

Modified SBA-15 synthesized using sugarcane leaf ash for nickel adsorption

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Highly ordered mesoporous variety of silica SBA-15 (Santa Barbara Acid – 15) has been prepared from sugarcane leaf ash by template assisted method and it has been successfully used as an adsorbent for nickel. Post-synthesis modification of the particle is done by grafting of carboxyl, amino, thiol and phenyl groups through siloxypropane tethers to the siliceous surface of SBA-15. Adsorption efficiency of products is estimated in batch mode and compared. Maximum percentage removal (92.5%) is obtained with amine functionalised SBA-15 with an initial Ni (II) concentration of 80 mg/L at a pH value of 5. The Freundlich isotherm model describes the equilibrium well.

Keywords: Adsorption, Nickel, Santa Barbara Acid-15, Sugarcane leaf ash

Removal of heavy metal ions from wastewaters has been an extensive industrial research subject, as these are highly toxic even at low concentrations¹. Nickel is one such known heavy metal pollutant, found mainly in effluents discharged from industries such as nickel-cadmium battery manufacturing², electroplating³, mineral processing, metal finishing⁴, etc. Apart from commercial adsorbents like activated carbon⁵ various low cost adsorbents have been explored by researchers for the removal of dyes and heavy metals in the recent past. However, these materials has low adsorption capacities and high equilibration time. For large scale applications, an adsorbent that rapidly removes the pollutant is necessary. Novel ordered mesoporous silica has been investigated as potential sorbents for adsorbing nickel form aqueous solutions.

Mihaela *et al.*⁶ reported that modified SBA-15 (Santa Barbara Acid-15) has a remarkable adsorption capacities for Cu²⁺, Co²⁺, Ni²⁺ and Zn²⁺ ions. The hybrid material showed higher adsorption selectivity for Cu²⁺ compared to other metal in the solution. Multi-amine functionalized mesoporous silicas have been prepared by a post-grafting process using siloxy propane tethers. These multi-amine grafted composites show almost equal affinity to heavy metal ions in wastewater samples and can effectively remove them rather completely. Among them the Pb²⁺ and Zn²⁺ concentrations are below the detection limit after the adsorption. Amine functionalized adsorbents

can be more favorable when more than one kind of metal ions needs to be removed⁷.

In literature, several methods for SBA-15 synthesis are reported using many silica precursors like tetra-alkoxysilane, fumed silica, water glass and sodium silicate⁸. The major downside is that they are expensive and also the precursors are highly toxic.

Limited amount of work has been done on converting ash into mesoporous silica materials. Sugarcane leaf ash has been used as a partial replacement of Portland cement due to its low cost and high SiO₂ content⁹. An alternative silica source obtained from sugarcane leaf ash is a promising option¹⁰. In the present work, nickel has been removed from wastewater by adsorption with amine functionalized SBA – 15 synthesized using sugarcane leaf ash, a low cost silica source.

Experimental Procedure

Materials

The production of mesoporous silica involves the use of sugarcane leaf ash as the silica precursor. The sugarcane leaves were obtained from nearby sugarcane field and incinerated in the muffle furnace at 400°C. Nickel chloride hexahydrate (99%, Aldrich), dimethyl glyoxime (99%, Aldrich), polyethylene glycol-polypropylene glycol- polyethylene glycol [Plutonic P123], a triblock co-polymer (PEO₂₀PPO₇₀PEO₂₀) were used as a template⁸. Alkoxysilanes selected for the functionalization¹¹ were phenyltriethoxysilane (EtO)₃Si-Ph, (98%, Aldrich),

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3-aminopropyltriethoxysilane ($(\text{EtO})_3\text{Si-PrNH}_2$, (98%, Aldrich), mercaptotriethoxysilane, $(\text{EtO})_3\text{Si-PrSH}$, (95%, Avocado) and 4-(triethoxysilyl)butyronitrile $(\text{EtO})_3\text{Si-PrCN}$, (98%, Aldrich). These reagents were purchased from Aldrich and used without further purification.

Preparation of pure silica SBA-15

Dried sugarcane leaves were cut into small pieces and weighed. The leaves were cut to ensure complete burning. They were incinerated in a muffle furnace at a temperature of 650°C .

