

Nanosilica synthesis and application for lead treatment in water

Nghiên cứu tổng hợp nanosilica và ứng dụng xử lý kim loại chì trong nước

Research article

Nguyen Xuan Huan*, Tran Nam Anh, Nguyen Thi Thuy Hang, Dao Thi Tuyet Nhung, Nguyen Van Thanh

Faculty of Environmental Sciences, VNU University of Science, Vietnam National University, Ha Noi, Vietnam

Lead is a naturally occurring element that has high atomic weight (207u) and density (11.3 g/cm³). Their multiple industrial, domestic, agricultural, medical and technological applications have led to their wide distribution in the environment, raising concerns over their potential effects on human health and the environment. At present, extensive application of nanosilica in environmental pollution treatment has led to the development of silica extraction methodologies out of various chemical and waste products. In this study, nanosilica is synthesized by sol-gel method from tetraethoxysilane (TEOS) with base catalysts and volumetric ratio TEOS/C₂H₅OH/H₂O/NH₄OH: 5/30/1/1 and identified characteristics by some modern techniques such as Energy-dispersive X-ray spectroscopy (EDX), Fourier Transformation Infrared (FTIR) and X-ray diffraction (XRD), Scanning electron micrograph (SEM), field emission scanning electron microscopy (FESEM). The results showed that the prepared SiO₂ nanoparticles were amorphous phase with the average size about 60-100 nm and can be used as an immediately utilization for lead treatment. At the pH of 5, shaking within 1 hours with speed 150rpm/min, lead treatment efficiency is 96.17% for initial Pb²⁺ concentration 10 mgPb²⁺/L. Maximum adsorption concentration Q_{max} = 30.3mg/g, and adsorbent and adsorbate constant b = 0.868 L/g. Therefore, extracted nanosilica from TEOS has high lead treatment efficiency. In addition, synthesis nanosilica from rice husk with similar characteristics is a new research approach to improve application and economic value of the material.

Chì là nguyên tố tự nhiên có khối lượng nguyên tử cao(207 đvC), tỉ trọng lớn (11,3 g/cm³) và được ứng dụng phổ biến trong công nghiệp, nông nghiệp, sinh hoạt, y tế và công nghệ. Việc sử dụng rộng rãi chì trong nhiều lĩnh vực làm tăng mối quan ngại về tác động tiềm tàng của chúng đối tới sức khỏe con người và môi trường. Hiện nay việc áp dụng rộng rãi nanosilica vào xử lý ô nhiễm môi trường đã và đang dẫn đến sự phát triển của các phương pháp tách chiết silica từ hóa chất và các phế phụ phẩm. Trong nghiên cứu này, nanosilica được tổng hợp bằng phương pháp sol-gel từ tetraetoxysilan (TEOS) với xúc tác bazơ theo tỷ lệ thể tích TEOS/C₂H₅OH/H₂O/NH₄OH là 5/30/1/1 và xác định các đặc tính bằng một số kỹ thuật hiện đại như phổ tán sắc năng lượng tia X (EDX), quang phổ hồng ngoại (FTIR) và nhiễu xạ tia X (XRD), kính hiển vi điện tử quét (SEM), kính hiển vi điện tử quét phát xạ trường (FESEM). Kết quả cho thấy các hạt nano SiO₂ tách chiết được có pha vô định hình với kích thước trung bình khoảng 60-100 nm và được sử dụng trực tiếp cho xử lý chì. Tại điều kiện pH=5, lắc trong 1 giờ với tốc độ 150 vòng/phút, hiệu quả xử lý chì đạt 96,17% đối với nước nhiễm kim loại chì có nồng độ ban đầu là 10mgPb²⁺/L. Lượng hấp phụ cực đại Q_{max} = 30,3mg/g; hằng số đặc trưng của chất hấp phụ và chất bị hấp phụ b = 0,868L/g. Như vậy, hiệu quả xử lý kim loại chì của vật liệu nano silica được tổng hợp từ TEOS là rất cao. Bên cạnh đó, nghiên cứu chế tạo nanosilica từ vỏ trấu với các đặc tính tương tự là một hướng đi mới giúp nâng cao tính ứng dụng và giá trị kinh tế của vật liệu.

Keywords: characteristic, efficiency, lead, nanosilica, rice husk, sol-gel method, TEOS

1. Introduction

In recent years, heavy metal has been an increasing ecological and global public health concern associated with aqueous environment. Lead is a significant element metal that contaminated the water by both natural and anthropogenic activities. It occurs naturally in the environment as natural weathering of the earth's crust. In addition, soil erosion and anthropogenic activities such as fossil fuels burning, mining, and manufacturing contribute to the release of its high concentrations.

Lead is chemical element which has been applied for many different industrial, agricultural and domestic activities. Exposure to lead occurs mainly via inhalation of lead-contaminated dust particles, ingestion of lead-contaminated food, and water. In the human body, the greatest percentage of lead is taken into the kidney, followed by the liver and the other soft tissues such as heart and brain. The nervous system is the most vulnerable target of lead poisoning. Headache, poor attention span, irritability, loss of memory and dullness are the early symptoms of the effects of lead exposure on the central nervous system. Lead polluted are dangerous to health and to the environment, therefore, it is necessary to remove them from the polluted water.

