Original Article
Bulletin of Pure and Applied Sciences.
Chemistry , Vol.42 C, No.1
January-June 2023: P.27-32

http://www.bpasjournals.com/chemistry
DOI: 10.48165/bpas.2023.42C.1.5
Print version ISSN 0970 4620
Online version ISSN 2320 320X

Adsorption of Cadmium & Zinc on Chemically modified Silica Gel functionalized with linear Poly (amido amine)

[1]Varun K Singh*, [2]Souvik Sur, [3]Ritika Kansal, [4]Ankit Kumar, [5]Praduman Rathi, and [6]Suman Shekhar

Author Affiliations
[1,3,4,5]Dept of Chemistry, Teerthanker Mahaveer University, Moradabad, Uttar Pradesh-244001, India
[2]Research and Development Center, Teerthanker Mahaveer University, Moradabad, Uttar Pradesh-244001, India
[6]Daudnagar College, Daudnagar (Aurangabad), Magadh University, Bodhgaya, Bihar-824113, India

***Corresponding Author**
Varun K Singh, Dept of Chemistry, Teerthanker Mahaveer University, Moradabad, Uttar Pradesh-244001, India
E-mail: vks2679@gmail.com

Received on 20.02.2023, Revised on 30.03.2023, Approved on 18.04.2023, Accepted on 27.04.2023, Published on 20.06.2023

ABSTRACT
The present investigation reports the adsorption of zinc & cadmium on silica surface chemically modified with linear poly (amido amine) a water-soluble polymer. The material is characterized by FTIR spectroscopy & Elemental Analyzer. The efficiency of metal binding of the adsorbent for Cd^{2+} and Zn^{2+} have been studied in aqueous solutions of corresponding metal ions. The results showed a valuable aspect of increasing trend.

Keywords: Toxicity, Metal ion, Adsorption, PAAs

How to cite this article: Singh V.K., Sur S., Kansal R., Kumar A., Rathi P., and Shekhar S. (2023). Adsorption of Cadmium & Zinc on Chemically modified Silica Gel functionalized with linear Poly (amido amine). *Bulletin of Pure and Applied Sciences-Chemistry,* 42C (1), 27-32.

INTRODUCTION

The toxicity of cadmium and zinc metals in ground/surface water bodies causes severe health hazards and directly affects the healthy living of organism and damaging the economy as well as natural environment (Sprynskyy et al. 2006; Lagadic et al. 2001). The bioaccumulation of these metal ions in living beings creates dangerous circumstances like bone and kidney's malfunctioning (Bortoleto et al. 2004; Ganjali et al. 2003). Some of them are carcinogenic, mutagenic, and teratogenic (Luo et al. 2023; Alloway et al. 1990). According to Pierson's theory, cadmium and zinc cations are soft in nature and possess strong affinity to combine with soft donor sites like Nitrogen and Sulfur. These soft N and S donors present on ligating sites can be incorporated on a variety of solid matrices and applied for separation & pre concentration of trace metallic cations (Jal et al. 2004; Dey[ab] et al. 2009, 2010). The utilization of solid phase extraction methods for the removal of cadmium and its determination has been reported earlier by Camel et al. (2003).

Various polymeric substances are also applied for metallic coordination, depending upon the

presence of different types of functional groups in the structural framework of macromolecules. Although due to some limitation this technique has constrained fruitful applications, however crosslinking of organic macromolecules led to emerge a new methodology in which organic functionalities grafted on inorganic backbone can be utilized to separate the metal ions (Hayashi et al. 1999; Tsubokawal N. 2007; Zhang et al. 2009).

Poly(amido amines) (PAAs), one of the synthetic water soluble organic macromolecules consists of amido and tertiary amino groups in its hydrocarbon chain arranged in a linear fashion which can be utilized for grafting onto silica surface (Dey[c] et al. 2009; Qu et al. 2008). Qu et al. (2008) had also studied Poly (amido amine) functionalized silica gel for the removal of Pd(II). Subsequently Dey[c] et al. (2009) had also discussed characterization and metal binding behavior of Ni^{2+} & Cu^{2+} on PAAs grafted on silica surface.

