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Two Step Functionalizing of Mesoporous Silica with L- Cysteine for Heavy Metals Removal

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Abstract

Mesoporous silica SBA-15 was synthesized by liquid crystal method and then was functionalized by amino acid L-Cysteine in presence of N,N'-Dicyclohexylcarbodiimide (DCC) as coupling agent. The functionalized nanoporous material has been utilized for adsorptive removal of heavy metals such as Copper, Cadmium, Silver, Cobalt, Nickel, and Lead cations from aqueous solution. The synthesized adsorbent has been also characterized by means of BET/BJH surface area, TEM and FT-IR methods. Moreover, adsorption capacities of the functionalized material were calculated by heavy metal ions analysis with atomic absorption spectroscopy (AA). The pH of the solution has been optimized for each element. The results explored the L-Cysteine functionalized mesoporous silica (SBA-15) is a suitable adsorbent for almost completely removal of Cu and Ag. It is also an efficient adsorbent for some other heavy metals. According to this study, adsorption capacity of the nanostructured material for heavy metals removal is (Cu^{+2}, 99.6%; Ag+, 99.4%; Cd^{+2}, 84.4%; Pb^{+2}, 89.2%; Ni^{+2}, 60.1%; Co^{+2}, 86.9%).

Keywords: Mesoporous Silica, Heavy Metals Removal, Amino Acid, L- Cysteine, DCC.

1. Introduction

The increasing level of heavy metals in water represents a serious risk to human health and ecological systems. Developing countries are the most affected areas by heavy metals [1]. Some of the harmful metals, e.g., Cd, Ni, Pb, Cu, Ag and Co, originated from industrial mining effluents, may be found in contaminated drinking waters [2]. Then, various methods including precipitation, coagulation/flocculation ion exchange, reverse osmosis, complexation-isolation, electrochemical and biological treatments are conventionally used for metal ions removal [3-4]. High cost of operation and energy consumption is however a big problem in all of them due to the co-exposure of drinking water to multiple heavy metals. In this due, application of the simple and scalable method namely, adsorptive removal of the hazardous contaminants, could be the best choice [5].
Although the sorbents such as activated charcoal, zeolites and clays conventionally are used in wastewater treatment systems [6], but many other adsorbents are like metalorganic frameworks (MOFs) [7] and mesoporous materials functionalized with certain ligands might be some of the most promising materials for removing heavy metals [8-13].
Application of 3-Aminopropyltrimethoxysilane (3-APTMS) and N-[3-(trimethoxysilyl)propyl]-ethylenediamine (MSDA) functionalized SBA-15 have been reported to have high affinity for adsorption of Cu^{+2} [5].

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The N-(Aminothioxomethyl)-2-Thiophen-carboxamide functionalized mesoporous silica has exceptional selectivity for adsorption of cadmium and copper from Water [14].
In this study mesoporous silica SBA-15 was synthesized by hydrothermal method and then functionalized with aminopropylsilane, following by linking amino acid L-Cysteine in the presence of DCC as coupling reagent. The functionalized material has been used as adsorbent for lead, copper, cadmium, cobalt, silver, nickel ions removal.

2. Materials and Methods

All of solvents and chemicals including TEOS as silica source, amino acid L-Cysteine and, amino-propylsilane as functionalizing reagents, trimethylamine (TEA) as proton scavenger, were analytical grade materials from Merck. The coupling agent N,N Dicyclohexylcarbodiimide (DCC) utilized for second step of functionalizing of silica was from Daejung, Korea.
The triblock copolymer, Genapol PF-10, produced by Clariant also used as soft template for preparation of mesoporous silica. The deionized water was used in all experiments.
Surface area was measured by BET Surface Area Analyzer: BELSORP MR (Japan). Infrared spectroscopy measurements were done by Perkin-Elmer and metal ions concentrations have been determined by Thermo- Scientific flame atomic absorption instrument. Microscopy analysis of sample representing porous structure of the SBA-

15 obtained by transmission electron microscopy (TEM), Philips, Netherlands.