A wide range of methods including chemical precipitation, solvent extraction, vacuum evaporation, membrane technologies, adsorption, ion exchange and membrane separation have been used to treat lead pollution environment (Ilka Gehrke et al. 2015 and Paul B Tchounwou et al. 2014). Using nanomaterials, for example, nanosilica is considered as new researching direction to treat lead pollution (Rahele Rostamian et al. 2011 and Rajesh Ghosh and Sounak Bhattacharjee. 2013). Nanosilica can be extracted from chemical or natural materials. Nanosilica was produced by various techniques including Stober technique (Gholami, Salavati-Niasari et al. 2013), sol-gel methods (Le et al. 2013), and water-in-oil nanoemulsion system (Park, Ho et al. 2003). However, few studies have been carried out using slow gelation technique and freeze-drying methods (Lu and Hsieh 2012).

In this study, nanosilica is synthesized by sol-gel method from TEOS and rice husk. This materials were characterized using Energy-dispersive X-ray spectroscopy (EDX), Fourier Transformation Infrared (FTIR) and X-ray diffraction (XRD), Scanning electron micrograph (SEM), Field emission scanning electron microscopy (FESEM). In other aim of this study is to investigate the nanosilica capacity to treat lead in different conditions such as time, pH, Pb²⁺ concentration and nanosilica concentration.

2. Materials and methods

2.1 Materials

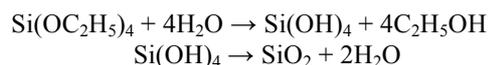
The chemicals used consist of tetraethoxysilane (TEOS, ≥98%, Merck), lead nitrate (Pb(NO₃)₂, ≥99.5%, Merck) as a lead source, ammonia solution (25%, Scharlau), ethanol (C₂H₅OH) (99.7%, China), hydrochloric acid (HCl, 37%, China), sodium hydroxide (NaOH, ≥96%, China), and

deionized water. And rice husk in the Red river delta was used as silica sources. Lead-contaminated water was made from Pb (NO₃)₂ to test the ability of the laboratory scale.

2.2. Methods

2.2.1 Nanosilica synthesis method from TEOS

Nanosilica is synthesized by sol gel method from TEOS with base catalysts and volumetric ratio TEOS/C₂H₅OH/H₂O/NH₄OH: 5/30/1/1. Precipitation of silica- chemical reaction involved:



Taking exactly 50mL TEOS into 300mL C₂H₅OH erlenmeyer flask. Stirring the solution in heating magnetic stirrer within 30 minutes. Adding gradually 10 mL deionized water and continuously stirring 30 minutes. Adding 10mL NH₄OH (25%) to obtain the solution with pH of 8 and stirring to form sol (Enrique C. Peresa et al. 2018; Ezzat Rafieel et al. 2012 and Farshid Ghorbanil et al. 2015). After that, evaporating naturally within 48 hours. Putting the sol in oven at 80°C within 15 hours then crushing. Annealing at 450-550°C in 3 hours, and crushing again to obtain final product.

2.2.2. Research on impact of time on Pb²⁺ treatment efficiency

Taking 100mL of 10 mg/L Pb²⁺ solution into 5 erlenmeyer flasks (250mL) and turning to pH=5. Weighing and taking 0.1 g nanosilica into each flask, then shaking with speed 150 rpm/min within time 20, 45, 60, 75, and 90 minutes, respectively. Centrifugating with speed 2500 rpm/min and determining remaining Pb²⁺ concentration by ICP-OES iCAP 6000 machine.

2.2.3. Research on impact of pH on Pb²⁺ treatment efficiency

Taking 100mL of 10 mg/L Pb²⁺ solution into 7 erlenmeyer flasks (250mL) and turning to pH of 3, 4, 5, 6, 7, 8, and 9, respectively by 0.01N HNO₃ and NaOH. Adding 0.1g nanosilica into each flask and shaking with speed 150rpm/min within 60 minutes. Centrifugating with speed 2500 rpm/min and determining remaining Pb²⁺ concentration by ICP-OES iCAP 6000 machine.

2.2.4. Research on impact of Pb²⁺ concentration on treatment efficiency by nanosilica

Taking 100mL deionized water into 8 erlenmeyer flasks (250mL). Diluting Pb(NO₃)₂ to obtain Pb²⁺ solution with concentration of 5, 10, 15, 20, 25, 30, 35, and 40 mg/L, respectively then turning them to pH of 5. Adding 0.1g nanosilica into each flask and shaking with speed 150 rpm/min within 60 minutes. Centrifugating with speed 2500 rpm/min and determining remaining Pb²⁺ concentration by ICP-OES iCAP 6000 machine.

2.2.5. Research on impact of nanosilica concentration on treatment efficiency by nanosilica

Taking 10mg/L Pb²⁺ solution with pH of 5 into 6 erlenmeyer flasks (250mL). Adding nanosilica in such a way that nanosilica concentration in each flask in a series of 0.1, 0.5, 1, 1.5, 2 and 2.5 g/L. Shaking them with speed 150 rpm/min within 60 minutes. Centrifugating with speed 2500 rpm/min and determining remaining Pb²⁺ concentration by ICP-OES iCAP 6000 machine.

3. Results and discussion

3.1. Characteristic of nanosilica extract from TEOS

3.1.1. Nanosilica extract composition

XRD image (Figure 1) shows that nanosilica contains high Si content with mass percentage 99.2465% and molecular weight percentage 99.425%. In addition, it also contains small amount of other elements such as P (0.3329%), Ca (0.4025%). It means the synthesized nanosilica is extremely pure and we can research and analyse material applications.

