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Cyclic Ligand Functionalized Mesoporous Silica (SBA-15) for Selective Adsorption of Co²⁺ Ion from Artificial Seawater

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Hard donor atoms (N and O) containing macrocyclic ligand was synthesized and further functionalized with mesoporous SBA-15 materials by chemical modification method. The modification was achieved by the immobilization of 3-chloropropyltriethoxysilane (CIPTES) onto mesoporous silica surface followed by post grafting route. The resulting material (Py-Cy-SBA-15) has been characterized by low angle X-ray diffraction (XRD), nitrogen adsorption–desorption isotherm, Fourier-transform infrared (FT-IR) spectroscopy, ²⁹Si and ¹³C CP MAS NMR spectroscopic analyses, Thermogravimetric analysis (TGA) and elemental analysis. The long range orders of the materials were identified by transmission electron microscopy (TEM). The functionalized material was employed to the heavy metal ions adsorption from aqueous solution containing Cu²⁺, Co²⁺, Zn²⁺, Cd²⁺ and Cr²⁺. The prepared hybrid material showed high selectivity and adsorption capacity for Co²⁺ ion at pH 8.0.

Keywords: Cyclic Ligand, Mesoporous Materials, Heavy Metal Ions, Selective Adsorption, Metal Coordination.

1. INTRODUCTION

In recent years the heavy metal contamination in the environmental water bodies is considerably increasing due to effluent discharging from various industries such as electroplating, mining, painting units containing heavy metal ions at high concentrations.¹ Also, water pollution includes insecticides, volatile organic compounds, chemical wastes and pollutants from live stock operations. Even though some of these metals in trace are recognized as nutrients required for animal and plant life, they are usually toxic at higher levels. The heavy metals include essential elements like iron and cobalt as well as toxic elements like cadmium, lead, copper and mercury.^{2, 3} Recently great attention has been paid to the removal of heavy metals from the aqueous solution. Conventional method for the heavy metal removal includes ion exchange,⁴ membrane separation,⁵ solvent extraction,^{6,7} precipitation⁸ and adsorption.9,10 Among these methods, adsorption is generally preferred for the removal of heavy metal ions because of the availability of various adsorbents, high efficiency, easy handling and cost effectiveness. A variety of new type of adsorbent materials are currently being explored, including activated carbon,¹¹ chelating resins,¹² bisorbents,13 and mesoporous silica materials.14 At present, searching for novel adsorbents for heavy metal adsorption with high removal efficiency with selectivity and low cost become the main interest in the research on the adsorption of heavy metal ions. Organically synthesized chelating ligand containing N, S and O donor atoms is of a special interest because of the variety of ways in which they are bonded to metal ions. A vast number of adsorbents exist with various types of ligand that deals with metal adsorption.¹⁵⁻¹⁸ Specific sorbents comprising of a ligand that can interact with the metal ion of interest and a solid support have been of our research interest since mesoporous silica materials^{19,20} including SBA-15 received a great interest as a solid support due to their large surface area, well defined pore size, excellent mechanical and chemical stability and easiness to modify.

In the present work, we have tried to develop chelating ligands containing more numbers of chelating sites for the assembly of basic functional groups and utilize them to modify SBA-15 to apply for heavy metal ions adsorption and synthesized ligands showing significantly high

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adsorption selectivity due to the presence of lone pair electrons from hard donor atoms (N and O) and the macrocyclic ligand having five coordination sites in the single molecule which makes a selective coordination with a specific metal ion.

2. EXPERIMENTAL DETAILS

2.1. Materials and Reagents

Poly(ethylene glycol)-block-poly(propylene glycol)-block-(poly ethylene)glycol (Pluronic P123) ($M_w = 5800$), tetraethyl orthosilicate (TEOS, 98%), 3-chloropropyltriethoxysilane (CIPTES, 95%) and salicylaldehyde, 2,6-diaminopyridine were purchased from Aldrich chemicals and used as received. Standard stock solution of all metals was prepared by dissolving salts form of metal nitrates in water. Artificial seawater was used in the preparation of standard stock solutions of metals. The general composition of the artificial seawater is as follows: NaCl-41.5%, MgCl₂-2.5%, CaCl₂-0.8%, KCl-0.9%, NaHCO₃-0.23%, KBr-0.08%, H₃BO₃-0.04%, SrCl₂-0.007%, NH₄Cl-0.01%, NaF-0.07%, NaSiO₃-0.002% and FePO₄-0.0005%.