The X-ray fluorescence (XRF) analysis of ash (in wt%) is given below:

Formula	Concentration (wt%)
SiO_2	: 80.14
CaO	: 6.06
MgO	: 5.02
K_2O	: 3.09
SO_3	: 2.25
Al_2O_3	: 0.89
Cl	: 0.67
Fe_2O_3	: 0.51
Na_2O	: 0.28
MnO	: 0.17
TiO_2	: 0.046
CuO	: 0.0067

The chemical composition of the ash shows the presence of Si, Ca, Mg, Al, Na, K and Fe as major components. One gram of finely ground ash was fused with sodium hydroxide in the ratio of 1:1.2 at 450°C for 1 h. The fused mass was diluted with water in the ratio of 1:4 followed by sonication to completely disperse the particles. The solution was then filtered repeatedly until a colourless filtrate was obtained¹². This sodium silicate solution (water glass) is viscous, transparent, colourless. Being an inexpensive silica source obtained from sugarcane leaf ash, it was used as a precursor for the synthesis of mesoporous SBA-15.

Five gram of P123 triblock copolymer was added to an acidified solution prepared by dissolving 1 g of 1N HCl in 43.2 g of demineralized water and stirred for 1 h at 35°C until a homogeneous solution was obtained. The pH of the solution was maintained well below pH 2 (iso-electric point of silica), as silica exists as SiO_2H^+ below 2 pH. This was done to maximize the condensation of silica over the triblock

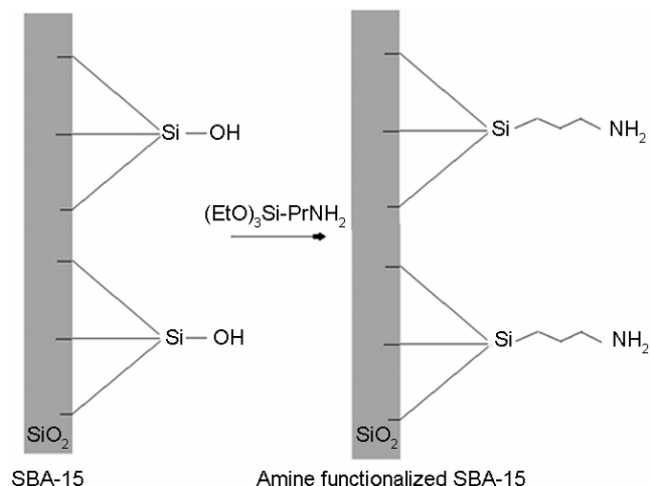
copolymer template. Then simultaneously, 12 g of sodium silicate obtained from sugar cane leaf ash was dissolved in dilute sodium hydroxide (0.27 g NaOH dissolved in 69.5 g demineralized water). This sodium silicate solution was added to the surfactant solution and stirred at 35°C for 24 h, resulting in the formation of dense white P123/ SiO_2 composite. The synthesis solution was then transferred to a teflon bottle and aged for 72 h at 120°C to obtain SBA-15. The white solid products (as-synthesized SBA-15) were filtered and washed repeatedly with de-ionized water, dried at room temperature for 24h and then calcined for 8h at 550°C in air. The aggregated SBA-15 particles were separated by wire mesh⁸.

Functionalization of SBA-15

Surface modification grafting of functional groups to the siliceous surface of SBA-15 through siloxy propane tethers was carried out according to a method described by Pallavi *et al.*¹¹ Here, 1 g of calcined SBA-15 was suspended in 30 mL of toluene Scheme 1. This was to be followed by the addition of 2 mmol of the functionalizing agent (triethoxysilane possessing the desired functional group) per gram of silica support and the reaction mixture was heated to reflux for 24 h. The white solid was then filtered off, washed with toluene and dried under vacuum. The samples were then named *psR*-SBA-15 where R is the functional group on the surface. For *psPrCOOH*-SBA-15, the sample of *psPrCN*-SBA-15 was refluxed in 1M HCl solution for 4 h¹³.

Characterization of mesoporous materials

The surface area, total pore volume, and pore size distribution were estimated using surface area and



Scheme 1—Amine functionalization of SBA-15

porosity analyzer (ASAP 2020, Micromeritics, USA). Microscopic observation of the mesoporous material was done by scanning electron microscope (6701 F, JEOL, Japan). FTIR spectra (spectrum 100, Perkin Elmer, USA) of mesoporous materials were observed for the SBA-15 surface.

