J. Adv. Chem. Sci. - Volume 3 Issue 2 (2017) 465–468

Share Your Innovations through JACS Directory

Journal of Advanced Chemical Sciences

Visit Journal at http://www.jacsdirectory.com/jacs

ISSN: 2394-5311

Chemically Modified Silica Microparticles as Sorbents for PCB Detection and Direct Fenton Oxidation

R. Vijayalakshmi*, R. Gayathri, S. Chenchurani, D. Abiya

Quaid E Millath Govt College for Women, Anna salai, Chennai – 600 002, Tamil Nadu, India.

ARTICLE DETAILS

Article history:
Received 29 April 2017
Accepted 25 May 2017
Available online 29 July 2017

Keywords:
Rice Husk
Silica Nanoparticles
Fenton Oxidation
Surface Modified Silica

ABSTRACT

A greener process involving sol-gel method was adopted to prepare structurally controlled non-crystalline silica particles from rice husk collected from the local regions of Tamil Nadu. The experimental conditions were optimized and silica particles were characterized by BET with surface area of 320 ± 10 m^2/gm and from the SEM measurements, the micro particles mean size range from 120 ± 10 nm respectively. The average pore size of the mesoporous powder obtained was measured to be 8 ± 2 nm. The mesoporous silica was surface modified hydrophobically utilizing phenyl triethoxysilane (PTEOS) and ultra-sonication. Using FTIR and SEM measurements the surface modifications were characterized. These silica sub micro particles with hydrophobic templates were used as sorbents for adsorption of PCB. Using the direct treatment of PCB sorbed chemically modified silica sub micro particles with fenton reagent, the degradation studies on PCB was performed. The degradation percentages dependence with sorbent feed loadings were measured by the analysis of the degraded products. The sub micro silica particles with surface chemical modifications have proved to be efficient solid matrix for the removal of PCB, in the aqueous phase at ambient conditions.

1. Introduction

The use of spherical nano silica particles as sorbents of eco deadlier pollutants and as well as a catalytic booster for the subsequent degradation of adsorbed pollutants has been a recent progress in advanced oxidation processes for environmental greener cleaning routes [1]. However stages involving cost effective synthesis of nanosilica particles, reduction in sorbent production time and effective degradation of hydrophobic pollutants are some of the challenges to be resolved [2-6]. Presently rice husk raw materials have been reported to contain nearly 20% of silica source [7,8]. In the present work employing rice husk, microporous nanosilica particles are prepared adopting pyrolysis followed by sol gel method involving ethanol, phosphoric acid and sequential precipitating procedures [9]. The nano silica microporous powders are size characterized by SEM and while the surface area data are measured using N_2 adsorptions/desorptions. The isotherm are constructed by an automatic surface area and pore size BET analyser.

In order to modify the surface of the as synthesized silica particles chemical modification process with phenyl triethoxysilane (PTEOS) was adopted [10]. Greener reaction pathway employing rice husk ash and PTEOS aqueous solutions aid the removal of eco-deadlier solvents, and hydrophobically template microporous nanosilica spheres [11]. The chemically surface modified silica nanopowders are analyzed using FTIR and SEM measurements. The hydrophobically surface modified nanosilica particles are used as sorbents for efficient adsorption of PCB followed by oxidative degradation of adsorbed PCB by decomposition by Fe^{3+} catalyst producing hydroxyl radicals. These radicals undergo a series of nonspecific oxidation of organic compounds (RH) via transitory organic radical intermediates [14,15].

$$H_2O_2 + Fe^{2+} \rightarrow OH^{\cdot} + OH^{-}\ Fe^{3+}$$

$$RH + OH^{\cdot} \rightarrow R^{\cdot} + H_2O$$

PCB sorbed hydrophobically surface modified microprorous nanosilica powders are treated with excess prestandardized fenton solution and the unconsumed Fe^{2+} is quantitatively assayed. The standard fenton procedure applied to the waste water estimations has been chosen [16]. The percentage fenton chemical oxidation proportionate to the PCBs are repeated without the nanosilica particles and the percentage of effective removal of PCBs are determined. The salient results are discussed.