In light of this, the aim of our study was to investigate the adsorption efficiency of Poly (amido amine) grafted silica surface which was prepared by homogenous process.

EXPERIMENTAL

Materials and Methods

Methylene-bis-acrylamide (Acros), Piperazine (Aldrich) and 3-chloropropyltrimethoxysilane were purchased from Aldrich. The doubly distilled water (DDW) was obtained from an ultra-pure Milli-Q 18.2 MV system. Solutions of Cd^{2+} / Zn^{2+} were prepared from reagent grade nitrate salt in DDW. Silica gel of particle size (0.063–0.200 mm, 60Å pore diameter, 2.82 g mL^{-1} pore volume and 422 m^2 g^{-1} surface area) was procured from Fluka chemicals.

PerkinElmer, model 2400, elemental analyzer was used for elemental analysis. KBr pellet method was used for FT-IR analysis using diffuse reflectance on a Bomem Spectrophotometer, MB-series. Atomic Absorption Spectrophotometer (AAS) Shimadzu, 680, apparatus was used to evaluate the concentration of metal ions after adsorption.

Preparation of Adsorbent Material:

The adsorbent material preparation has been done via homogenous procedure as adopted earlier by Dey et al. (2009) for grafting of polymer material onto silica surface. PAAs was first prepared by mixing 7.7 g of MBA with 4.51 g of piperazine in 50 ml of DDW. The reaction mixture was kept for 72 h at room temperature (25ºC) at slow stirring rate. 2.0 g of the organo-chloro functionalized silica gel (SiCl) was added to the suspension of PAA followed by addition of 2.0 mL triethylamine. The suspension was finally stirred for 48 h at a temperature of 60ºC. The preparation of organo-chloro functionalized silica gel was done by adding 09 cm^3 of 3-chloropropyltrimethoxysilane into a suspension of 4.5 g of dry activated silica gel in 100 cm^3 of dry xylene. The prepared adsorbent material was filtered, washed with ethyl alcohol, vacuum dried and finally used for adsorption studies.

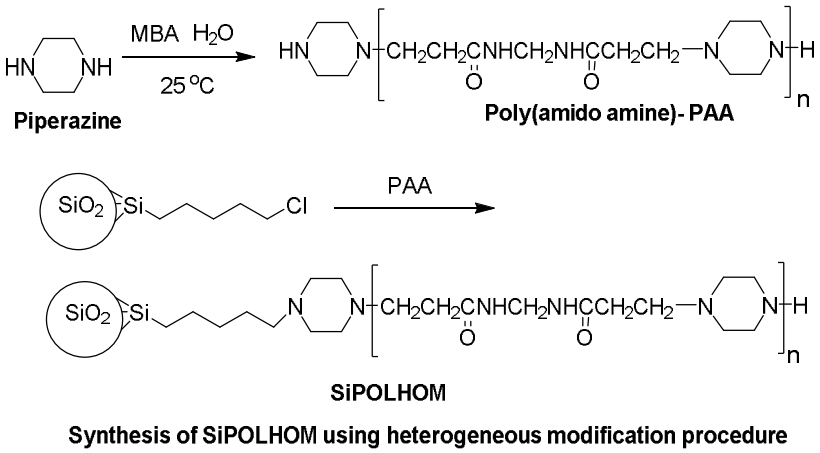

Figure 1: Preparative route of Poly (amido amine) functionalized silica surface

RESULT & DISCUSSION

Elemental Analysis

The elemental analysis showed that the adsorbent material contains C= 2.5%, H= 5.2%, N= 12.0 %. The estimated and calculated ratio of C: N is found to be approximately 2.69: 2.55. The results confirm the adherence of organic molecules on the surface of the silica.