Adsorption of nickel

Stock solution of nickel was prepared by dissolving required amount of nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) in double distilled water. For each run, 80 mL of nickel solution of known concentration was taken in a 250 cm^3 conical flask. SBA-15 (1 g/L) was added to the mixture and the flask was agitated in an orbital rotary shaker at constant temperature (303 K), pH (5) and rpm (175). Aliquots were taken after 4 h and filtered to remove the adsorbent particles. Concentration of nickel ion in the supernatant solution was determined by analyzed using UV-Visible double beam Spectrophotometer (Systronics 2201, India) at 440 nm and dimethylglyoxime as a reagent¹⁴. All the experiments were conducted in duplicates and average values were taken. The amount of nickel adsorbed per unit mass of the adsorbent at equilibrium (q_e , mg/g) was calculated using the following expression¹⁵:

$$q_e = \frac{(C_o - C_e)}{m} \quad \dots (1)$$

where C_o and C_e are the initial and equilibrium nickel concentrations in mg/dm^3 ; and m , the amount of SBA-15 in g/dm^3 . The percentage nickel adsorption (% R) was calculated using the following expression:

$$\%R = \frac{(C_o - C_e)}{C_o} \times 100 \quad \dots (2)$$

Equilibrium data were analyzed with most popularly used Langmuir and Freundlich isotherms models¹⁶.

Adsorption studies

Adsorption studies were performed using modified and bare SBA-15 in batch studies to select the best functional group for nickel adsorption. A comparative study was done on the four chosen groups, along with bare mesoporous silica. Nickel solution (80 mL) of 80 ppm was taken in a 250 cm^3 conical flask and 0.1 g of adsorbent was added to the mixture, the flask was agitated in an orbital rotary shaker at constant

temperature (303 K), pH (5) and rpm (175). The process was repeated until equilibrium was attained.

Results and Discussion

Nickel removal by adsorption

Adsorption studies using SBA-15 with different functional groups were conducted in batch mode. Maximum percentage adsorption is 92.5% for amine functionalized SBA-15. Corresponding percentage nickel removal by other SBA-15 are bare SBA-15 (77.5); COOH-functionalized porous silica (68.75); thiol functionalized SBA-15 (86.25) and phenyl functionalized SBA-15 (76). It is observed that amine grafted SBA-15 shows higher adsorption compared to other products.

Characterization of SBA-15

Figure 1 shows the FTIR of the functionalized SBA-15 samples. Characteristic peak observed at 3451.55 cm^{-1} confirms the presence of hydroxyl group (bare group) in the sample. Peak observed at 1087.23 cm^{-1} confirms the asymmetric stretching vibration of Si-O-Si¹⁷. The primary amine band observed at 1523.63 cm^{-1} confirms the presence of amine group in amine functionalized SBA-15¹⁸.

From SEM analysis (Fig. 2), it can be seen that SBA-15 has the typical wheat-like morphology and consists of aggregates of uniform rope-like particles. The image was observed at resolutions of 1 nm and 100 nm.

The Bruanauer-Emmett-Teller (BET) surface area has been experimentally determined to be 632 m^2/g . For each sample the average pore size is estimated at 0.838 cm^3/g . Barrett- Joyner-Halenda (BJH) adsorption average pore diameter is 6.61 nm. Table 1 gives a comparison of the surface area,

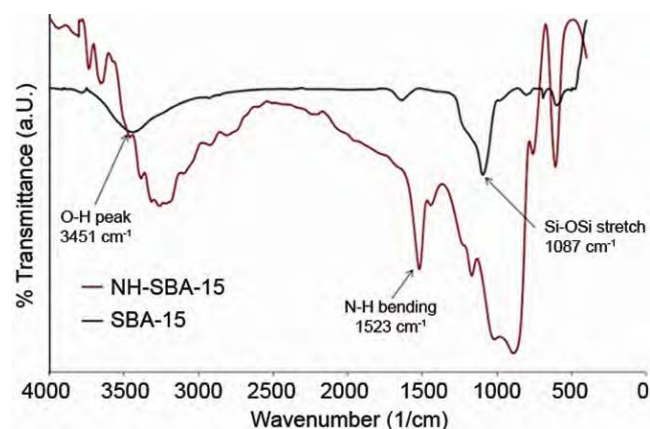


Fig. 1—FTIR spectra of bare and amine functionalized SBA-15



Fig. 2—SEM image of SBA-15

Table 1—Surface area, pore volume and pore diameter of SBA-15

Specific surface area $\text{m}^2 \text{g}^{-1}$	Pore volume $\text{cm}^3 \text{g}^{-1}$	Pore diameter nm	References
574	0.838	6.61	This study
790	1.44	9.1	13
710	0.11	2.9	19
645	0.85	6.1	20
571	0.85	7.9	21

pore volume and pore diameter of the SBA-15 reported in literature.

