RJC

RASĀYAN J. Chem.
Vol. 13 | No. 1 |249 - 254| January - March | 2020
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

SILICA EXTRACTION FROM BEACH SAND FOR DYES REMOVAL: ISOTHERMS, KINETICS AND THERMODYNAMICS

M. Lutfi Firdaus[1,*], Fitri E. Madina[1], Sasti Yulia F.[1], Rina Elvia[1], Soraya N. Ishmah[2], Diana R. Eddy[2], Abigail P. Cid-Andres[3]

[1]Graduate School of Science Education, University of Bengkulu, Bengkulu 38371, Indonesia
[2]Department of Chemistry, Universitas Padjadjaran, Jatinangor 45363, Indonesia
[3]Department of Physical Sciences, College of Science, Polytechnic University of the Philippines, Manila 1016, Philippines
*E-mail: lutfi@unib.ac.id

ABSTRACT

Beach sand is an abundant natural resource that contains silica minerals with many benefits. One of the uses of silica is to remove synthetic dyes that are toxic to biota in the environment. The goal of this research was to extract and characterize the silica from Bengkulu beach sand and to apply it as dyes adsorbent. The extraction of silica consisted of two steps that were potassium silicate formation and gel formation. The gel was formed by adding strong acid into a potassium silicate solution. Silica's particle size and crystallinity were characterized using PSA and XRD, respectively. SEM-EDS was used to characterize the morphology and chemical composition of extracted silica. The effect of the different experimental settings, like pH, temperature, contact time, the concentration of dyes and adsorbent weight, on adsorption of dyes were monitored as well as the study of adsorption isotherms, kinetics, and thermodynamics. At equilibrium, synthetic dyes adsorption to silica suited to the Freundlich model producing correlation coefficients (R^2) of 0.853 and 0.976 for remazol blue and congo red, respectively. At optimum conditions, maximum adsorption capacities for remazol blue and congo red were 133 and 131 mg/g, respectively. The research implied that adsorption of dyes to silica fitted the pseudo-second-order model with thermodynamic values of ΔG°, ΔH°, and ΔS° were -4.04 to 2.19 kJ/mol, -13.53 to -4.726 kJ/mol, and 0.019 to 0.021 J/mol.K, respectively. By using these results, we resolve that the adsorption of dyes trends was exothermic and spontaneous. In addition, the reaction increases the system's entropy. This study emphasizes the potential of silica from the sand beach as a substitute economical adsorbent for the toxic dyes removal.

Keywords: Silica, Remazol Blue, Congo Red, Adsorption, Isotherms, Kinetic, Thermodynamics

INTRODUCTION

The current rapid population-growth is accompanied by a decline in environmental quality caused by the massive exploitation of resources to meet human needs. One of the causes of damage to the environment is the intensive use of various synthetic chemicals to make clothes that are comfortable and attractive. Synthetic dyes are widely used in the textile industry to dye clothing and other textile products, such as curtains and sheets, cord and twine, carpets and rugs, towels, furniture and automotive upholstery.[1,2] Once these synthetic dyes enter the water body, they are difficult to degrade by microorganisms in the environment owing to their complex chemical structures. Most of the synthetic organic dyes have aromatic rings that also toxic to biota in environments. The rings are even harder to degrade due to its stability, and it is foreign to living things in the surroundings, known as xenobiotics.[3] Therefore, it is important to treat the synthetic dyes first before it is discharged to the river system. Various physicochemical treatment have been used to reduce dyes from textile's wastewater, such as precipitation, filtration, coagulation, oxidation, and photochemical reactions.[4–6] While those of biochemical methods

http://dx.doi.org/10.31788/RJC.2020.1315496

include aerobic-anaerobic treatment[7,8] and activated sludge treatment.[9] However, most of these methods have the complicated procedure, high cost, and produce toxic chemical compounds. Nowadays, adsorption is the most frequently used method to remove dyes from textile industries waste-water owing to its low-cost, simple, fast, and effective removal processes. Several adsorbents have been used for this purpose, such as activated carbon, biomaterials, chitosan, zeolite, etc.[2,10,11] For this purpose, extracted silica from beach sand has several advantages over other adsorbents used in dyes removal.[12]
Beach sand is a granular material arranged of fine rock and mineral particles. The most common composition of beach sand is silica (silicon dioxide, or SiO_2), normally in the form of quartz, that has been carried away during weathering and deposition process on a geologic time scale. The result of weathering then carried by wind and water and settled at the edges of the sea. Quartz sand is mixed with oxide groups and other impurities which blended during the natural sand formation and weathering process. Quartz sand is mainly composed of SiO_2, Al_2O_3, Fe_2O_3, TiO_2, MgO, K_2O, and CaO.[13] Here, we report silica extraction from beach sand and evaluate its potential as a low-cost adsorbent to remove synthetic dyes from textile industries waste-water.