2.2. Synthesis of Organic Ligand Precursor

Synthesis of macrocyclic pyridine ligand precursor was carried out by two steps as following; ed by Publishing Tech

2.2.1. Synthesis of 1,6-Bis(2-Formyl Phenyl) Ethanerican The macrocyclic ligand was prepared according to the published procedure with slight modification.^{21, 22} In the first step, salicylaldehyde (6.0 g, 50 mmol) was dissolved in 50 ml of DMF and K_2CO_3 (3.2 g, 20 mmol) was added. To this, 1,2-dibromoethane (5.2 g, 30 mmol) in 15 ml DMF was added dropwise to the reaction mixture. The resultant yellow solution was kept under stirring at 150-155 °C for 5 h at room temperature for 5 h (Scheme 1(a)). Then, 200 ml of distilled water was added and the mixture was kept in a refrigerator. After 1 h, the precipitate was filtered and washed with 500 ml water. Then, the obtained precipitate was recrystallized by ethanol. Yield: 8.7 g, (67%). ¹H NMR (CDCl₃, δ ppm): δ 2.2 (s, 4 H), δ 7.2 (d, 1 H), δ 7.5 (t, 2 H), δ 7.8 (d, 1 H), δ 10.3 (s, 2 H). ¹³C NMR (CDCl₃, δ ppm): δ 68.7 (CH₂CH₂), δ 187.5 (CHO), δ 113–161.5 (aromatic).

2.2.2. Synthesis of Cyclized Compound

In the second step, the cyclized compound was prepared using the first step product as a starting material. A solution of 2,6-diaminopyridine (1.2 g, 11 mmol) in methanol (30 ml) was slowly added to the reaction flask containing 1,6-bis(2-formyl phenyl)ethane (0.65 g, 2.0 mmol) in methanol (40 ml). After the the addition was completed, stirring was continued for further 6 h. A yellow precipitate was filtered and washed with methanol and



Scheme 1. (a) Synthesis of Py-Cy derivative and (b) functionalization of Py-Cy ligand onto SBA-15 surface.

dried ovenight. The C=N bond was reduced to C-N by NaBH₄ (Scheme 1(a)). The final product was labeled as Py-Cy-ligand. Yield: 0.35 g (54%). ¹H NMR (DMSO, δ ppm): δ 1.5 (s, 4 H), δ 2.0 (s, 1 H), δ 2.8 (s, 1 H), δ 7.2 (t, 2 H), δ 7.5-8.0 (mt, 4 H). ¹³C NMR (DMSO, δ ppm): δ 68.0 (CH₂CH₂), δ 189.4 (C=N_{py}), δ 113.0-160.8 (aromatic).

2.3. Preparation of Mesoporous Silica SBA-15 Adsorbent

Mesoporous silica SBA-15 was prepared using Pluronic P123 triblock copolymer as a surfactant template and TEOS as a silica source in acidic conditions.²³ In a typical synthesis, 4 g of triblock copolymer was dissolved in 125 g of de-ionized water and 20 g of con. HCl was added under stirring at ambient temperature (25–30 °C) for 1 h. 8.5 g of TEOS was added to the homogeneous surfactant solution and the mixture was stirred at 35 °C for 24 h. Then, it was allowed to stand for crystallization under static hydrothermal conditions at 100 °C for 24 h in a Teflon-lined autoclave reactor. The crystallized product was filtered, washed with water and dried. Finally, the occluded template was removed by calcination at 550 °C.

2.4. Immobilization of SBA-15 with Py-Cy-Ligand

Immobilization of Py-Cy-ligand onto SBA-15 was carried out using a post grafting method as following steps;

In a typical procedure, approximately 2.0 g of SBA-15 material was pre-treated at 140 °C for 3 h and then immersed into 50 ml toluene and 10 ml (0.05 M) of CIPTES in a 250 ml flask. Then, the reaction mixture was kept for reflux at 80 °C for 24 h under nitrogen atmosphere.

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Upon completion, the solid product was filtered, washed with 100 ml ethanol, and dried in oven at 60 °C for 6 h to obtained a triethoxysilylpropylchloride functionalized SBA-15 materials (CIPTES-SBA-15) (Scheme 1(b)).

2.4.1. Immobilization of Py-Cy-Ligand with SBA-15

Chemically synthesized Py-Cy-ligand (0.5 g, 1.78 mmol) was added to CIPTES-SBA-15 (1.0 g) in chloroform (60 ml) in the presence of triethyamine base to scavenge the HCl generated by the derivitazation reaction (Scheme 1(b)). The resultant pale yellow solid was filtered off, washed with chloroform and dried at 60 °C under vacuum and stored under inert atmosphere. The obtained product is labeled as Py-Cy-SBA-15.

