

Polysaccharide assisted synthesis of mono dispersed silicate nanospheres and their application in removal of Cr (VI) from aqueous solution

Babita Sehgal*

Applied Chemistry Department, Faculty of Technology and Engineering, The Maharaja Sayajirao University of Baroda, Vadodara, India. babitasehgal-appchem@msubaroda.ac.in

Abstract- In the present work yeast has been used as a pore forming agent in presence of naturally occurring polysaccharide starch. The non-surfactant technique employed here, facilitates the formation of monodispersed silicate nanospheres . The nanospheres after amino functionalization showed a maximum Cr(VI) removal efficiency at 45°C .The nanospheres were further characterized by XRD, SEM , FTIR and BET. The adsorption equilibrium data was modeled using the Langmuir , Freundlich and Temkin isotherms at 2 pH and temperatures of 25°C, 35°C and 45°C respectively. The data was found to fit more satisfactorily to Langmuir isotherm at all the temperatures, indicating unilayer adsorption.

Key words - starch, yeast, amino functionalized silica, Cr (VI) adsorption, kinetics.

I. INTRODUCTION

Removal of contaminants from waste water or other water sources continue to be a focus of research. This becomes more significant especially when concentration of the contaminant is low and water volume is high. Chromium is one of the toxic metals that exists in two states i.e. Cr (III) and Cr(VI). Out of the two, Cr(VI) shows higher mobility and hence considered to be more toxic to humans. Since hexavalent chromate (CrO_4^{2-}) and dichromate oxyanions ($\text{Cr}_2\text{O}_7^{2-}$) are soluble in water hence their removal from groundwater has been a subject of challenge. Adsorption of toxic species like hexavalent chromium largely depends on pore size of the adsorbent. Though a large number of conventional porous materials like zeolites [1], clays [2] , activated carbon [3] are available but their major disadvantage is low adsorption ability or poor selectivity.

Porous silica is one of the ideal rigid supports that can be made with large and narrow pore size distribution and later functionalized by various groups so as to increase their interaction with Cr(VI). A few investigators have studied

Cr(VI) adsorption on MCM-41 [4] ,SBA-1and SBA-15 [5] ,HMS [6] , modified clinoptilolite [7] and ZSM-5 zeolites [8] but the Cr(VI) loading capacities were not more than 0.573 mmol/g. A maximum loading of 3.32 mmol/g was achieved using NN functionalized silica [9] . Amine-functionalized bimodal mesoporous silica nanoparticles were used in solid phase extraction to obtain a maximum Cr(VI) removal of 3.69 mmol/g [10] . In all the cited examples, the mesoporous material was synthesized using molecular surfactant route that offered limited pore size. The only way to attain higher pore sizes is to employ

swelling agents that involve complicated synthesis and irreproducibility. Therefore, it is highly desirable to develop a facile method to synthesize a material with controllable porosities. Recently, new environmentally safe materials prepared using polysaccharides for adsorption of heavy metal ions represent a new category of hybrid nano composites. Compared to chemically synthesized surfactants, polysaccharides have a higher biodegradability and lower toxicity. Moreover they are highly water soluble and could be easily extracted out of the pores by simple washing with water thus eliminating the need for high temperature calcination and organic solvent extraction that often lead to collapse of the pore structures at high temperatures [11-13] .The non-surfactant template method thus provides a very economical, environment friendly and highly biocompatible route to mesoporous material synthesis[14] showed that non-surfactant organic molecules, e.g., optically active organic compounds such as D-glucose, acts as a template for the formation of mesoporous silica material with large surface areas and pore volumes and narrow pore size distribution. A comprehensive review of the chemistry and various approaches used in cyclodextrin-based silica materials has already been explained in literature [15]. While a few authors have shown the uptake of heavy metals from synthetic aqueous solutions using modified PEI-silica gel [16], others have proposed the use of cyclodextrin bonded silica for adsorbing p-nitrophenol [17] . A maximum adsorption capacity ($q_m= 45.8$) for removal of Acid blue was obtained using silica beads containing cyclodextrin [18]. Later, yeast cells were used as a template to prepare mesoporous aluminophosphate particles from aluminum alkoxide and phosphoric acid solution via a precipitation

method [19]. A facile fabrication of $\text{Cd}(\text{OH})_2$ -yeast hybrid microspheres was shown using yeast [20]. For the first time starch-yeast based foaming technique was used for facile synthesis of porous ceramic [21].