2.1. Synthesis of Mesoporous Silica SBA-15

In a typical reaction, 6 g of Genapol-PF10, as template, was dissolved in 195 mL of 0.4M HCl by gently stirring at 35 ºc for 5 h. Then, 12.5 g of TEOS as silica precursor was added to this solution and stirred again at 35ºc for 24h. Then, aging was performed at 95ºc for 24h. The resultant precipitate filtered and washed by deionizer water until pH > 5, and dried at 110 ºc for 10h. The product was calcinated at 550 ºc for 4h for template removal.

2.2. Functionalization of Mesoporous Silica SBA-15 by Amino Propyl Triethoxysilane (APTS)

1 g SBA-15 was dispersed in 50ml Toluene, and 1ml of APTS) was added. Then the reaction mixture was refluxed for 24 h at 80 ºc. The solid was then filtered, washed by toluene and dried at 55 ºc. This product was named SBA-15-APTS.

2.3. Functionalization of SBA-15-APTS by Amino Acid L-Cysteine

1g of functionalized SBA-15-APTS was dispersed into a solution of 0.5ml triethylamine dissolved in 40 ml dichloromethane. The whole mixture was stirred for 45 min, then 0.5gr DCC was added to this solution and stirring was continued at room temperature for 45min. Finally, 1g amino acid L-Cysteine was added to this solution and stirred at room temperature for 24h. The solid product was filtered, washed with dichloromethane and dried at room temperature. Fig. 1. shows the two - step functionalizing of silica.

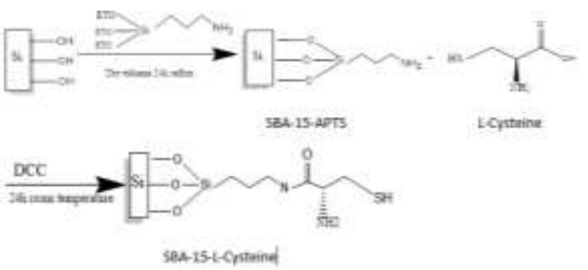

Fig. 1. Functionalizing of silica with amino-propyl-silane and L-Cysteine.

3. Results and Discussion
3.1. Adsorbent Characterization

FTIR spectra of different samples are illustrated in (Fig. 2). According to (Fig. 2.a) the large broad band between 3700 and 3200 cm^{-1} is referred to O–H bond stretching of the surface silanol groups which is one of the main features of the spectrum . A strong peak between 1090 and 1010 cm^{-1} is related to the band of siloxane, –Si–O–Si–. Another peak relating to siloxane band is between 625 and 480 cm^{-1} (Fig. 2.b) [15]. After functionalization with aminopropyl groups, new peaks can be attributed to both symmetric and asymmetric stretching of CH_3 and CH_2 groups 2928 cm^{-1}. A band at 1560 cm^{-1} ($\delta_{N\text{-}H}$) was also identified. These results confirm the successful functionalisation of SBA-15 with aminopropyl groups [16]. Comparison of the spectra SBA-15 functionalization by amino acid L-Cycteine (Fig. 2.c) with spectra amino acid, confirm functionalization SBA-15 by amino acid L-Cycteine.

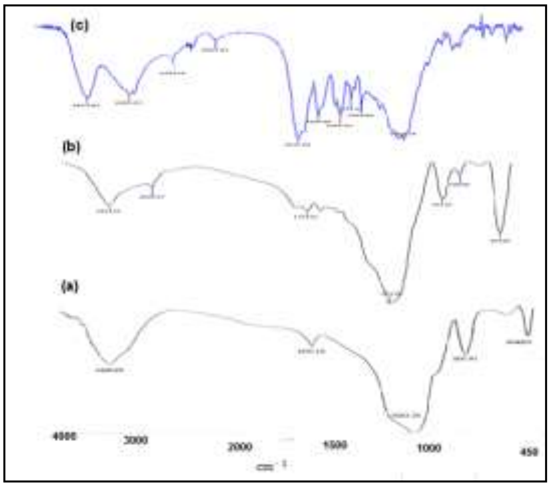

Fig. 2. FTIR spectra of (a) SBA-15 (b) NH2-SBA-15 (C) L-Cysteine-SBA-15.