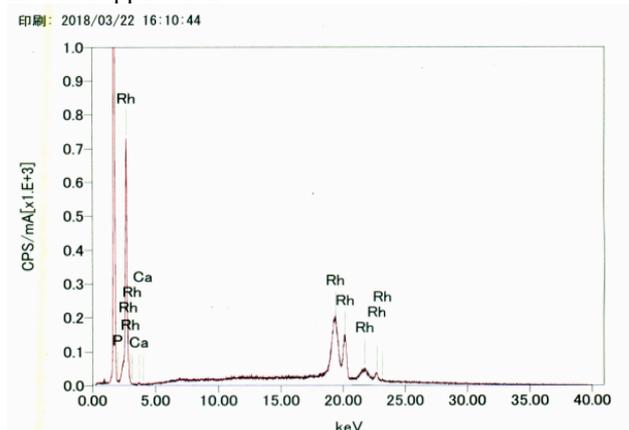


Figure 1. Energy-dispersive X-ray spectroscopy of nanosilica

3.1.2. Nanosilica extract functional group

The adsorption peak around 3250-3750 cm⁻¹ indicates the existence of free hydroxyl groups. The vibration around 1634 cm⁻¹ indicates the presence of H₂O. The peaks around 1105 cm⁻¹, 808 cm⁻¹, and 470 cm⁻¹ correspond to Si-O and Si-O-Si stretching, respectively. Therefore, synthesized nanosilica is high purity.

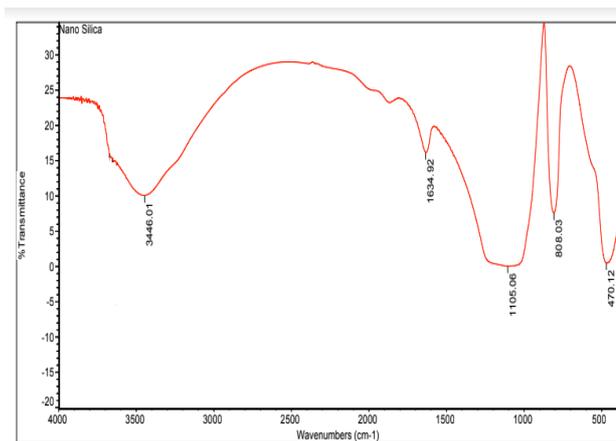
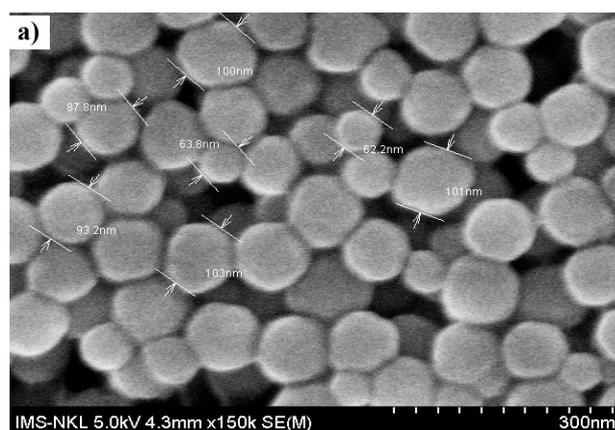


Figure 2. Fourier-transform infrared spectroscopy-graph of nanosilica

3.1.3. Nanosilica extract morphology and particle size

Figure 3 presents nanosilica FESEM result by HATACHI S-4800 machine (Vietnam Academy of Science and Technology). It shows that nanosilica has average particle size about 60-100 nm. With base catalyst (pH=8), TEOS hydrolytic reaction is easy to form Si(OH)₄ because OH⁻ ion can infiltrate into Si atom immediately and replaces -OC₂H₅ group of TEOS molecules. Thus, when ≡Si(OH) precipitated, silica gel groups have a preferential branching structure for all sides, the result is the nanosilica material is usually spherical, as shown in Figure 3.

The particles distinguish clearly which do not have adhesion together, disperse uniformly to make large surface area and wide contact area. It leads to high adsorption ability and high polluted treatment efficiency. Comparing with nano particles (Thai Hoang at el., 2012) showed that the particles in this report distribute better and distinguishable clearly.



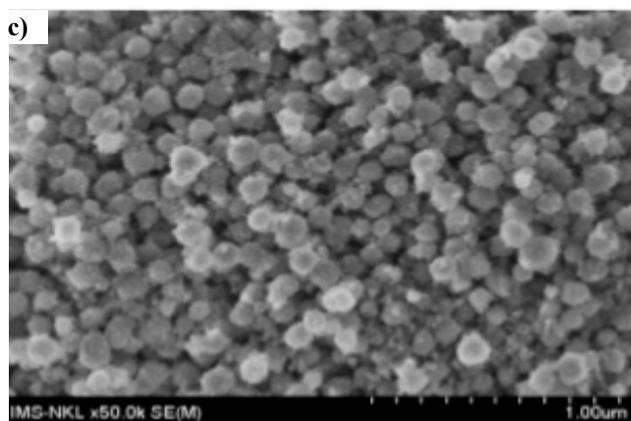
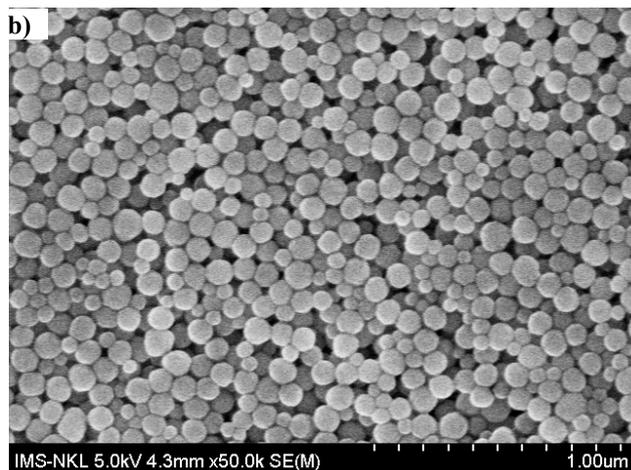