Though, many silica nano composites have been reported in the literature using polysaccharides but their application in chromium adsorption has not been much explored. This study aims to fabricate a porous silicate with controllable porosity where silica network was allowed to grow around a naturally occurring polysaccharide like starch in the presence of a biological frothing agent (e.g., yeast) under mild conditions of pH and temperature. This is the first time that biological foaming agents are being used for synthesis of mesoporous silica as per our knowledge.

II. EXPERIMENTAL

A. Reagents

Tetraethyl orthosilicate (TEOS, 99%) was obtained from Sigma Aldrich. 25% ammonia solution (purity 99.5%, Merck), ethanol (purity 99.5%, Merck) were used without purification. Deionized water and active dry yeast were used throughout the experiment. Yeast extract powder special grade of Loba Chemie, soluble starch used as a template was obtained from Himedia. All chemicals, reagents used were of analytical grade and were used as received without further purification.

B. Synthesis of mesoporous silicates

Mesoporous silicate was prepared using starch as template, yeast as a foaming agent and a silica precursor tetraethylorthosilicate (TEOS). A mixture of alcohol and water was used as a solvent for suspending yeast with TEOS. Ammonia was used as a catalyst. Firstly, 0.02 moles of TEOS in ethanol was added to a mixture of 0.02 moles of ammonium hydroxide in water (15 ml) in a two-necked 500-ml round-bottomed flask fitted with a thermometer and reflux apparatus. The mixture was stirred for 30 minutes at room temperature under nitrogen. Once the solution became clear and homogeneous the reaction mixture was refluxed at 65 °C for 12 hours. Later the reaction mixture was allowed to cool down to room temperature. Water and ethanol produced as byproduct during hydrolysis of TEOS were removed under vacuum so that the original sol reached 50% of its original volume. To this reduced solution, starch-yeast slurry was added with slow stirring for six hours. % Weight of added starch was calculated from the reaction stoichiometry, assuming complete conversion of TEOS to silica. By-products were separated using rotary evaporator and later subjected to washing at least 5-6 times with water to remove un-reacted yeast/starch. The samples were further dried in a vacuum oven at 110 °C. Drying was continued until a constant weight was achieved. This was followed by calcination at a slow temperature increase (1 °C/min) up to 550 °C for 6 hours to get SY20, SY30, SY40, SY50 and SY80 samples.

The same procedure was repeated without starch to get respective Y40, Y50 and Y80 samples. In all the performed experiments the wt % of starch was kept constant as 50%. For comparison, two samples with 40 wt% and 60 wt% starch were also prepared as shown in Table 1 and abbreviated as S40Y50 and S60Y50.

C. Preparation of Starch- yeast Slurry

In order to add yeast, it was first dissolved thoroughly in 1:1 distilled water by weight. The resulting yeast solution was introduced with stirring into an appropriate amount of starch to form slurry. The slurry was later poured into a 250 ml beaker and covered with a glass cover and simultaneously heated to 40 °C inside an oven for 2-3 hours so that fermentation sets in and foaming develops. Later the foamed starch-yeast slurry was added to the refluxed TEOS. Keeping the amount of starch constant, the increments of yeast used were varied as 20%, 30%, 40%, 50% and 80% with respect to starch by weight and the samples were denoted as SY20, SY30, SY40, SY50, and SY80 respectively as seen from Table 1. In order to see the effect of yeast, a few samples were prepared using similar procedure without starch but using variable amount of yeast and were abbreviated as Y40, Y50, Y80 where the number shows the amount of yeast added in %.

D. Synthesis of Amino Functionalized Silica (FSY)

Amino Functionalized Silica was prepared as per the method of Ho et al [22]. In this method 2.5 g of calcined SY50 was refluxed with 2.5 g of 3-aminopropyltrimethoxy silane (APTMS) in a 100 ml RBF containing 50 ml of n-hexane for about 6-7 hrs. Later the mixture was washed with isopropanol and dried at room temp and denoted as FSY50.