Adsorption studies

Effect of pH

Percentage nickel removal has been found to increase with increase in solution pH till pH 5 and then found to decrease with further increase in solution pH. Thus, optimum pH is found to be 5. The effect of pH can be explained considering the surface charge on the adsorbent material. At low pH, due to high positive charge density the electrostatic repulsion will be high, resulting in lower uptake of positively charged metal ions. At a higher pH, the nickel ions are precipitated as their hydroxides which decreases the rate of adsorption and subsequently the per cent removal of metal ions²².

Equilibrium studies

The Freundlich model described the system better than the Langmuir model (Fig. 3)²⁰. The Langmuir isotherm parameters determined by least square method are: q_{max} (81.812 mg g^{-1}); K_L (0.700 L/mg); R^2 (0.994). The Freundlich isotherm parameters are: n (0.212); K_F ($42.169 \text{ mg g}^{-1} (\text{dm}^3/\text{mg})^{1/n}$); R^2 (0.985).

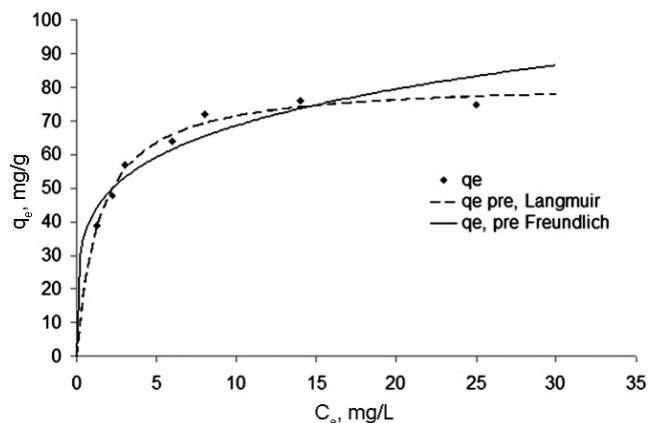
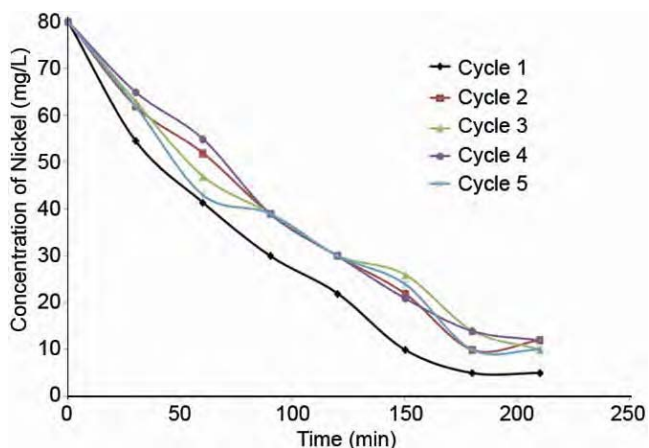


Fig. 3—Comparison of Langmuir and Freundlich isotherms

Fig. 4—Adsorption of nickel ion on $-\text{NH}$ functionalised SBA-15 for five cycles (C_0 – 80 mg/L; m – 0.1 g/L; Contact time– 180 min)

The Langmuir monolayer capacity of the adsorbent (81.813 mg/g) is found to be higher than many alternate adsorbents reported in literature^{14,15,23}.

Regeneration

Reusability of the adsorbent is one of the major characteristic requirements for a good adsorbent. Functionalised SBA-15 can be easily recovered by adjusting the pH. In this work, the functionalised SBA-15 is recovered by adjusting the solution pH to 7.5. Figure 4 shows reusability of SBA-15. It is evident from this figure that the SBA-15 is stable after several cycles of adsorption. Thus, it can be used as suitable adsorbent in the large scale applications.

Conclusion

Functionalized SBA-15 mesoporous silica particles have been successfully synthesized from sugarcane leaf ash. Resulting SBA-15 has very high surface

area (632 m²/g). Amine functionalized SBA-15 has shown maximum adsorption capacity of 81.8 mg/g. Optimum pH for the removal of Ni (II) by amine functionalized SBA-15 from aqueous solution is found to be 5. The modified SBA-15 could easily be regenerated and reused. The adsorption effectiveness could be retained even after five regeneration cycles.

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