2. Experimental Methods

2.1 Materials and Methods

Commercial samples of PCB from Fluka and rice husk fresh samples from the paddy mills of Poonamalle Township, near Chennai, Tamilnadu were purchased. Fenton reagent from Fischer chemicals was procured and standardised. PTEOS and phosphoric acid were sigma samples. The experimental procedures for the preparation of nanosilica powders from rice husk by sol-gel method was followed as reported in literature [9, 17-23]. The procedure for chemical modification of the nanoparticles with PTEOS is discussed below. Oxidative degradation of the sorbed PCBs onto the surface modified nanosilica particles by direct fenton process are exactly followed as reported in the literature [10].

2.2 Preparation of Sodium Silicate from Rice Husk

The rice husk was treated with diluted HCl to remove the metallic impurities. The solution was filtered, and the residue was dried in an oven for 12 hrs at 110 °C. The dried rice husk was placed in an electric furnace for 5 hrs at 60 °C for complete combustion to produce the rice husk ash (RHA). The dried ash was added to a teflon flask containing 10 wt% of NaOH and boiled at 90 °C for 1 hr with constant stirring. Finally the mixture was cooled and filtered to obtain the sodium silicate.

2.3 Preparation of Silica Particles

Sodium silicate and ethanol was mixed in the ratio as 1:0.25 mL and stirred for 10 minutes after the addition of water. The mixture was titrated with phosphoric acid until a gel was formed. Also the pH was adjusted to neutral value. The yellowish gel obtained, was centrifuged and washed with water to remove the impurities. The sample was dried and calcined in a furnace to obtain the silica powder.

---

*Corresponding Author
Email Address: vijiradha68@gmail.com (R. Vijayalakshmi)

Cite this Article as: R. Vijayalakshmi, R. Gayathri, S. Chenchurani, D. Abiya, Chemically modified silica microparticles as sorbents for PCB detection and direct fenton oxidation, J. Adv. Chem. Sci. 3(2) (2017) 465–468.

2.4 Surface Modification of Mesoporous Silica Particles with PTEOS

With few grams of silica powder 20 mL of ethanol, 10 mL of deionized water, 5 mL of phosphate buffer, 2 mL of ammonium hydroxide solution were added and rotated in a rotator for 2 hrs at room temperature. This solution was named as solution "A". In another tube 30 mL of ethanol, 5 mL of deionized water, 2.5 mL of PTEOS and 2 mL of ammonium hydroxide was added and rotated for ½ an hour at room temperature. This solution was named as solution "B". After 2 hrs solution A was removed centrifuged and the supernatant decanted. Now the B solution was added to the A solution and rotated overnight at room temperature. The solution was centrifuged and the supernatant was decanted. The modified particles was washed with 20 mL of 50:50 ethanol and rotated for 5 minutes. The process was repeated with 30:70 mL of ethanol and deionized water and 0.1 M phosphate buffer was used to adjust the pH to neutral condition. The supernatant was discarded and particles were transferred to 100 mL evaporating basin and oven dried overnight. Once dried the soft lumps of the fine powder was broken and stored in an air tight container for further use.

2.5 Characterization

Types of bonds present in the particles were determined using FTIR. The spectra were recorded using a Perkin – Elmer spectrometer. X – Ray diffraction (XRD) of the synthesized silica nanoparticles was obtained by using an (XRD Brucker diffractometer). The diffraction patterns were obtained in the 2θ range from 3°-50°. The Morphology of silica particles was observed by scanning electron microscopy (SEM) using HITACHI S4800 microscope.

2.6 Adsorption Studies

Adsorption of PCB on to the chemically modified silica nanoparticles are carried out to obtain the equilibrium data. Various concentrations of freshly prepared solution of the PCBs in ethanol, and modified silica nanoparticles was prepared. Adsorption was achieved by adding a known amount of adsorbent, adsorbate (PCB), pH and temperature. After stirring and equilibration for 1hour the supernatant liquid is analyzed using UV-spectroscopy, at a wavelength of 215 nm. The percentage adsorption and amounts of PCBs adsorbed at equilibrium are calculated using the following equation.

$$\text{Adsorption } \% = (C_0\text{-}C_t/C_0) \times 100$$

$$Qe = (C_0 – C_e)/m \times V$$

where C_0, C_t, C_e are the concentrations at the initial, at a time t, and at equilibrium, V is the volume of the solution in liters and m is the adsorbent mass in grams.