E. Material Characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT D/Max-2500 powder diffraction system using Cu K α radiation of 0.15406 nm wavelength. The nitrogen sorption experiments were performed at -196 °C on a Micromeritics ASAP 2020 system. Prior to the measurement, the samples were out-gassed at 120 °C for 6 h. The BET (Brunauer–Emmett–Teller) specific surface areas were calculated using adsorption data in a relative pressure range of P/P0 = 0.05–0.25. Pore size distribution curve was calculated using BJH (Barrett–Joyner–Halenda) method. The total pore volumes were estimated from the amounts adsorbed at a relative pressure (P/P0) of 0.99. Scanning electron microscopy (SEM) was performed using Jeol, JSM 5600 microscope operated at 15 kV. The samples were coated with Au prior to SEM examination. Infrared (IR) spectra were recorded on a Perkin-Elmer Infrared spectrophotometer. UV measurements were performed using Shimadzu Spectrophotometer. Elemental analysis was done using Euro Vector EA 3000 Analyzer.

F. Adsorption Experiments

1) Adsorption Isotherms experiments: Stock solution of 1000 mg/L of standardized Cr(VI) was prepared from K₂Cr₂O₇ in double distilled-deionised water. Adsorption experiments were carried out using a temperature controlled incubator shaker set at 100 rpm maintained at 25°C for 6 h. A known amount of functionalized adsorbent (100 mg) was thoroughly mixed with 100 mL of respective Cr(VI) solution keeping the concentrations in the range of 10 - 500 mg/l and 2 pH using either hydrochloric acid (5 N) or sodium hydroxide (1 M). The solution (ml) to adsorbent (g) ratio was kept as 1000. The mixtures were stirred at 25, 35 and 45° C. After shaking the flasks for the required time, the suspensions were filtered through Whatman 0.45 mm filter paper and the filtrates were analyzed for Cr(VI) concentration using DNPH method and analyzed by UV spectrophotometer. The % of metal ions removed was calculated by the following equation:

$$R = (C_0 - C_e / C_0) \times 100 \dots \dots \dots (1)$$

The equilibrium adsorption of metal ion solution by amino functionalized silica was measured after 6 hrs of contact time. The amount of Cr (VI) adsorbed per gram of the adsorbent was calculated by the difference between the initial and the final readings using equation (2).

$$q_e \text{ (mg/g)} = (C_0 - C_e \text{ (mg/L)}) \times V \text{ (L)} / W \text{ (g)} \dots \dots \dots (2)$$

where q_e is the equilibrium adsorption capacity of adsorbent in mg of metal /g of adsorbent, C₀ and C_e are the initial and equilibrium concentration of metal ions in mg/L respectively, V is the volume of metal ions and W is the weight of adsorbent in gram. The analysis of equilibrium data was carried out using linear form of Langmuir, Freundlich and Temkin equations. The linear forms of the Langmuir, Freundlich and Temkin equations are

$$C_e / q_e = 1 / Q_0 b + C_e / Q_0 \dots \dots \dots (3)$$

$$\log q_e = \log k_F + 1/n \log C_e \dots \dots \dots (4)$$

$$q_e = A + B \ln C_e \dots \dots \dots (5)$$

Where b (L/mg) is the Langmuir adsorption constant and Q₀ (mg/g) is the Langmuir monolayer sorption capacity. 1/n is the Freundlich constant related to surface heterogeneity and k_F (mg/g) is the Freundlich sorption capacity. q_e and C_e are previously denoted, while A and B are Temkin constants.

III. RESULT AND DISCUSSION

A. Surface Area

The porosity of the synthesized silica with variable % of yeast (20%-80%) was investigated by nitrogen sorption analysis. A remarkable increase in surface area, pore size and pore volume was seen on adding yeast. As seen from Table.1, the BET specific surface area shows a consistent increase from 204.5 to 342.6 m² g⁻¹ while pore volume increased from 0.279 to 0.867 cm³ g⁻¹ as the % of yeast increased from 20% to 50%. It was observed that SY50 showed a maximum surface area with 50% yeast, while SY80 showed a reduced value (157.2 m² g⁻¹) of surface area and pore volume (0.411 cm³ g⁻¹). The increased surface area can be attributed to the formation of spherical, isolated nanospheres with increased density of pores leading to higher pore volume and surface area in the silica matrix. In contrast, the samples containing only yeast showed a substantial increase in pore diameter and a maximum pore diameter of 21.14 nm was obtained for Y80 compared to samples containing starch and yeast. Moreover the samples without starch were not spherical but displayed a structure of