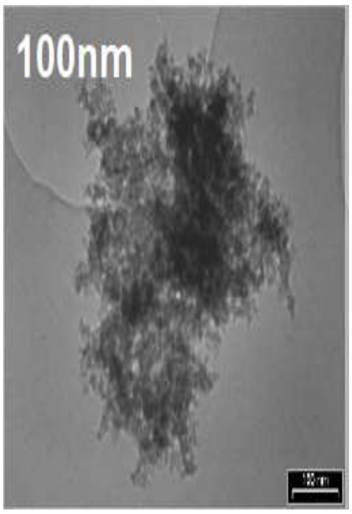

Fig. 3. TEM image of SBA-15.

Microscopic investigation of the bare SBA-15 confirmed the porous structure of this material. The TEM image of the sample is shown in Fig. 3. The porous behavior of this material is confirmed by further investigation using BET/BJH surface area analysis. The N_2-adsorption/desorption measurements were determined at 77 K. The

specific surface areas were calculated using multiple point Brunauer–Emmett–Teller (BET) method. The pore size distributions were calculated using desorption branches of the isotherms by Barrett–Joyner–Halenda (BJH) method.
According to BET model, the main pore diameter and surface area of the sample were 4.06 nm and 505.20 m^2/g, respectively (Fig. 4.).

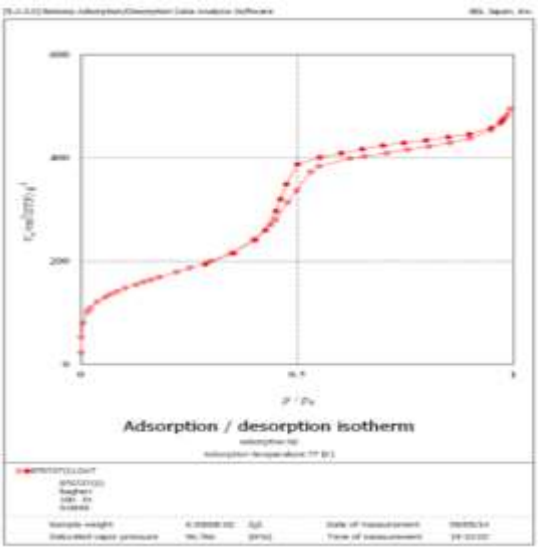

Fig. 4. Adsorption/Desorption isotherm of SBA-15.

3.2. Metal ions Adsorption

Different values of metal ions, 0.05g of SBA-15-L-Cystein and 2ml buffer solution was stirred at room temperature for 2h. Then solution was filtered and metal ions concentration in filtrate solution, was analysed by FAAS. The adsorption capacity(q_e) and adsorption percent were calculated by the following Eq. 1. and Eq. 2[17]. :

$q_e = (C_o - C_e)\, V/w$ Eq. (1).

$\text{Adsorption\%} = [(C_o - C_e)/(C_o)] \times 100$ Eq. (2).

C_o is the initial concentration of the metal ions (mg/L), C_e is the equilibrium concentration (mg/L), V is the volume of the solution, (L), w is weight of the adsorbent (g).

3.3. Optimization of the pH for Metal Ions Adsorption

Acetate and phosphate buffers prepared before starting the experiments. In a typical reaction, L-Cysteine-SBA-15 (0.05 g) was suspended in 2 ml acetate or phosphate buffers (pH values 3.6-7) containing desired amount of the transition metal cation. After stirring the mixture for 120 min at room temperature, the solid adsorbent has been filtered off and concentrations of the metal ion in the filtrate was measured by flame atomic absorption spectrometry. Fig. 5. and Fig. 6. illustrate the pH optimization curves for various metals studied in this work. The optimum pHs obtained for heavy metal ions is reported at Table. 1. Finally, the adsorption capacity of any ion has been determined at optimized pH of each ion. Table. 2. lists the comparative adsorption capacity of metal ions investigated by this method. The same results are visualized in Fig. 6. that shows comparative adsorption behaviour of various metal ions in presence of L-Cysteine modified SBA-15.

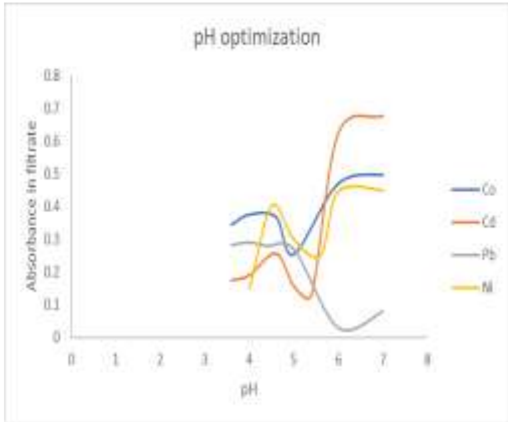

Fig. 5. PH Optimizing for Co, Cd, Pb and Ni ions.