Figure 1. a, b) Field emission scanning electron micrograph (FESEM) of Nanosilica at different resolution scale; c) FESEM of Nanosilica (Thai Hoang at el., 2012)

3.1.4. Nanosilica extract structure

Nanosilica X-ray diffraction pattern shown in Figure. 7 shows that the major component of this material is high purity nanosilica, which is not confused by other impurities. Comparing with X-ray diffraction pattern of nanosilica obtained from the study of nanosilica’s XRD (Xuejing Chen at el., 2014), it only appears one wide peak at $2\theta = 22.5^\circ$, which indicates that nanosilica particles have small particle size and weak intensity, form in amorphous, crystal clear. Compared with crystalline silica, amorphous silica has more advantages such as non-toxic and better interaction and polluted absorbent (Xuejing Chen et al., 2014)

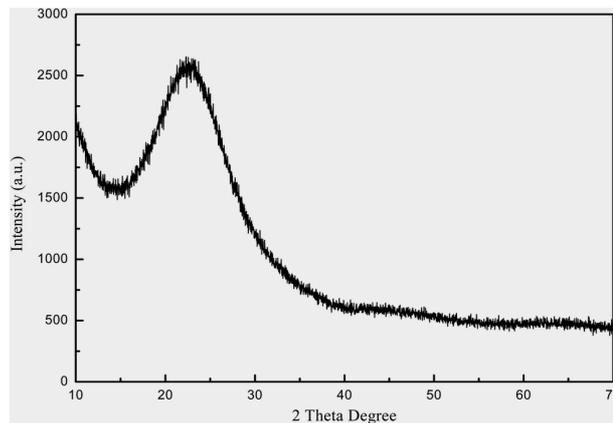
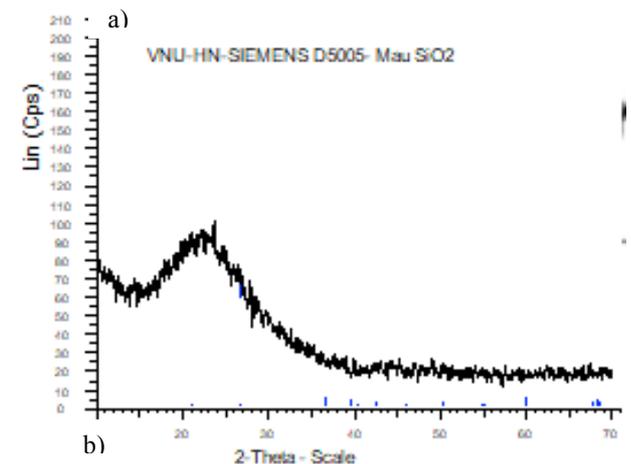


Figure 4. a) X-ray diffraction pattern of Nanosilica; b) X-ray diffraction pattern of Nanosilica (Xuejing Chen et al., 2014)

3.2. Pb^{2+} treatment efficiency of nanosilica at different conditions

3.2.1. Impact of treatment time on Pb^{2+} treatment efficiency

Pb^{2+} treatment result of 0.1g nanosilica in different duration of time, with the pH of 5 and initial concentration 10 $mgPb^{2+}/L$ is represented in Figure 5.

At first 20 minutes after treating, the efficiency raises quickly and reaches to 90.97%. The longer time the higher treatment efficiency, it gets 96.17% after 60 minutes and remaining Pb^{2+} concentration is 0.383 $mgPb^{2+}/L$. After 90 minutes, almost Pb^{2+} is adsorbed completely and and remaining Pb^{2+} concentration is 0.002 $mgPb^{2+}/L$. Thus, the range of time from 60 to 90 minutes is the optimal condition to carry out the next experiments.

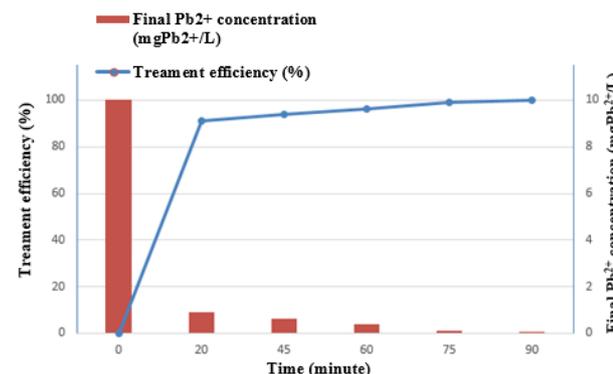


Figure 5. Pb^{2+} concentration and efficiency treatment at different time

3.2.2. Impact of pH on Pb^{2+} treatment efficiency

Pb^{2+} treatment result of 0.1g nanosilica at different pH, initial concentration 10 $mgPb^{2+}/L$, and shaking within 60 minutes is represented in Figure 6.