TABLE I TEXTURAL CHARACTERISTICS OF SILICA AND FUNCTIONALIZED SILICA

Sample Name	Weight % of added starch	Weight % of added Yeast	Pore diameter (nm)	BET Surface area (m2/g)	Pore volume (cm3/g)
SY20	50	20	6.06	204.5	0.279
SY30	50	30	6.93	212.7	0.367
SY40	50	40	7.46	243.5	0.367
SY50	50	50	8.01	342.6	0.867
SY80	50	80	8.93	157.2	0.411
Y80	0	80	21.14	45.3	0.189
FSY50	50	50	2.98	51.0	0.145

A large decrease in pore volume and pore diameter after functionalization in FSY50 can be attributed to higher extent of functionalization (2.86 mmol g⁻¹) confirming that the functionalization must be occurring inside the mesopore channels. The controllable synthesis protocol and the mesoporous structure with high pore diameter and tunable pore volume makes them a suitable material in the

field of catalysis and adsorption. It was found that when starch content was lowered, then the slurry showed a low viscosity and the bubbles generated during foaming created interconnected pore network . This type of pore network might have generated during foaming, allowing the bubbles to coalesce with each other. In contrast, on increasing the % of starch, the high viscosity of the slurry

hindered foam enlargement resulting in smaller and irregular pore sizes.

B. FTIR

Fig. 1 shows the FTIR spectra of un-calcined silica (USY50), calcined silica (SY50), Functionalized silica (FSY50) without and with adsorbed chromium (FSY50Cr). All the samples show two strong absorption bands around 1100 cm^{-1} , 790 cm^{-1} attributed to asymmetric and symmetric stretching of Si-O-Si bonds while an Si-O bending vibration is seen at 478 cm^{-1} [23, 24]. The stretching vibration of Si-OH observed around 983 cm^{-1} was most prominent for uncalcined samples, less intense after functionalization and was found to shift to 993 cm^{-1} after Cr(VI) adsorption indicating that most of the Si-OH bonds on the inner surface of SY50 got occupied during modification. As supporting evidence, (Fig 1c) shows a few characteristic bands after functionalization like NH_2 scissor bands around 1097 cm^{-1} and 1558 cm^{-1} , increased intensity of C-H stretching vibrations at 2883 cm^{-1} after functionalization. The band at 896 cm^{-1} seen in (Fig 1d) signifies the presence of Cr(VI) bound silica [25].

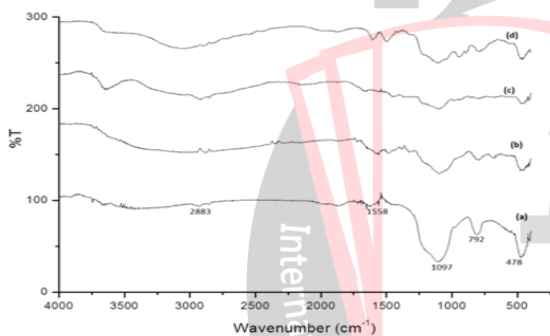


Fig.1 FTIR spectra of (a) un-calcined silica (USY50), (b) calcined silica (SY50), (c) Functionalized silica (FSY50), (d) Functionalized silica with adsorbed chromium (FSY50)

C. TGA

TGA analysis for the as synthesized SY50 is shown in Fig. 2. The analysis was done between 25 and $750\text{ }^\circ\text{C}$ and three distinct weight losses were observed. The first weight loss due to adsorbed water occurred at temperature of 105°C . The second weight loss around $270\text{--}310\text{ }^\circ\text{C}$ may be associated with the release of water and residual organic substrate like yeast and starch. The third weight loss observed from $390\text{ to }490^\circ\text{C}$ is attributed to the thermal decomposition of organic substrate.

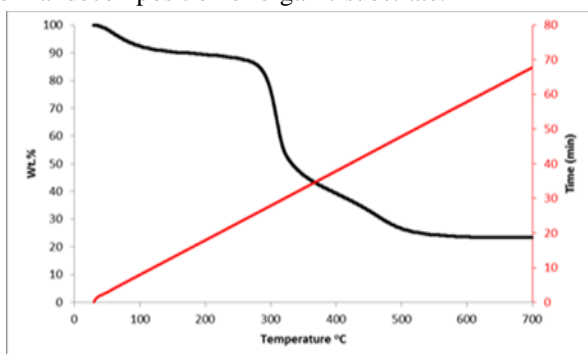


Fig. 2 Typical TGA profile for SY50

D. XRD

XRD patterns in Fig. 3 shows a prominent peak at $2\theta = 1.0\text{--}4.0^\circ$ and some broad peaks at $2\theta = 4.0\text{--}10.0^\circ$. An intense peak (100) is observed at 2θ value of 1.5° for SY50 along with a weak (110) reflection. These reflection patterns are attributed to 2D hexagonal structure of mesoporous material. However after amine functionalization as seen from Fig 3b, a significant decrease in intensity was observed for (100) reflection ..