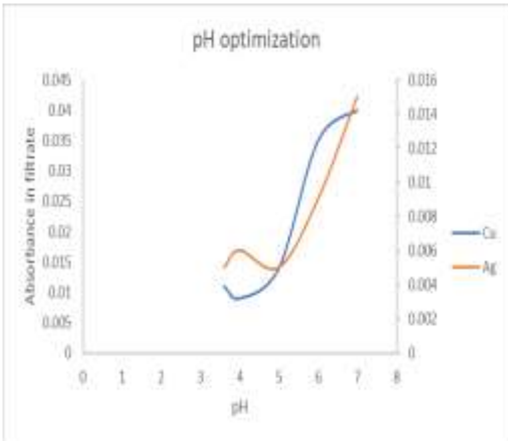

Fig. 6. PH Optimizing for copper and silver ions.

Table. 1. Optimum pH for adsorption of metal ions.

Cation	Optimum pH
Cu^{+2}	4
Ag^{+}	5
Cd^{+2}	5.4
Co^{+2}	5
Pb^{+2}	6
Ni^{+2}	5.6

Table. 2. Adsorption percent and Adsorption capacity of different metal ions.

Metal Ion	Adsorption Capacity (mg/g)	Adsorption (%)
Ag^+	198.9	99.4
Cu^{2+}	160.4	99.6
Pb^{2+}	25.6	89.2
Cd^{2+}	24.2	84.4
Ni^{2+}	18.8	60.1
Co^{2+}	24.8	86.5

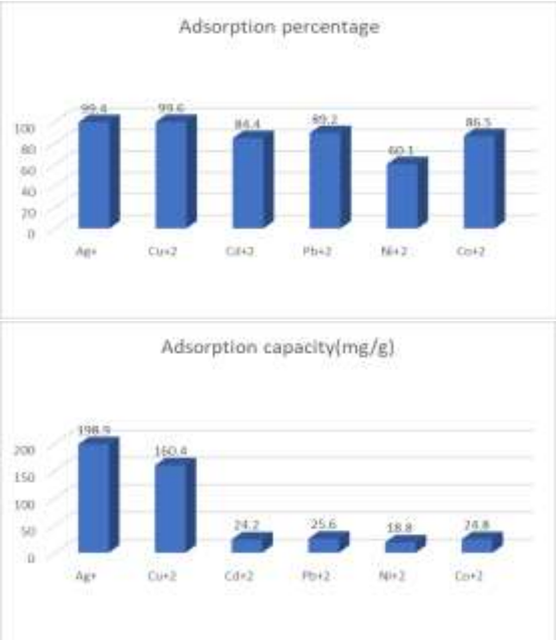

Fig. 7. Comparison between the adsorption behaviour of heavy metal ions onto the L-Cysteine modified SBA-15

Table. 3. The Langmuir equation data.

Cation	Q $_{max}$	R^2
Ag^+	200.3	0.9960
Cu^{+2}	178.6	0.9895
Pb^{+2}	26.2	0.9944
Ni^{+2}	15.3	0.9966
Co^{+2}	26.4	0.9821
Cd^{+2}	27	0.9998

The Langmuir model was used for investigation of adsorption isotherm based on Langmuir equation (Eq. 3) [17].

$$C_e/q_e=1/q_{max}K_L+C_e/q_{max} \qquad \text{Eq. (3)}$$

C_e is the equilibrium concentration, q_e and q_{max} are the adsorption capacity and theoretical maximum adsorption capacity respectively. Table. 3. lists the Langmuir data. Herein, R^2 values point to adsorption isotherm fitted to Langmuir model and monolayer adsorption of cations.

4. Conclusion

In this study, mesoporous silica functionalized by amino acid L-Cysteine was used for removal of heavy metals. Two step functionalized mesoporous silica showed acceptable adsorption capacity for several ions but nickel that slightly weak adsorption obtained for this ion. The best results found for Ag^+ and Cu^{+2} amongst six ions studied in this work.

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