2.5. Determination of Metal Adsorption Capacity

Approximately 250 mg adsorbent sample of Py-Cy-SBA-15 was suspended in 5 ml of metal solution from stock $(1 \times 10^{-3} \text{ M})$ was stirred (300 rpm) for 12 h. Then, the adsorbent was separated by filtration and the filtrate was collected and analyzed for metal ion concentration by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) analysis.

The heavy metal adsorption process was carried out at pH 8.0. The amounts of each metal ion adsorbed by Py-Cy-SBA-15 were calculated as below,

$$q_e = \frac{(C_0 - C_e)V}{W \times \text{metal atomic weight}} 40.176 \text{ On: The second se$$

where q_e is the adsorption capacity (mmol g⁻¹) of the adsorbent at equilibrium; C_0 and C_e are the initial and equilibrium concentrations of solution (ml) and W is the mass of the gram adsorbent used (g).

2.6. Characterization

X-ray diffraction (XRD) measurements were performed by using a Bruker AXS using Cu K α radiation ($\lambda = 1.5418$ Å) at 40 kV and 40 mA in the 2 theta range of 1.2-10°. Transmission electron microscopy (TEM) images were obtained with a JEOL 2010 electron microscope with an acceleration voltage of 200 kV. The BET (Brunauer-Emmett-Teller) method was used to calculate the specific surface area. The pore size distribution curve was obtained from an analysis of the adsorption branch using the Barett-Joyner-Halenda (BJH) method. Before the measurement the sample were degassed at 120 °C for 2 hrs in vaccuo. ¹³C cross polarization (CP) and ²⁹Si MAS NMR spectra were obtained with a Bruker DSX 400 spectrometer with a 4 mm of Zirconia rotor spinning at 6 kHz (resonance frequencies of 79.5 and 100.6 MHz for ²⁹Si MAS and ¹³C CP MAS NMR, respectively; 90° pulse width of 5 μ s, contact time 2 ms, recycle delay 3 s for both ²⁹Si MAS and ¹³C CP MAS NMR). Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer Pyris Diamond TG instrument at a heating rate of 10 °C min⁻¹ in air. Elemental analysis (% C, % N, % O and % S) was performed at the Perkin Elmer 2400 Series II CHN Elemental analyzer. Quantitative determination of metal ions was performed by ICP-AES (ACTIVA, JY HORIVA, Japan).

3. RESULTS AND DISCUSSION

3.1. Adsorbent Characterization

Figure 1 shows the XRD patterns of the SBA-15 and the Py-Cy ligand functionalized SBA-15 samples. All the samples show a well ordered hexagonal structure representing that the ligand modification process does not affect the mesostructural order of the materials. The XRD patterns show two well resolved peaks (110) and (200) in the 2θ range between 1.6° and 2.1°, and the *d*-spacing values for the two peaks were 54.6 and 48.1 Å, respectively. No obvious changes in the XRD patterns were observed after ligand functionalization. This indicates that the ligand modification did not affect the structure of the materials.

Figure 2(A) shows the nitrogen adsorption-desorption isotherms for SBA-15 and Py-Cy-SBA-15 materials. The isotherm curves belong to type IV pattern and have an H1 hysteresis loops that is representative for the class of mesoporous materials. The inflection position in the ligand functionalized SBA-15 shifted slightly towards lower relative pressure and the volume of nitrogen adsorbed was decreased with ligand modification, which indicates the reduction of pore size. Table I shows the structural parameters, such as BET surface area, total pore volume and pore diameter for SBA-15 and Py-Cy-SBA-15. BET surface area, pore volume and pore diameter was decreased after surface modification and ligand functionalization process (Table I). These changes can be attributed to the presence of pendant groups on the mesoporous SBA-15 surface that partially blocks the adsorption of nitrogen molecules. The surface functionalization of SBA-15 also results in the shrinkage of the BJH pore diameter (Table I), which was ascribed to the lining of pore wall with the organic functional groups (Fig. 2(B)).



Figure 1. XRD patterns of (a) SBA-15 (b) Py-Cy-SBA-15.





Figure 2. (A) Nitrogen adsorption–desorption isotherms and (B) Pore size distribution profiles of (a) SBA-15 and (b) Py-Cy-SBA-15.