The presence of a broad (100) diffraction peak as well as weak (110) reflection in both functionalized as well as non-functionalized sample indicates that functionalization did not change the mesoscopic order. Apart from a nominal decrease in $d(100)$ value from 6.52 to 5.76 nm and a small change in unit cell parameter from 7.54 to 6.65 nm , no other change was observed in XRD pattern. Hence it can be concluded that an ordered structure must have been maintained after functionalization.

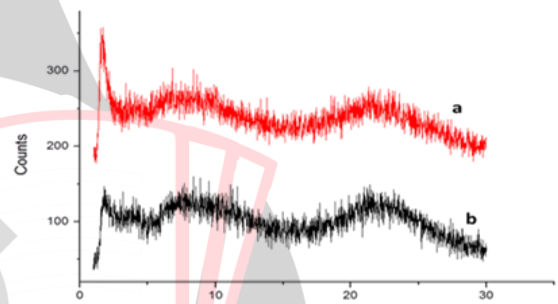
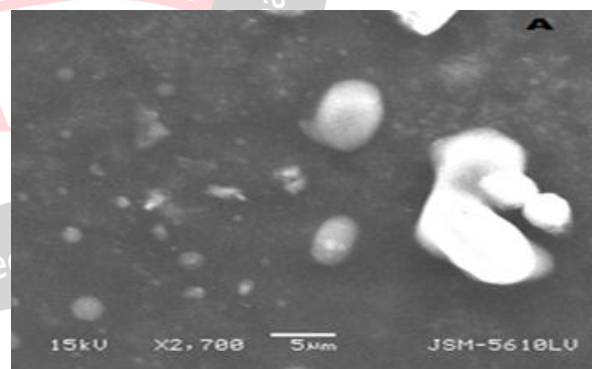


Fig. 3 XRD patterns of (a) silica (SY50) calcined at $550\text{ }^\circ\text{C}$ and (b) Functionalized silica (FSY50).

D. Morphology Studies



SEM micrograph of SY50 as shown in Fig 4 A shows that all the silica particles are in nanometer range. The calcined samples retained the morphology even after the biotemplate was removed. The functionalization did not led to bulky silica nanoparticles. However, as seen from Fig 4B, the morphology of the particles of the solid obtained with low % of yeast shows large agglomerated particles with irregular morphology along its non-porous surface.

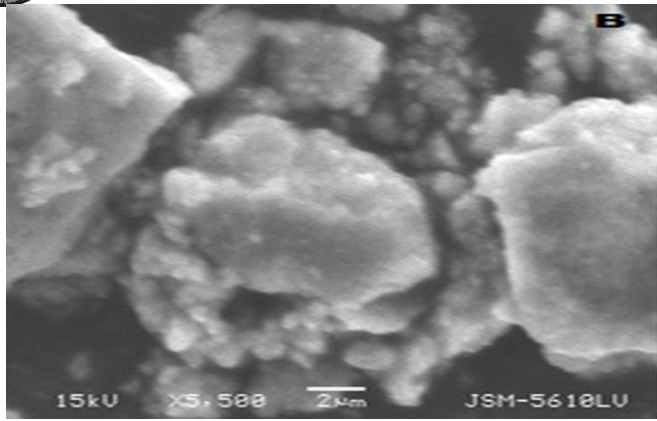


Fig. 4 SEM images of silica prepared:(A) SY50 (B) FSY50

E. Adsorption of Cr(VI)

Adsorption isotherm: Fig.5 shows the equilibrium adsorption isotherms of Cr(VI) on FSY50 adsorbent at 2 pH under different temperatures. The adsorption capacity increased significantly with the equilibrium Cr(VI) concentration from 0 to 300 mg/ L. There was a steep increase seen in adsorption capacity up to 96.8 mg/g but was relatively slow when equilibrium Cr(VI) concentration was increased. This was suggestive of favorable adsorption of Cr(VI) at concentrations around 100 mg/l. The isotherm data was fitted using the Langmuir, Freundlich and Temkin isotherm models. Table. 2 shows the calculated adsorption parameters and correlation

coefficient (R^2) for the three isotherm models by linear regression.