EXPERIMENTAL

Material and Methods

The natural sand used as raw material was obtained from Panjang Beach, Bengkulu. All chemicals used in this research were of analytical grade or of the highest purity available supplied by Merck Ltd. (Darmstadt, Germany). Synthetic dyes, i.e. remazol blue and congo red, were obtained from local textiles home-industry. All glassware was washed with detergent (5%), 4 M HCl, and deionized water before use. The decolorization rate of dyes was monitored by UV-Visible Spectrophotometer (B-One, Messgerate). The synthesized silica was characterized by Particle Size Analyzer (PSA 1190, CILAS), X-Ray Diffractometer or XRD (Smart Lab 3 kW, Rigaku) and Scanning Electron Microscopy / Energy Dispersive X-Ray Spectroscopy or SEM/EDS (JSM 6510 LA, JEOL).

Silica Extraction

Initially, beach sand was filtered using a 100-mesh sieve followed by soaking in 10 M HCl for 20 h to remove unwanted minerals other than silica. The residue was washed using distilled water until pH neutral. A 30 g of cleaned beach sand was then mixed with KOH 10 M and heated at 360°C for 4 h, as alkali fusion reaction with K_2SiO_3 as a product. Further, K_2SiO_3 was dissolved in 500 mL distilled water, stirred and let stand for 24 h. The mixture was filtered and then the filtrate was added by HCl 10M dropwise until the pH of the mixture was between 1 to 2, which was also characterized by white gel formation. The formed gel was then filtered and washed with distilled water until pH neutral and dried at 60°C for 18 h until no moisture detected. The resulted silica powders (SiO_2) were characterized using various instruments and ready for further experiments as dyes adsorbent.

Dyes Adsorption Experiments

Batch adsorption experiments were performed using a thermostat shaker with a mixing speed of 150 rpm. Stock solutions of synthetic dyes were prepared by dissolving weighed remazol blue and congo red accurately in pure water to obtain a stock solution with a concentration of 1,000 ppm. The working standards were then made by dilution of stock solution to obtain concentrations of 50, 100 and 150 ppm. A 10 mL initial concentration of dyes at 100 ppm and 0.20 g of silica adsorbent was applied. The mixture was maintained at an assigned temperature and shaken until equilibrium was achieved. The effect of pH on dyes removal was evaluated by adjusting solutions pH from 2.0 to 7.0 using HCl 0.1 M or NaOH 0.1 M. The influence of contact time on dyes removal was carried out from several minutes to several hours. The effect of temperature and adsorbent weight on dyes decolorization was also carried out on several variations. An aliquot of the sample was then sampled, filtered and analyzed with a spectrophotometer on the visible wavelength.[14]

RESULTS AND DISCUSSION

The Yield and Silica Characterization

Initially, we compared NaOH and KOH as agent for alkali fusion, to extract silica from Bengkulu beach sand. However, KOH produced a higher yield than NaOH. Therefore, we chose KOH as extractant to obtain the best result herein. As seen from Table-1, we found that the best ratio to obtain the highest yield was 15 % sand in 85 % KOH 10 M. Potassium silicate (K_2SiO_3) generated from this initial stage was then dissolved in water to form silicate acid ($Si(OH)_4$) that after addition of HCl and heated, silicate acid was become precipitate. After decantation and filtration, the separated silicate acid was heated to form silica (SiO_2) that used for further experiments. Conversion yield from beach sand to silica was 90%, with SiO_2 purity as high as 99.5%. The results are in accordance with previously issued values.[13,15] The total reaction of silica extraction from beach sand is as follows:

$$SiO_{2(s)\ sand\ powder} + 2KOH_{(s)} \rightarrow K_2SiO_{3(aq)} + H_2O_{(g)}$$
$$K_2SiO_{3(aq)} + H_2O_{(aq)} + 2HCl_{(aq)} \rightarrow Si(OH)_{4(s)} + 2KCl_{(aq)}$$
$$Si(OH)_{4(s)} \rightarrow SiO_{2(s)} + 2H_2O_{(g)}$$

Table-1: Yield of K_2SiO_3 Extraction from Beach Sand

Sand : KOH Ratio (% Weight)	Yield (%)
20 : 80	21.00
15 : 85	51.17
10 : 90	45.00

Figure 1 shows that the largest number of extracted silica's particle sizes lies between 6.5 nm to 10.09 nm with average particle size was 8.241 nm. This result confirmed that the product was nano-silica. The X-ray diffraction patterns of extracted silica were characterized by the appearance of angular diffraction peaks of 2θ at 23.74°, as shown in Figure 2. This peak widens at 2θ between 20-30° which indicates that the extracted silica was amorphous. The result of SEM analysis shows that the extracted amorphous silica has a homogeneous shape and size. In addition, EDS data shows that the extracted silica composed of 18.45% Si and 48.77% O, which is the constituent of SiO_2.