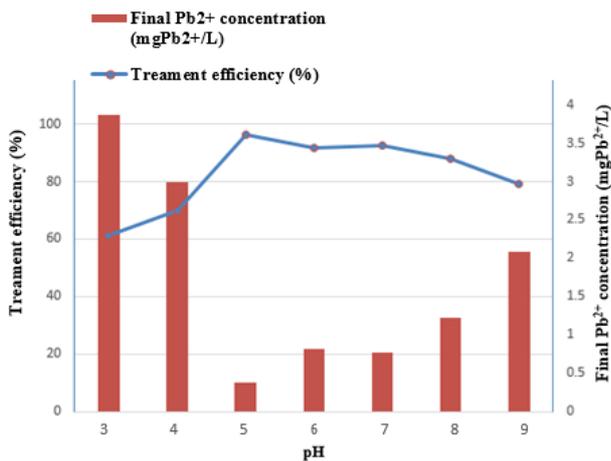


Figure 6. Pb²⁺ concentration and efficiency treatment at different pH

The result shows that lead (Pb²⁺) treatment efficiency raises when pH increases from 3 to 5. At pH = 5, the treatment efficiency is highest (approximately 96.17%), the remaining lead in solution is 0.383 mg Pb²⁺/L. According to Ahmed and RAM (1992), hydroxyl groups on SiO₂ exist at acid- base balance such as:

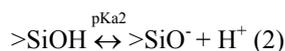
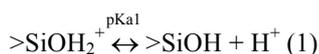


Table 1. Pb²⁺ concentration after treatment and setting up Langmuir’s adsorptive isotherm equation

Initial Pb ²⁺ concentration (mg/L)	Final Pb ²⁺ concentration (mg/L)	Treated Pb ²⁺ concentration Q _e (mg/g)	C _e /Q _e (g/L)	Pb ²⁺ treatment efficiency (%)
5	0.173	4.827	0.036	96.54
10	0.383	9.617	0.040	96.17
15	1.196	13.804	0.087	92.03
20	2.141	17.859	0.120	89.30
25	3.537	21.463	0.165	85.85
30	5.462	24.538	0.223	81.80
35	8.011	26.989	0.297	77.11
40	12.452	27.548	0.452	68.67
QCVN 40:2011 /BTNMT (B)	0.5	-	-	-

The Langmuir’s adsorptive isotherm equation:

$$Q_e = Q_{max} \frac{b.C_e}{1 + b.C_e} \quad (*)$$

Where:

C_e - equilibrium concentration of adsorbed substance (mg/L);

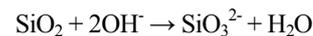
Q_e - adsorptive capacity (mg/g);

Q_{max} - maximum adsorptive capacity calculated by theory (mg/g);

b - Langmuir equations coefficients (determined from experiments).

To determine the constants in the Langmuir’s isotherm equation, the graph method converting equation (*) into

From reaction (1) and (2), it indicates that when pH raises, the balance move following increasing negative charge tendency on SiO₂ (>SiO⁻) surface. It causes a strong electrostatic attraction between the positive lead-adsorbed material (Pb²⁺) and the negative charge of SiO₂ adsorbent so the capacity and adsorption efficiency increase. In contrast, when pH decreases, balance will move following increasing positive charge on SiO₂ (>SiOH₂⁺) and make capacity and adsorption efficiency decrease (Ahmed M. N. and R. N. Ram., 1992). When pH is in range of 5 to 7, treatment efficiency is negligible change. At pH=7, the efficiency reaches 92.34%. When pH is larger than 7, the high OH⁻ ion concentration leads to react slowly.



Absorbed ability of SiO₃²⁻ ion is lower than nanosilica (SiO₂). SiO₃²⁻ ion making lead treatment ability of material decreases. Thus, when pH is larger than 8, the efficiency begins decreasing.

3.2.3. Impact of initial Pb²⁺ concentration on Pb²⁺ treatment efficiency

Pb²⁺ treatment result of 0.1g nanosilica at different Pb²⁺ concentrations, the pH of 5, and shaking within 60 minutes is represented in Table 1.

linear equation, in which C_e/Q_e depends on first order of C_e as the following:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}}.C_e + \frac{1}{b.Q_{max}} \quad (**)$$

Depending on Langmuir model, maximum adsorption concentration Q_{max} = 30.3mg/g, and adsorbent and adsorbate constant b = 0.868 L/g.

As a result, treatment efficiency reduces when initial Pb²⁺ concentration raises because nanosilica surface is occupied fully by lead molecule when adsorption system reaches equilibrium. With nanosilica concentration 1g/L, treatment time 60 minutes, the pH of 5 and initial Pb²⁺ concentration ≤10mg/L, Pb²⁺ concentration after treatment fit for QCVN 40:2011/BTNMT (column B)- National Technical Regulation on Industrial Wastewater

(column B: values are applied for industrial wastewater discharged into urban drainage systems, residential areas without centralized waste water treatment plants).