Fig. 6 shows single continuous Langmuir isotherm plots at different temperatures as compared to nonlinear Freundlich and Temkin graphs. Based on the correlation coefficient (R^2) value it was found that the experimental data of Cr(VI) adsorption could be described best by the Langmuir model. The correlation coefficient of the isotherm models followed the order: Langmuir > Temkin > Freundlich. The value of Q_{max} was found to increase with increasing temperature, thus confirming the involvement of endothermic process for the removal of chromium. Langmuir capacities were calculated using eq.3. Hence the adsorption must be taking place through a monolayer coverage following Langmuir adsorption isotherm. The large pore size generated by pore forming agent yeast facilitated ion diffusion and increased adsorption. Table 3 shows a comparative analysis on Cr(VI) adsorption capacities of FSY50 adsorbent compared to other adsorbents.

TABLE II LANGMUIR, FREUNDLICH AND TEMKIN CONSTANTS FOR CHROMIUM (VI) ADSORPTION ON FSY50 ADSORBENT

Temp (°C)	Langmuir Isotherm			Freundlich Isotherm			Temkin isotherm		
	Q_{max}	b	R^2	n	K_f	R^2	A	B	R^2
25°C	250	0.085	0.999	2.315	26.3	0.907	37.21	33.35	0.978
35°C	250	0.125	0.999	2.392	32.2	0.885	50.53	35.19	0.984
45°C	333	0.136	0.998	2.398	38.9	0.879	72.4	37.06	0.987

TABLE III COMPARATIVE ADSORPTION CAPACITIES OF VARIOUS SILICA BASED ADSORBENTS USED FOR Cr(VI) ADSORPTION

Adsorbent	Pore size (nm)	Pore volume ($cm^3 g^{-1}$)	SBET ($m^2 g^{-1}$)	Nitrogen content (mmol of N/g)	Maximum loading (mmol of Cr (VI) g^{-1})	Reference
ZSM 5	---		215		0.205	8
NN- Silica	4.4	0.09	54.5	2.73	3.32	9
N-MCM-41	2.8	0.238	1037	1.46	1.017	5
NN-MCM-41	2.63	0.135	586	2.76	0.79	5
NSBA-1	2.66	0.158	689	1.9	1.8	5
NN SBA-1	2.48	0.139	606	3.33	1.54	5
NNN SBA-1	2.4	0.036	126	4.05	1.1	5
NH ₂ UVM-7	2.62	0.27	626	4.83	3.69	10
FSY50	2.98	0.145	51	2.86	3.8	This study