3. Results and Discussion

3.1 Characterization of Microporous Nano Silica Particles

Figs. 1(a, b) depicts the SEM images of nanosilica particles and the chemically modified silica particles using PTEOS in the as synthesized conditions. The average size of the approximately 300 particles considered for measurement fall in the range of 120 ± 1 nm. Fig. 1(c) shows the SEM images of chemically modified particles. Difference in the Fig. 1(b) and (c) images clearly depicts the difference in the chemically modified samples of the nano silica spheres from that of the PCB sorbed chemically modified nanosilica spheres.

Fig. 2 exhibits the XRD pattern of amorphous nano silica powder to evaluate the amorphous nature of the silica nanoparticles X–Ray diffraction studies were done. The results showed that the material was 98% of the amorphous form. The XRD patterns show a broad peak centered 2 = 22°, which is associated with amorphous silica. The lack of sharp peaks indicates the absence of any ordered crystalline structure. The fact that the absence of a peak around 26° 2 confirms the absence of crystalline quartz.

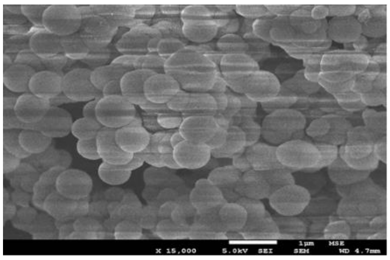

Fig. 1(a) SEM images of nano silica particles

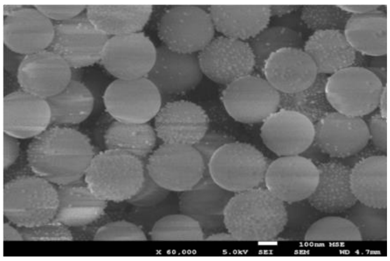

Fig. 1(b) SEM images of chemically modified nano silica particles using PTEOS

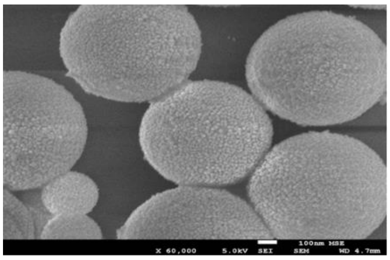

Fig. 1(c) SEM images of PCB sorbed modified nano silica particles

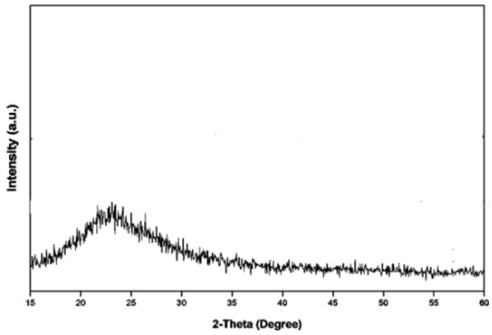

Fig. 2 XRD pattern of amorphous nano silica powder

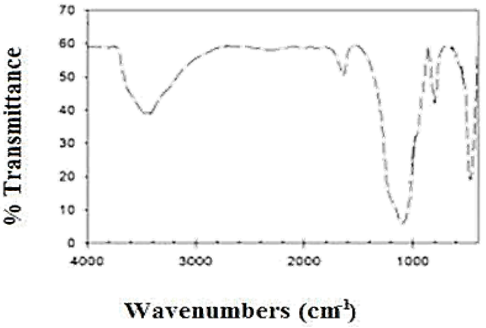

Fig. 3(a) FTIR spectrum of silica nano particles in KBr pellets at 25 °C

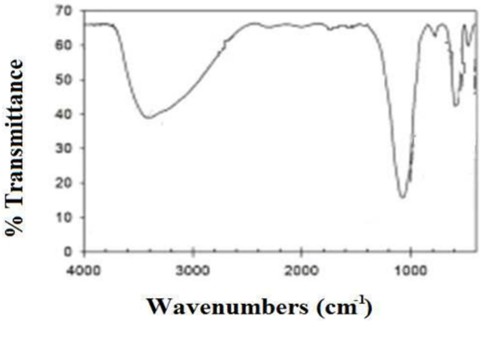

Fig. 3(b) FTIR spectrum of PCB adsorbed modified silica nano particles

Fig. 3(a) presents the infrared spectra of the silica that was examined by FTIR in the range of 4000 – 400 cm^{-1}, the major chemical groups of silica are identified. The predominant absorbance peaks at ≈1107 cm^{-1} corresponds to the symmetric vibrations of the siloxane bond, Si – O – Si. The bands located at ≈802 cm^{-1} and 477 cm^{-1} are assigned to the Si -O symmetry stretching vibration and bending vibration respectively. The band at 3200 cm^{-1} is ascribed to the SiO– H asymmetry stretching vibration and bending vibration respectively. The band at 1635 cm^{-1} belonged to the