The TEM image in Figure 3(a) revealed the well order hexagonal pore arrangement in the (100) direction. The TEM image in Figure 3(b) also displayed the pore arrangement parallel to each other in the (100) or (010) directions, clearly indicating that the ligand modification process did not affect the long-range order of the mesoporous adsorbents. Figure 4(a) shows the ²⁹Si MAS NMR data and the two groups of singals appeared on the spectrum indicating the presence of both the inorganic and organic silane functionalities in the materials. The Q^4 (-110 ppm), Q^3 (-101 ppm) and Q^2 (-87 ppm) peaks represent the fully and partially condensed inorganic silica source, while the T^3 (-67 ppm) and T^2 (-49 ppm) peaks are assigned to the terminal and cross-linked organosilane functionalities in the pore surface. Figure 4(b) shows ^{13}C CP MAS NMR spectra in the solid state for the Py-Cy ligand

Table I. Textural properties of SBA-15 and Py-Cy-SBA-15 adsorbents.

Material	Specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore size (Å)	Py-Cy ligand (mmol/g) ^a	C/N^a
SBA-15	750	0.92	39.9	_	_
Py-Cy-SBA-15	330	0.58	35.4	1.8	3.5

Note: a Elemental analysis

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(a) (b) (100) 50 nm (110) 50 nm Figure 3. TEM images of Py-Cy-SBA-15 taken at (100) (a) and (110)

Figure 3. TEM images of Py-Cy-SBA-15 taken at (100) (a) and (110) direction (b).

functionalized SBA-15. The alkyl group resonance signals are assigned as (1), (2) and (3) appearing at 18.8, 32.0 and 45.2 ppm, respectively. The aromatic carbon resonance signals arise at 160.0 and 210.3 ppm, assigned to the phenyl and pyridine groups that are labeled (5), (6) and (7) present in the ligand.³⁰ These results confirm the successful modification of SBA-15 by Py-Cy ligand. The quantity of the ligand molecules attached to the SBA-15 surface ($L_0 = 1.80 \text{ mmol/g}$) was calculated from the percentage of nitrogen in the functionalized mesoporous silica, as estimated by elemental analysis (Table I), using the following expression:

$$L_0 = \frac{\% \text{ of } N \times 10}{\text{Nitrogen atomic weight}}$$

The molar ratio of C/N was calculated from the elemental analysis of the Py-Cy-SBA-15 indicates a 2:1 stoichiometry between the silanol groups on the silica surface and the ligand. The result confirms a high efficiency in the functionalization of the SBA-15 surface.



Figure 4. Solid-state (a) ²⁹Si and (b) ¹³C CP MAS NMR spectra of Py-Cy-SBA-15.



Figure 5. Thermogravimetric curve of Py-Cy-SBA-15.

Thermogravimetric analysis of Py-Cy-SBA-15 was performed (Fig. 5). The stepwise weight loss of the adsorbent indicates that the adsorbent contains various chemical compositions obtained from each step of the modification. The Py-Cy ligand modified adsorbent shows the initial weight loss 2 wt% of physisorbed water at 100 °C. In the second step, decomposition of the organic ligand resulted in the weight loss of 10.6 wt% at 200–550 °C. This major weight loss was mainly attributed to the degradation of Py-Cy ligand molecule present in the SBA-15 materials. The degradation of the silica network occurred between 551–800 °C, leading to a weight loss of 7 wt%.

3.2. Adsorption of Heavy Metal Ions

The adsorption capacities of heavy metal ions from aqueous solutions were measured to determine the capability of functionalized ligand molecules present in the mesoporous adsorbents. Targeted heavy metal ions including Co^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Cr^{2+} were utilized to study the effect of various parameters towards the adsorption, and the selectivity of the heavy metal ions by Py-Cy functionalized SBA-15 was also determined.



Figure 7. Amounts of adsorption of heavy metal ions (Cu²⁺, Co²⁺, Zn²⁺, Cd²⁺ and Cr²⁺) on Py-Cy-SBA-15 at pH 8 after 12 h of adsorption.