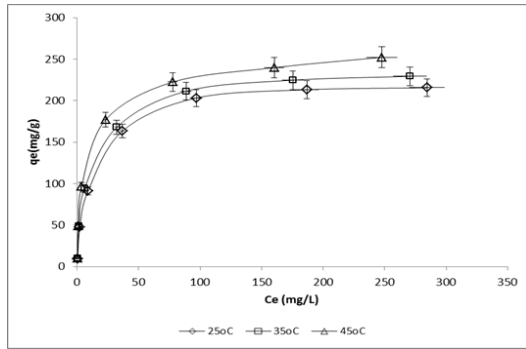


Fig. 5 Equilibrium adsorption isotherms of Cr(VI) onto FSY50

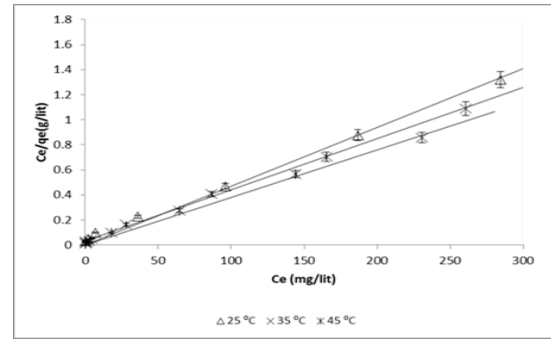


Fig. 6 Langmuir isotherm model of Cr(VI) onto FSY50 at 25°C, 35°C and 45°C

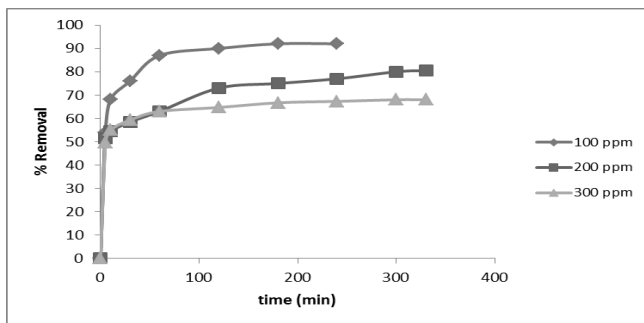


Fig. 7 Percentage removal of Cr(VI) on FSY50 adsorbent as a function of contact time

IV. CONCLUSION

Amino functionalized silica nanospheres have been successfully synthesized with tunable pore diameter of 8.01 nm, specific surface area of $\sim 342.6 \text{ m}^2/\text{g}$ and a pore volume in the range of $0.867 \text{ cm}^3/\text{g}$ having a maximum amino loading of 2.86 mmol/g. In the present work the large pore size of the adsorbent generated by green synthesis, facilitated a much better Cr(VI) adsorption due to increased ion diffusion. 92.3 % of Cr(VI) was removed in less than 300 min. Isotherm data related to adsorption of Cr(VI) onto the FSY50 at various temperatures ranging from 25 to 45 °C showed good linearity with a high correlation coefficient ($R^2=0.999$). The material may find its application in other areas including catalysis and separation.

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REFERENCES

[1] G.M. Haggerty, R.S. Bowman, Sorption of chromate and other inorganic anions by organo-zeolite, Environ. Sci. Technol. Vol 28, no.3, pp 452-458, March 1994.
[2] Z. Li, R. Bowman, Counterion effects on the sorption of cationic surfactant and chromate on natural clinoptilolite, Environ. Sci. Technol. Vol 31, no.8, pp 2407-2412, July 1997.

[3] I. Han, M.A. Schlautman, B. Batchelor, Removal of hexavalent chromium from ground water by granular activated carbon, Water Environ. Res. Vol 72, no.1, pp 29-39, Jan 2000.
[4] X Feng, G.E. Fryxell, L.Q. Wang, A.Y. Kim, J.K. Liu, M. Kenner, Functionalized Monolayers on Ordered Mesoporous Supports, Science Vol 276, no. 5314, pp 923-926, May 1997.
[5] J.M. Rosenholm, A. Peninkangas, M. Linden. Amino-functionalization of large-pore mesoscopically ordered silica by a one-step hyperbranching polymerization of a surface-grown polyethyleneimine Chem Commun. Vol 37, pp 3909-3911, 2006.
[6] H. Yoshitake, T. Yokoi, T. Tatsumi, Adsorption of Chromate and Arsenate by Amino-Functionalized MCM-41 and SBA-1, Chem Mater Vol 14, no.11, pp 4603-4610, Nov 2002.
[7] L. Mercier, T.J. Pinnavaia, Access in mesoporous materials: Advantages of a uniform pore structure in the design of a heavy metal ion adsorbent for environmental remediation Adv Mater. Vol 9, no. 6, pp 500-503, Jun 1997.
[8] M. Ghiaci, R. Kia, A. Abbaspur, F. Seyedejn-Azad, Adsorption of chromate by surfactant-modified zeolites and MCM-41 molecular sieve, Sep. & Purif. Technol. Vol.40, no.3, pp 285-295, Dec 2004.
Li. Jiansheng, M. Xiaoyu, H. Yanxia, Z. Jiangyan, S. Xiuyun, W. Lianjun. Synthesis, amino-functionalization of mesoporous silica and its adsorption of Cr(VI), Journal of Colloid and Interface Science. Vol.318, no. 2, pp 309-314, Feb 2008.
[9] H. Shir Khanloo, A. Khaligh, F. Golbabaei, Z. Sadeghi, A. Vahid and A. Rashidi, On-line micro column preconcentration system based on amino bimodal mesoporous silica nanoparticles as a novel adsorbent for removal and speciation of chromium (III, VI) in environmental samples, Journal of Environmental