- OH stretching vibration of the silanol or adsorbed water molecules on the silica surface [24].

Fig. 3(b) depicts the FTIR spectrum of the PCB adsorbed chemically modified silica nanoparticles using PTEOS. Absence of the band at 1635 cm^{-1} due to the absorbed water molecules and the presence of the additional peak at 634 cm^{-1} confirms the modification of silica particles by PTEOS and adsorption of PCB. Fig. 4 shows the nitrogen adsorption isotherm for the synthesized nanosilica particles. The physical properties of the silica nanoparticles are shown in Table 1.

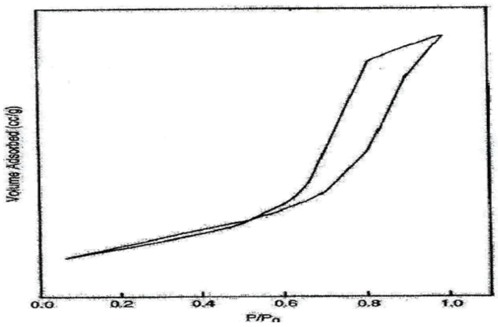

Fig. 4 Nitrogen BET adsor ption spectrum of synthesized silica nano particles

Table 1 Surface area of as synthesized silica nanoparticles obtained by BET and their textured properties

BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
327	0.81	8.2

According to the IUPAC classification, the prepared silica can be classified as mesoporous materials because the pore size was in the range of 2 – 50 nm [25, 26]. Thus the characterization results confirm that the amorphous silica of high purity and relatively high surface area can be prepared from rice husk ash and will have a greater potential for adsorption on its surface.

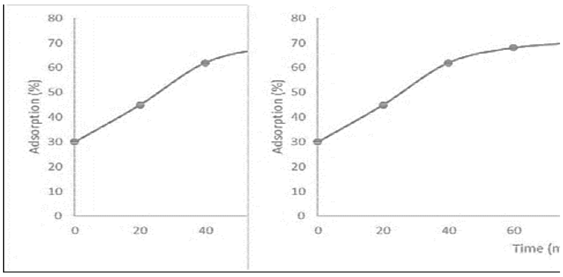

Fig. 5 Effect of equilibration time on PCB adsorption on to modified silica nano particles at 25° C. mo dified silica [1 mg], PCB 6 mg/L

Fig. 5 depicts the effect of contact time on PCB adsorption to the modified silica nano particles in order to optimize the equilibration time. 1 mg of the adsorbent was treated with 250 mL of PCB solution with 6 mg/L concentration at 25 °C. The mixture was shaken during different times and left for 2 hrs and then analyzed. Rapid adsorption was observed during the first 30 min of contact time and no significant change in PCB was observed after 60 minutes. Therefore, 60 min was selected as the equilibrium time. The PCB sorbed chemically modified mesoporous nano silica particles are collected and solvent dried.

The adsorption of PCB carried out at different initial concentration from 2 mg/L to 10 mg/L on to the chemically modified silica nanoparticles at 25 °C. As shown in Fig. 6 when the initial concentration increases from 2 to 6 mg/L, the adsorption increases from 32% to 70%. Thus the equilibrium concentration is maintained as 6 mg/L.