3.2.1. Effect of pH of the Adsorption Medium

Solution pH is one of the important parameters that influence the adsorption of metal ions from aqueous solution, since it affects the solubility of metal ions and the ligand functionality. To measure the pH effect on heavy metal ion adsorption, pH was selected at pH 4, 6 and 8. The metal adsorption profiles (Fig. 6(a)) show the metal ion adsorption varied depending on the pH of the adsorption medium. The efficiency of metal ion adsorption is lower at lower pH. In contrast, the metal uptake efficiency increased with the increase of the medium pH. At pH 8, functionalized material showed equilibrium degree of adsorption. Co²⁺ ion showed the higher amount of adsorption at pH 8 than the competitive metal ions. The optimum pH for Co²⁺ ion adsorption ranged from 5 to 8. At low pH, it is expected that the coordination sites of the ligand undergo protonation to varying degree in the adsorption medium. Due to the protonation of the ligand, a competition existing between protons and heavy metal ions causes a decreased complexation ability of metal ions with ligand molecules.17,24



Figure 6. Effects of pH (a) and time (b) on the adsorption of Cu^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} and Cr^{2+} ions.



Figure 8. Effects of ionic strength (a) and metal ion concentration (b)on the adsorption of Co²⁺ ion.

3.2.2. Effect of Time on Heavy Metal Adsorption

The adsorption efficiency of ligand increased with respect to the contact time before equilibrium is reached at 25 °C. Figure 6(b) revealed that the Co^{2+} ion adsorption efficiency increased gradually up to 90% and reached equilibrium when the contact time was increased 30 min to 4 h. Similarly, the adsorption rate of other metal ions such as Cu^{2+} , Zn^{2+} , Cd^{2+} and Cr^{2+} also shows various percentage of adsorption. The adsorption almost reached equilibration, when the adsorption time reaches at 2 h. This indicates that the heavy metal ion adsorption takes place on the Py-Cy-SBA-15 as fast adsorption at the initial stage followed by the slow adsorption in which the metal cations diffuse into the SBA-15 adsorbents and coordinate with functionalized ligand molecules. The adsorption amounts of Co²⁺, Cu²⁺, Zn²⁺, Cd²⁺ and Cr²⁺ after 12 h of adsorption were 29.8×10^{-2} mmol/g, 13.0×10^{-2} mmol/g, 10.4×10 10^{-2} mmol/g, 6.3×10^{-2} mmol/g and 6.2×10^{-2} mmol/g, respectively, for the Py-Cy ligand functionalized SBA-15, as shown in Figure 7. The difference in the amount of adsorption of various heavy metal ions in the same adsorbents mainly depends on the ionic radii, electronegativity of the donor atoms and coordination tendency and geometry of the ligand-metal complex.²⁵⁻²⁷

3.2.3. Effect of Ionic Strength of Metal Ion Solution

Ionic strength of the adsorption medium may be an important factor that influences aqueous phase equilibrium between heavy metal ions and adsorbent materials. In general, the rate of adsorption decreases with increasing ionic strength of the adsorption media which can attribute to the presence of coordination sites of different affinities.²⁸ NaCl is one of the major compositions in the artificial seawater. The effect of ionic strength on the adsorption efficiency of Co^{2+} ion was investigated. The result (Fig. 8(a)) indicates that the ionic strength at higher concentration (1.0 M) marginally affected on the adsorption of Co^{2+} ion onto the Py-Cy-SBA-15. The effect of an excess of NaCl on the

adsorption of Co^{2+} ion was not significant in the formation of selective coordination of Co^{2+} ion with the Py-Cy ligand.

3.2.4. Effect of Initial Metal Ion Concentration

The metal ion uptake mechanism mainly depends on the initial metal ion concentration in the aqueous medium. At low concentration, the metal ions are adsorbed by specific functional groups present in the adsorbent materials whereas an increasing the metal concentration cause lower adsorption, due to the saturation of the adsorption sites resulting in the equilibration between metal ions and binding sites.²⁹ Figure 8(b) shows Co²⁺ ion adsorption, where a decreased rate of adsorption was observed from 98% (for Co²⁺ = 100 mg/L) to 78% (for Co²⁺ = 1000 mg/L).

4. CONCLUSIONS

Py-Cy ligand functionalized mesoporous silica SBA-15 material was synthesized by post grafting method. The prepared material was characterized by XRD, N₂ adsorption desorption, ²⁹Si and ¹³C CP MAS and TGA analysis. The adsorption capacity and selectivity of the modified materials was tested with various heavy metal ions from artificial seawater solution at pH 8. Py-Cy-SBA-15 showed a selectivity and higher adsorption capacity towards Co²⁺ ion $(29.8 \times 10^{-2} \text{ mmol/g})$ than the competitive metal ions such as Cu^{2+} (13.0×10⁻² mmol/g), Zn²⁺ (10.4×10⁻² mmol/g), Cd^{2+} (6.3 × 10⁻² mmol/g) and Cr^{2+} (6.2 × 10⁻² mmol/g). The selectivity is mainly due to the ionic radii of metal ions, electronegativity of donor atoms and the cooperative effect of nucleophilic pyridine and electron rich nitrogen and oxygen donating sites existing in the ligand, which makes a more preferable octahedral coordination with cobalt ions than the other competitive metal ions.