FTIR Analysis

The FTIR spectrum of adsorbent material demonstrates a broad band around 3412 cm^{-1} due to O–H stretching of silanol group. A peak around 2964 cm^{-1} attributed to C–H stretching of the tetrahedral carbon confirms the attachment of the long PAA chain onto the backbone of silica surface (Sales et al. 2006). The appearance of another peak at 1112 cm^{-1} has been assigned to siloxane stretching vibrations, ν(Si–O–Si) and the Si–H bending vibration centered at 965 cm^{-1} (Dey et al. 2008). Furthermore, stretching vibrations at 1645 cm^{-1} are associated with the carbonyl group vibration which indicates the incorporation of the long PPA chain.

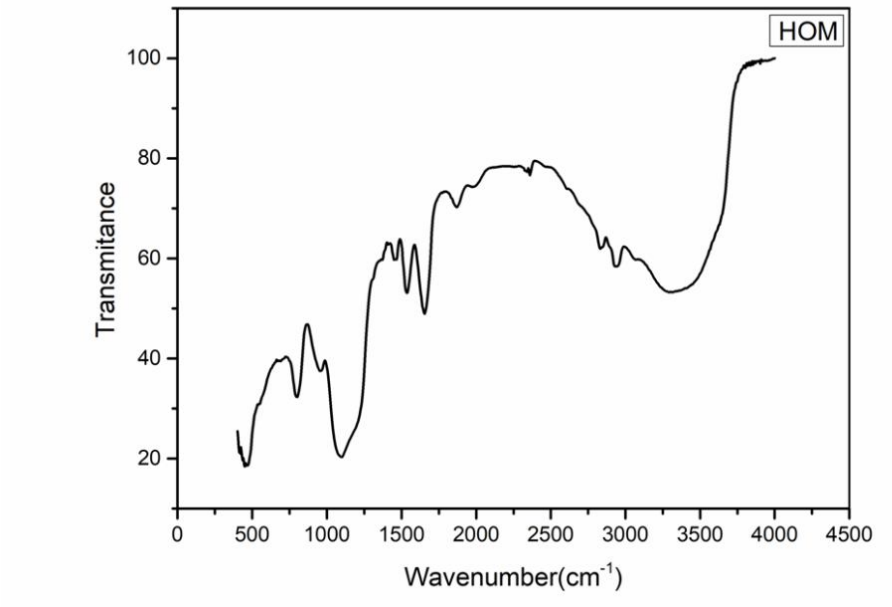

Figure 2: FTIR spectra of Poly (amido amine) functionalized silica surface

Adsorption of Cd^{2+} and Zn^{+2}:
The adsorption efficiency of chemically modified silica surface with long chain PAAs molecule was analyzed towards the adsorption of Cd^{2+} and Zn^{+2}. In order to evaluate the adsorption efficiency of inorganic-organic hybrid material, batch adsorption method was applied for adsorption of Cd^{2+} and Zn^{2+} from aqueous dilutions. For adsorption study, 50 mg of hybrid material was mechanically stirred with 25.0 mL of aqueous solutions of metal cation with varying concentration (01–15 ppm) for 24 h at room temperature. The solid samples were separated by centrifugation and the supernatant was analyzed using AAS. The amounts of metal ion adsorbed on the inorganic-organic hybrid surface were calculated using the following formula Dey[d] et al. (2008).

$$A_f = \frac{Ai - As}{m} \quad (1)$$

Where, A_f = Amount of metal ion adsorbed on the surface of inorganic-organic hybrid material, A_i and $A_{s=}$ initial and final concentration of metal ions in solution and in the supernatant at equilibrium, m= is the mass of the inorganic-organic hybrid material used in the adsorption studies.