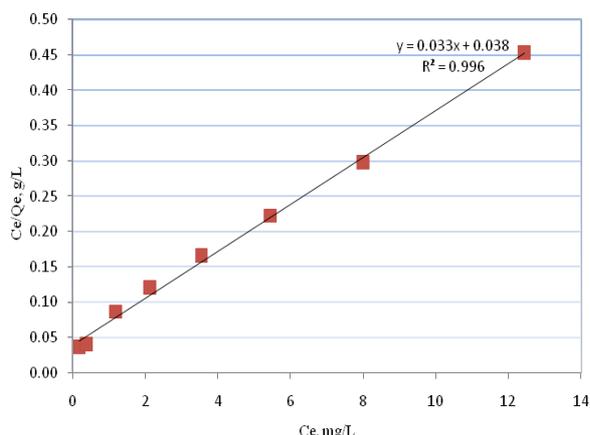


Figure 7. The Langmuir's adsorptive isotherm equation on lead removal by nanosilica

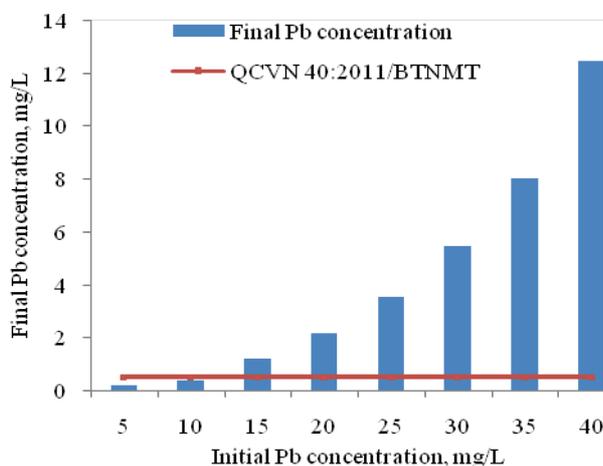


Figure 8. Pb²⁺ treatment efficiency with different initial Pb²⁺ concentrations

3.2.4. Impact of nanosilica concentrations on Pb²⁺ treatment efficiency

Pb²⁺ treatment result of different nanosilica concentrations at initial concentration 10 mgPb²⁺/L, the pH of 5, and shaking within 60 minutes is represented in Figure 9.

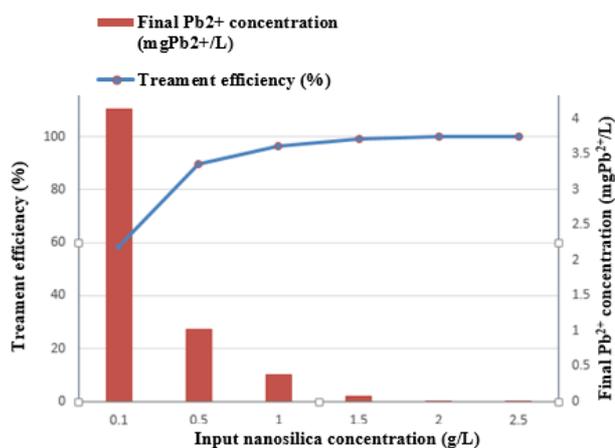


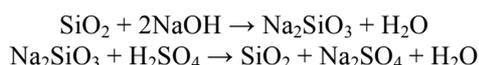
Figure 9. Pb²⁺ treatment efficiency of nanosilica at different input concentrations

Figure 9 shows that treatment efficiency grows up after adding nanosilica. When nanosilica concentration reaches 1 g/L, almost Pb²⁺ concentration is removed at efficiency 96.17%, and Pb²⁺ remaining concentration is 0.383 mgPb²⁺/L. Nanosilica concentration in the range of 1-2.5 g/L leads to negligible change in Pb²⁺ treatment efficiency.

3.3. Nanosilica synthesis from rice husk

At present, nanoscale silica materials are prepared using several methods, including vapor-phase reaction, sol-gel and thermal decomposition technique. However, their high cost of preparation has limited their wide application. In contrast, rice husk (RH) is an agricultural waste whose major constituents are organic materials and hydrated silicon. Because the silicon atoms in the rice husk have been naturally and uniformly dispersed by molecular units, very fine particle size, with very high purity and surface area silica powder can be prepared under controlled conditions. In addition, the reaction can occur easier than the conventional experimental technique. This process has the benefit not only of producing valuable silica powder but also of reducing disposal and pollution problems.

Precipitation of silica- chemical reaction involved (Tzong-Horng Liou, Chun-Chen Yang., 2011 and U. Kalapathy et al., 2000):



Nanosilica is synthesized by sol-gel method with 4 main steps:

Washing and dry: Rice husk was washed thoroughly with water to remove the soluble particles, dust, and other contaminants present, whereby the heavy impurities such as sand are also removed. It was then dried in an air oven at about 110°C for 24 h.

Acid treatment: An acid washing step was used to remove the small quantities of minerals prior to silica extraction

from rice husk ash (RHA). Ten grams of RHA samples were dispersed in 60 ml of HCl 1N.

Thermal treatment: A weighed RH as well as RH were subjected to heat treatment to obtain the ash. Samples were burned inside a programmable furnace (Nabertherm controller B 170, Nabertherm GmbH, Lilienthal, Germany) at different temperatures (500, 700, and 1000°C) and optimal temperature 700°C in 6h.

Silica extraction: A sample of 2.5 g RHA was stirred in a 250mL, 0.5M sodium hydroxide solution. The solution was heated in a covered beaker by stirring constantly and was allowed to stand at room temperature then filtered
Nanosilica preparation: HCl was added until neutralized. The precipitate silica was washed repeatedly with warm, deionized water and then was centrifugated with speed 5000 rpm within 10mins repeated in 3 times. The product is dried at 110°C for 24 h in the oven and crystallization in a programmable furnace at 450°C in 1h. Then crushed them to collect nanosilica.

Nanosilica extract composition

EDX elemental spectra of rice husk showed major element silicon (Si) and impurities Rhodium (Rh), lead (Pb), iron (Fe) and Arsenic (As). Silica content of the xerogels was estimated from the EDX data based on the assumption that all of the silicon was in the form of silica. The silica content of xerogels produced from washed RH were 99.5%. It is interesting to note that impurity elements were also present in a lower concentration even detected in the nanosilica. The color of nanosilica was white after synthesis.