- Health Science & Engineering.Vol 13,no.47,pp , Dec2015.
- [10] E.V. Datskevich, V.I. Shutova, V.V.Goncharuk, Determination of the conditions of the sol-gel synthesis of biosorbents for water treatment, Russ. J. Appl.Chem. Vol.80, no.9, pp.1529-1534, Sep 2007.
- [11] R.M. Grudzien, B.E. Grabicka and M. Jaroniec, Adsorption studies and thermal stability of SBA-16 mesoporous silicas, Applied Surface Science, Vol.253, no. 13, pp. 5660-5665, Jan 2007.
- [12] T. Clark, J.D. Ruiz, H. fan, C.J. Brinker, B. I. Swanson, A.N. Parikh, A New Application of UV–Ozone Treatment in the Preparation of Substrate-Supported, Mesoporous Thin Films, Chem. Materials, Vol.12, no.12, pp. 3879-3884, Dec 2000.
- [13] L. Xiao, J. Li, H. Jin, R.Xu, Removal of organic templates from mesoporous SBA-15 at room temperature using UV/dilute H₂O₂, Microporous and Mesoporous Materials. Vol.96, no 1-3, pp. 413-418, Nov 2006.
- [14] Y. Wei, D. Jin, T. Ding, W. Shih, X. Liu, S.Z.D. Cheng, Q. Fu, A Non-surfactant Templating Route to Mesoporous Silica Materials, Advanced Materials, Vol. 10, no. 4, pp.313-316, March1998.
- [15] G. Crini, M. Morcellet, Synthesis and applications of adsorbents containing cyclodextrins. J Sep Sci .Vol. 25, no.13,pp. 789–813, Sept 2002.
- [16] M.Ghoul, M. Bacquet, M. Morcellet.Uptake of heavy metals from synthetic aqueous solutions using modified PEI-silica gels. Water Res.Vol.37, no. 4, pp. 729–734, Feb 2003.
- [17] Y.Fan, Y.Q. Feng, S.L.Da,. On-line selective solid-phase extraction of 4-nitrophenol with β-cyclodextrin bonded silica. Anal Chim Acta.Vol.484,no.2, pp.145–53, May 2003.
- [18] T.N.T.Phan, M.Bacquet, M.Morcellet, Synthesis and characterization of silica gels functionalized with monochlorotriazinyl b-cyclodextrin and their sorption capacities towards organic compounds, J Inclusion Phenom Macrocylic Chem.Vol.38, no. 1, pp.345–359, Dec 2000.
- [19] A. B. Sifontes, , G.Gonzalez,E. Canizales,N.V. Gustavo. Biosynthesis of amorphous mesoporous aluminophosphates using yeast cells as templates, Materials Research Bulletin,Vol.48,no.2,pp.730–738, Feb 2013.
- [20] B. Bai, W. Guan, Z. Li, G. Li Puma, Bio-template route for facile fabrication of Cd(OH)₂-yeast hybrid microspheres and their subsequent conversion to mesoporous CdO hollow microspheres.Mater. Res. Bull. Vol.46, no.1, pp.26–31,Jan 2011.
- [21] L. Ruben. Menchavez , Lori-Ann S. Intong Red clay-based porous ceramic with pores created by yeast-based foaming technique, J Mater Sci Vol.45, no.23, pp.6511–6520, Dec 2010.
- [22] K.Y. Ho, G McKay, K.L.Yeung, Selective Adsorbents from Ordered Mesoporous Silica, Langmuir Vol.19, no.7,pp. 3019-3024, April 2003.
- [23] A.Skaf, G. Nassar, F.Lefebvre, B. Nongaillard, A new acoustic technique to monitor bread dough during the fermentation phase, J Food Engg, Vol.93, no.3,pp.365-378,Aug 2009.
- [24] A.Jitianu, M. Crisan, A.Maghea, M.Zaharescu, Influence of the silica based matrix on the formation of iron oxide nanoparticles in the Fe₂O₃–SiO₂ system, obtained by sol–gel method, J Mater. Chem.Vol.12, pp. 1401-1407, 2002.
- [25] J.S.Beck, J.C.Vartuli, W.J.Roth, M.E. Leonowicz,C.T.Kresge, K.D.Schmitt.et al., A new family of mesoporous molecular sieves prepared with liquid crystal templates,J. Am. Chem.Soc., Vol.114, no. 27, pp.10834-10843,Dec 1992.