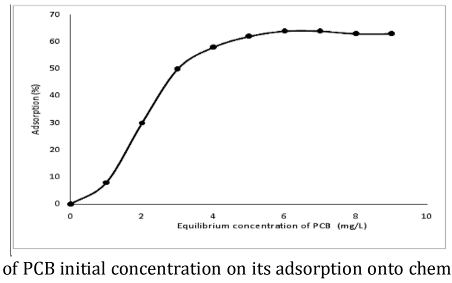

Fig. 6 Effect of PCB initial concentration on its adsorption onto chemically modified silica nano particles at 25° C. contact time 60 min , modified silica [1 mg]

3.2 Direct Fenton Oxidation

Prior studies on fenton oxidation of PCBs, H_2O_2 in fresh solutions are estimated by means of Merkoquant test, which detects peroxides accurately in the concentration range 1 to 100 mg/L of H_2O_2 .The standard experiment was carried out with 10% H_2O_2 and 400 ppm Fe solution for 10 mL of 10 mM PCB solution. After equilibration with 4 hrs. 85% removal of PCB was detected, in the absence of nano silica powder sorbents. Upon adopting same experimental conditions and incorporating 1 mg of silica nanoparticles for 10 mL of 10 mM of PCB solution within 1 hour of equilibration period 92% removal of PCB was detected. These results motivated us, to directly treat the PCB sorbed chemically modified nano silica particles with fenton oxidation process. By doing so, it was found out that 99% removal of PCB was detected. The PCB removed nanosilica powders are tested for recycling capacity and PCB sorption studies are repeated. Nearly 4 times the surface modified nanosilica powders can be recycled and further usage reduced the PCB degradation to 80% efficiency. The reason for decreasing activity may be due to agglomeration of nano silica and as well as due to pore blocks, leading to decrease in the micro porosity of nanosilica powders. In Table 2, the removal percentages of PCB by direct fenton process under various conditions of sorbents are given. It was also found out that the equilibration time for 99% removal of PCB is also decreased considerably from 4 to 1 hour, when the modified nanosilica sorbents are used at ambient temperature conditions.

Table 2 Removal percentage of PCBs under various sorbents conditions with direct fenton oxidation at 25 °C [PCB]=6 mg/L

S.No	Category	Time of equilibration	% fenton chemically oxidation	No. of cycles
1.	10% H_2O_2 and 400 ppm Fe^{3+}	4 hrs	85%	-
2.	Microporous nanosilica particle	1 hrs	93%	2
3.	Surface modified microporous nanosilica paticles	1 hrs	99%	4

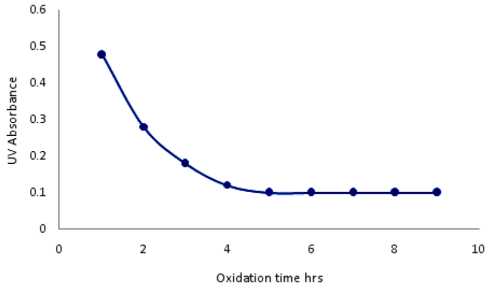

Fig. 7 UV$_{215}$ Absorbance of oxidation of PCB at various reaction times at 25 °C

4. Conclusion

The results of the present study demonstrated the efficient (> 98%) removal of PCBs by simple direct fenton process by utilising chemically modified microporous nanosilica powders. Size characterizations of nano silica powders prepared from rice husk materials followed by surface modification with hydrophobic groups are carried out and confirmed from SEM measurements. Hydrophobically surface modified nanosilica powders sorbed PCBs are thus activated and were degraded efficiently when subjected to direct fenton process.

Acknowledgment

The authors acknowledge the financial support from Tamil Nadu State Council of Higher Education, Tamil Nadu.

References

[1] P.T. Williams, N. Nugranad, Comparison of products from the pyrolysis and catalytic of rice husks, Ener. 25 (2000) 493-513.

[2] S. Rengaraj, M. Seuny- Hyeon, R. Sivabalan, Agricultural solid waste for the removal of organics: adsorption of phenol from water and waste water by Palm seed coat activated carbon, Waste Management 22 (2002) 543-548.