Nanosilica extract functional group

FTIR spectroscopy was used to detect the presence of functional groups in the silica nanoparticle (SNPs). The major chemical groups present in silica are identified by the FTIR spectra shown in Figure 5. Six functional groups are found in samples: hydroxyl groups, C-H stretching, C=C stretching, Si-O-Si stretching, Si-H groups, and -OCH₃ stretching.

The adsorption peak around 3447.27 cm⁻¹ indicates the existence of free hydroxyl groups. In rice husk, the C-H stretching vibration around 2924.02 cm⁻¹ indicates the presence of alkane functional group. The C=C stretching vibrations between 1636.44-1653.91 cm⁻¹ indicates alkenes and aromatic functional groups. The peaks around 1077.8-1097.58 cm⁻¹, 800.12 cm⁻¹, and 466.76- 470.37 cm⁻¹ correspond to Si-O-Si stretching, Si-H groups, -OCH₃ stretching, respectively. The presence of polar groups on the surface is likely to provide the considerable cation exchange capacity to the adsorbent.

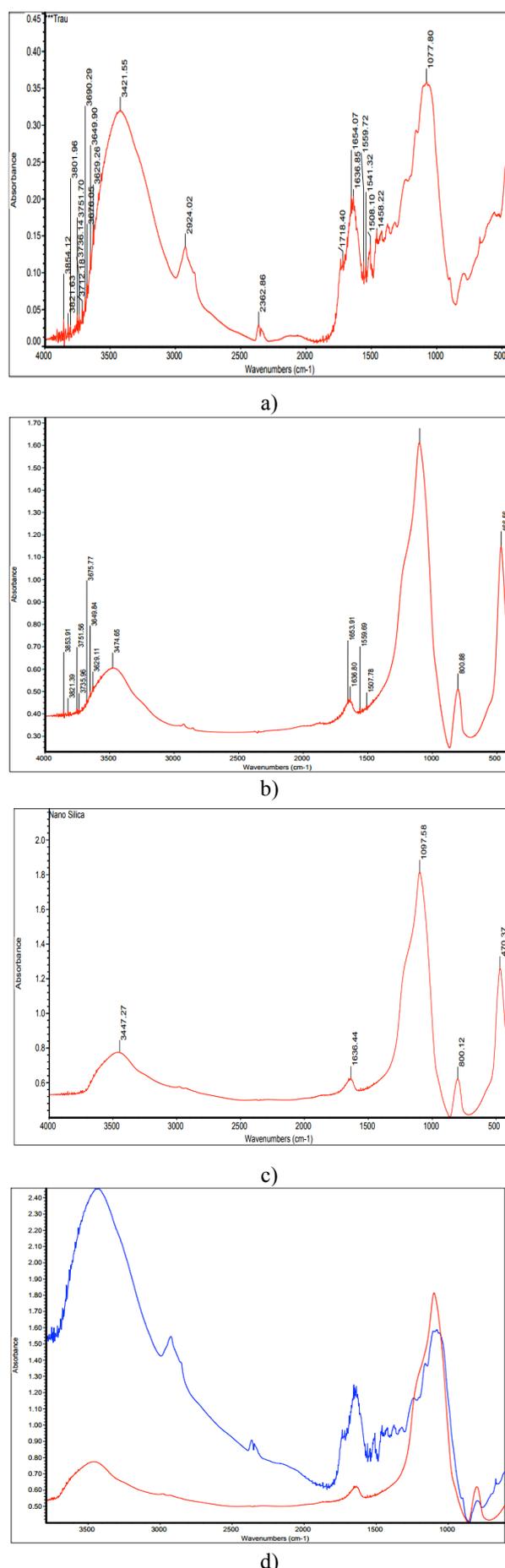


Figure 10. Fourier-transform infrared spectroscopy-graph of a) rice husk, b) rice husk ash, c) nanosilica from rice husk d) comparison a and c

Compared to rice husk, synthesized nanosilica resulted in a loss of C-H stretching band and a addition of Si-H. These were decreased in the primary functional groups of OH and C=C and increased in silica functional groups of Si-O-Si.

Nanosilica extract morphology and particle size

Figure 11 illustrates the SEM images of SNPs samples. It presented that synthesized nanosilica have spongy structure. Particle size and morphology of synthesized silica were examined by FESEM with high enlargement. It can be observed that SNPs have a circular shape with average particle size of 30-100 nm.

