of metal ions (Fe, Mn, Cr, Zn) and verification of Langmuir (for Zn only) using silica-4-hydroxybenzaldehyde
B:Fe, C:Mn D:Cr, E:Zn