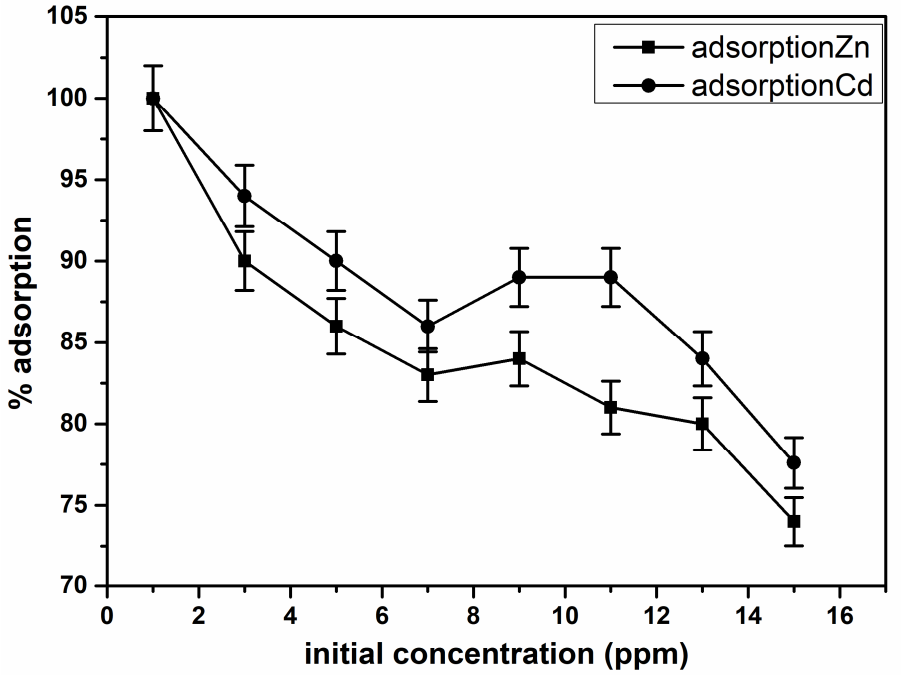

Figure 3: Adsorption of Zn and Cd on PAA modified silica surface.

The Figure 3 depicts the adsorption percentage of Cd^{2+}/ Zn^{2+} on the surface of inorganic-organic hybrid material. It can be clearly observed (Figure 3) that the adsorption percentage of metal ions on the surface of adsorbent is decreasing as the equilibrium concentration of cadmium & zinc increase however the amount of metal ion adsorb on the surface of hybrid materials have increasing trend and at lower concentration almost 100% efficiency is achieved. The result obtained are enough encouraging and it provide immense scope for utilizing this material for separation & pre concentration of toxic metal ions at micro/trace level. The comparative study shows that the adsorption of cadmium on the hybrid material is on higher in comparison to zinc. The higher amount of adsorption of Cd^{2+} in comparison to Zn^{2+} may be attributed to the nature of donating sites i.e., due to hardness &

softness of acid (Lazarin et al. 2007). Dey[c] et al. (2009), has also obtained similar type of observations in their investigation on adsorption of Cu^{2+} & Ni^{2+} in aqueous solutions on the surface of PAA modified silica gel. The adsorption efficiency increases with an increase coordination sites on the silica surface because of presence of long chain organic molecule. Also, the polymer attached on surface of silica facilitate to swell and the long chain of polymer molecule gradually become unfolded in suitable solvent. The increase in concentration of metal ions adsorbed depends on the availability of coordination sites on the adsorbent material and the nature of the solvent medium (Samal et al. 1999).

CONCLUSION

The present study gives a fruitful direction to apply the chemically modified silica gel for adsorption and pre concentration of toxic metallic cations on its surface. The prepared adsorbent material was characterized by Elemental Analysis and FT-IR spectroscopy for confirming the attachment of organic group on inorganic backbone of silica surface. The results of Elemental analysis & FT-IR spectra give agreement that the linear PAA chain has successfully immobilized on to the inorganic backbone of silica surface. The applicability of adsorbent material was investigated for adsorption of metallic cations of Cd^{2+} & Zn^{2+} in aqueous solutions. The overall result provides further encouragement & possibility for applicability of this material as an adsorbent for industrial & domestic uses.

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