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References and Notes

- 1. H. Arslanoglu, H. S. Altundogan, and F. Tumen, *J. Hazard. Mater.* 164, 1406 (2009).
- V. J. Inglezakis, M. D. Loizidou, and H. P. Girigorupoulou, Water Res. 36, 2784 (2002).
- 3. M. A. Maheswari and M. S. Subramanian, Anal. Bioanal. Chem, 379, 519 (2004).
- 4. P. C. Nagajyoti, K. D. Lee, and T. V. M. Sreekanth, *Environ. Chem. Lett.* 8, 199 (2010).
- 5. A. C. Templeton, F. P. Zamborini, W. P. Wuelfing, and R. W. Murray, *Langmuir*, 16, 6682 (2000).
- M. Kashiwa, S. Nishimoto, K. Takahashi, M. Ike, and M. Fhjita, J. Biosci. Bioeng. 89, 528 (2000).
- M. G. Hankins, T. Hayashita, S. P. Kasprzyk, and R. A. Bartsch, *Anal. Chem.* 68, 2811 (1996).
- J. Kostal, A. Mulchandani, and W. Chen, *Macromolecules*, 34, 2257 (2001).
- S. M. Kraemar, J. D. Xu, K. N. Raymond, and G. Sposito, *Environ. Sci. Technol.* 36, 1287 (2002).
- Y. G. Ko, U. S. Choi, J. S. Kim, and Y. S. Park, *Carbon*, 40, 2661 (2002).
- A. R. Latha, P. Frailie, D. Hua, M. Darsillo, and D. Bhattacharyya, J. Membrane. Sci. 326, 460 (2009).
- 12. C. Y. Chen, M. S. Lin, and K. R. Hsu, J. Hazard. Mater. 152, 986 (2008).

- 13. S. Zakhama, H. Dhaouadi, and F. M. Henni, *Bioresource Technol*. 102, 786 (2011).
- 14. H. Yang, R. Xu, X. M. Xue, F. T. Li, and G. T. Li, *J. Hazard. Mater.* 152, 690 (2008).
- I. H. Gubbuk, R. Gup, and M. Ersoz, J. Colloid Interf. Sci. 320, 376 (2008).
- B. Lee, Y. Kim, H. Lee, and J. Yi, *Micropor. Mesopor. Mater.* 50, 77 (2001).
- 17. M. Puannagam and F. Unob, J. Hazard. Mater. 154, 578 (2008).
- D. Perez-Quintanilla, I. del Hierro, M. Fajardo, and I. Sierra, J. Environ. Monitor. 8, 214 (2006).
- 19. P. K. Jal, S. Patel, and B. K. Mishra, Talanta 62, 1005 (2004).
- J. Chwastowska, A. Rogovuska, E. Sterlinska, and J. Dudek, *Talanta* 49, 837 (1999).
- S. Ilkan, H. Timel, I. Yilmaz, and M. Sekerci, J. Organomet. Chem. 692, 3855 (2007).
- 22. I. Yilmaz, S. Ilhan, H. Temel, and A. Kilic, J. Incl. Phenom. Macro. 63, 163 (2009).
- 23. D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, and G. D. Stucky, J. Am. Chem. Soc. 120, 6024 (1998).
- 24. B. L. Rivas and A. Moureira, *Macromol. Symp.* 270, 143 (2008).
- 25. C. Y. Zhu, R. M. Izaff, T. M. Wang, P. Huszthy, and J. S. Bradshaw, *Pure Appl. Chem.* 65, 1485 (1993).
- 26. J. Koresh and A. Soffer, J. Electchem. Interfacial. Electchem. 147, 223 (1983).
- 27. Z. Sadowski, Minerals Engg. 14, 547 (2001).
- 28. A. K. Bhattacharya, S. N. Mandal, and S. K. Das, *Chem. Engg. Journal* 123, 43 (2006).
- 29. L. N. H. Arakaki, J. G. P. Espinola, M. G. da Fonseca, S. F. de Olivera, A. N. de Sousa, T. Arakaki, and C. Airoldi, J. Colloid. Interf. Sci. 273, 211 (2004).

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