[3] M. Street, J.W. Patrick, M.J. Camporroperez, Sorption of phenol and p-cholorophenol from water using convention and novel activated carbons, Water Sci. Res. 29 (1995) 467-471.

[4] Z. Assu, J. Yen, A comparative adsorption/biosorption study of Mono-cholorinated phenols on to various sorbent, Waste Manag. 21(2001) 695-702.

Cite this Article as: R. Vijayalakshmi, R. Gayathri, S. Chenchurani, D. Abiya, Chemically modified silica microparticles as sorbents for PCB detection and direct fenton oxidation, J. Adv. Chem. Sci. 3(2) (2017) 465–468.

[5] S. Kumar, S.N. Upadhyay, Y.D. Upadhyay, Removal of phenols by adsorption on fly ash, J. Chem. Technol. Biotechnol. 37 (1987) 281-286.

[6] S. Srivastava, R. Tyagi, N. Pal, D. Mohan, Process development for removal of substituted phenol by carbonaceouse adsorbent obtained from fertilizer waste, J. Environ. Engg. 123 (1997) 842-848.

[7] N. Khalid, S. Ahmad, A. Toheed, J. Ahmad, Potential of rice husk for antimony removal, Appl. Radiat. Isotopes 52 (2000) 30-38.

[8] W. Nakbanpote, Preconcentration of gold by rice husk ash, Mineral. Engg. 13 (2000) 391-400.

[9] A.B. Ismail Rahman, D. Mohanmad, A. Husein, A green sol-gel route for the synthesis of structurally controlled silica particles from rice husk for dental composite filter, University of Science Malaysia, Ceramic Int. 39 (2013) 4559-4567.

[10] Prashanta Kumar Jal, Sabita Patel, Bilay Kumar Mishra, Chemical modification of silica surface by immobilization of functional groups for extractive concentration, Talanta 62 (2004) 1005-1028.

[11] S.K. Parida, P.K. Mishra, B.K. Mishra, Adsorption behaviour of cationic dyes on silica gel and on modified silica gel, Ind. J. Chem. 38 A (1999) 639-642.

[12] J.M. Quiroga, A. Rlaza, M.A. Manzano, Chemical degradation of PCB in the contaminated soils slurry: direct fenton oxidation and desorption combined with the photo-Fenton process, J. Enivron. Sci. Health A 44 (2009) 1120-1126.

[13] J.X Ravikumar, M.D. Gurol, Chemical oxidation of chlorinated organics by hydrogen peroxide in the presence of sand, Environ. Sci. Technol. 28 (1994) 394-400.

[14] R. Androzzi, V. Caprio, A. Insol, R. Marotta, Advanced oxidation processes (AOPs) for water purification and recovery, Catal. Today 53 (1999) 51-59.

[15] V.Y. Kavitha, K. Palanivelu, The role of ferrous ion fenton and photo-fenton processes for the degradation of phenol, Chemosphere 55 (2004) 1235-1243.

[16] E. Lipezynska-Kochany, Degradation of aqueous nitrophenols and nitrobenzene by means of the Fenton reactions, Chemosphere 22 (1991) 529-535.

[17] D. An, Y. Guo, B. Zou, Z. Wang, A study on the consecutive preparation of silica powders and active carbon from rice husk ash, Biomass bioener. 35 (2011) 1227-1234.

[18] Y. Liu, Y. Guo, Y. Zhu, D. An, Gao, A sustainable route for the preparation of activated carbon and silica from rice husk ash, J. Hazard. Mat. 86 (2011) 1314-1319.

[19] L. Dawei, Z. Xifeng, Short-period synthesis of high specific surface area silica from rice husk char, Mat. Lett. 65 (2011) 1528-1530.

[20] L. Dawei, D. Chen, X. Zhu, Reduction in time required for synthesis of high specific surface area silica from pyrolyzed rice husk by preparation at low pH, Biores. Technol. 102 (2011) 7001-7003.

Cite this Article as: R. Vijayalakshmi, R. Gayathri, S. Chenchurani, D. Abiya, Chemically modified silica microparticles as sorbents for PCB detection and direct fenton oxidation, J. Adv. Chem. Sci. 3(2) (2017) 465–468.