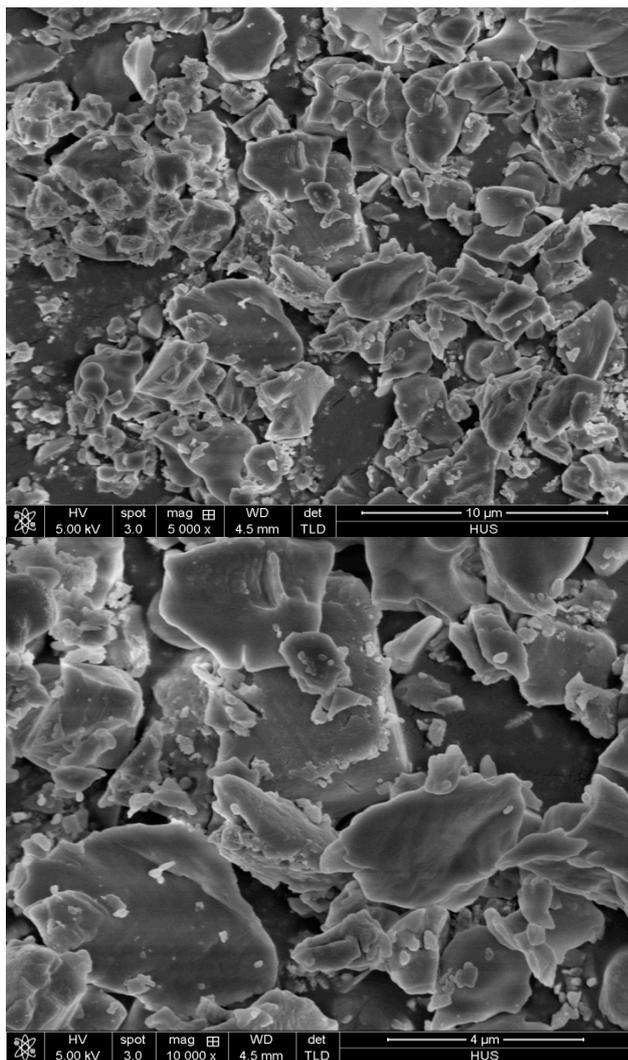


Figure 11. Scanning electron micrograph (SEM) of nanosilica from rice husk

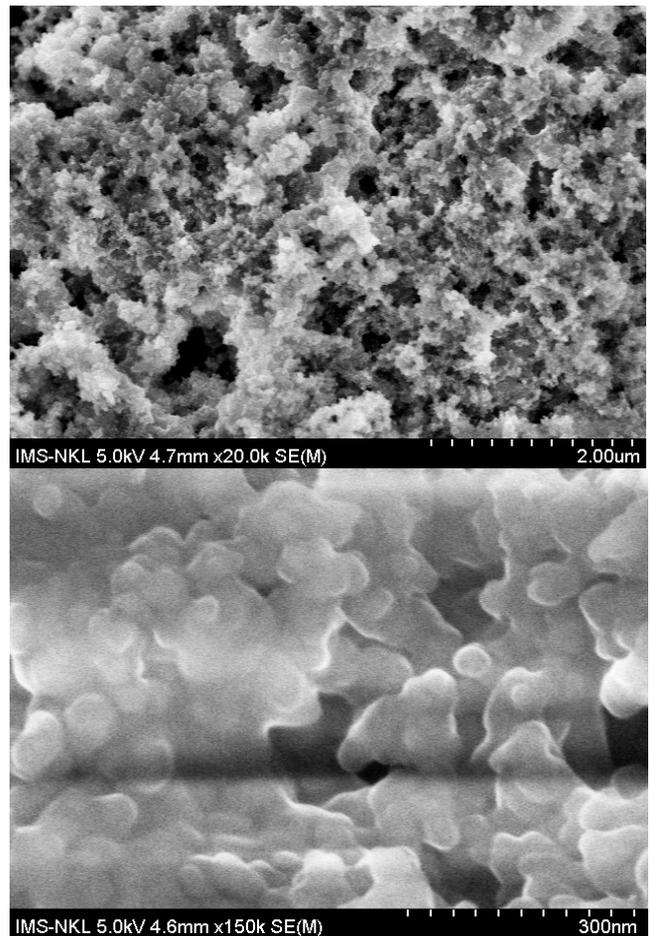


Figure 12. Field emission scanning electron micrograph (FESEM) of nanosilica from rice husk

Nanosilica extract structure

X-ray diffraction pattern of extracted silica is presented in Figure 13. Hill like peak in the range of $[2\theta] = 21$ to 24 , indicates the absence of any ordered crystalline structure and highly disordered structure of silica and extracted nanosilica is purity.

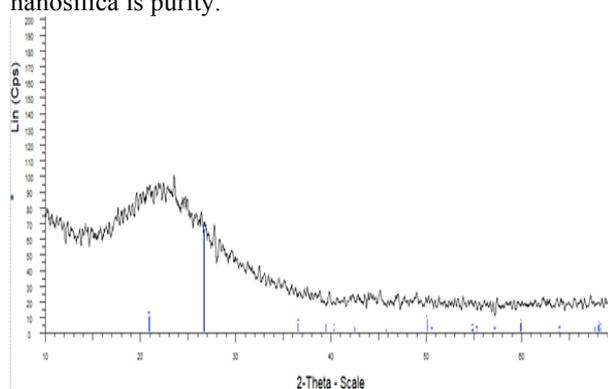


Figure 13. X-ray diffraction pattern of nanosilica

4. Conclusion

Purity nanosilica (60-100 nm) is synthesized by sol-gel method from TEOS with base catalysts and volumetric ratio TEOS/C₂H₅OH/H₂O/ NH₄OH: 5/30/1/1 and can be applied efficiency to treat lead in water. Pb²⁺ treatment efficiency increases following time, accelerates within first 20 minutes and then raises slowly and the highest

efficiency is 96.17% after 60 minutes. It increases in the range of pH 3-5. The highest is 96.17% at the pH of 5 and the remaining concentration is 0.383 mgPb²⁺/L. When pH is larger than 8, the efficiency starts decreasing. As a result, maximum adsorption concentration Q_{max} = 30.3 mg/g, and adsorbent and adsorbate constant b = 0.868 L/g. The higher nanosilica concentration seems being adsorbed completely. In addition, nanosilica also can be synthesized from rice husk with similar characteristics such as particle size 30-100 nm, spongy structure, and clean material and has orientation to apply to treat lead in water in future research.

5. References

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