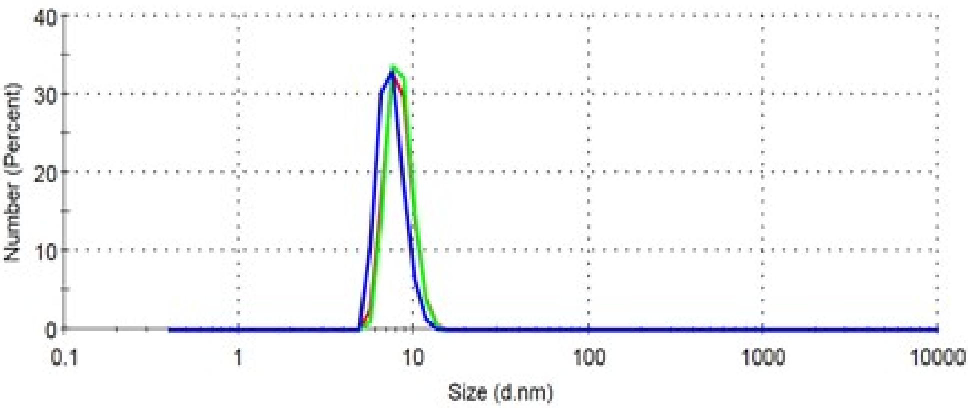

Fig.-1: Size of Extracted Silica as measured by PSA

Application of Silica as Dyes Adsorbent

Optimum Adsorption Conditions and Adsorption Isotherms

Preliminary experiments show that the optimum pH, contact time, adsorbent mass, and temperature for remazol blue were at pH 2, 60 min., 75 g, and 303 K, respectively. While those of congo red was at pH 2, 40 min., 75 g, and 303 K, respectively. In contrary to other reported papers, wherein adsorption of dye at pH 2.0 is negligible, the result is interesting.[16] By using these optimum conditions, most of the synthetic dyes (more than 90%) were absorbed onto silica. Unless otherwise stated, further experiments were conducted at these optimum conditions.

In order to examine the adsorption mechanism, the adsorption isotherm experiments were conducted in this study. The model of Freundlich's and Langmuir isotherms were selected. The isotherm of Freundlich is an empirical equation applied to characterize heterogeneous systems as physisorption.

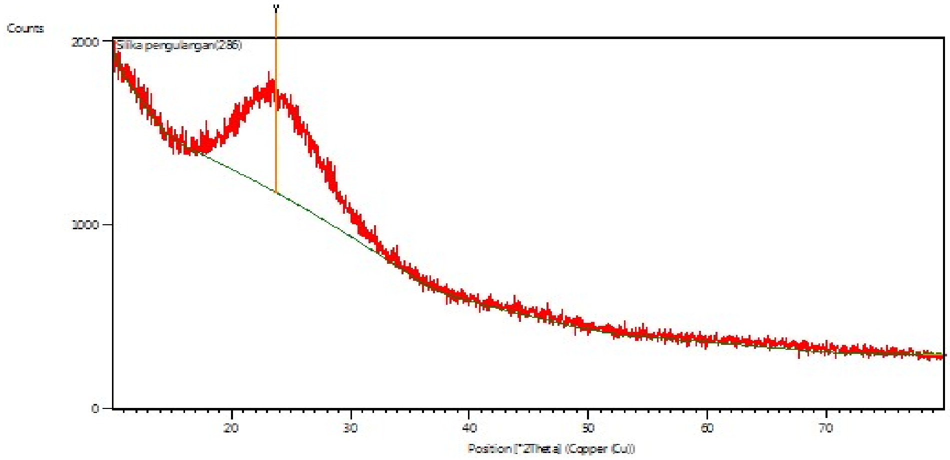

Fig.-2: X-Ray Diffractogram of Extracted Silica

The equation for Freundlich isotherm is shown below [2,17]:

$$\log q_e = \log K_F + \frac{1}{n} \log C$$

Where q_e is the amount of adsorbed dye at equilibrium (mg/g), K_F is a constant that related to the bonding energy, and 1/n is intensity of adsorption that indicates the isotherm type to be unfavorable ($1/n > 1$), favorable ($0 < 1/n < 1$) and irreversible ($1/n = 0$). For Langmuir isotherm, based on the assumption that adsorption is a chemical process as monolayer adsorption, is written as follows [2,18]:

$$\frac{Ce}{q_e} = \frac{1}{q_{max}.K_L} + \frac{Ce}{q_{max}}$$

Where q_e is the amount of adsorbed dye at equilibrium (mg/g), q_{max} is maximum adsorption capacity (mg/g), C_e is dye concentration at equilibrium (ppm), and K_L is Langmuir constants (L/mg).

Table-2: Constants for Isotherm Model for Dyes Adsorption

Synthetic Dyes	Freundlich Parameter			Langmuir Parameter		
	K_F	N	R^2	K_L	q_{max}	R^2
Remazol Blue	1.117	0.133	0.853	0.303	133	0.578
Congo Red	1.736	0.526	0.976	0.089	131	0.567

Table-2 shows adsorptions of both remazol blue and congo red onto silica were favorable with high adsorption capacity. At equilibrium, coefficient of determination results shows that both dyes adsorption onto silica tends to obey isotherm model of Freundlich, with maximum capacities of adsorption for remazol blue and congo red were 133 and 131 mg/g, respectively. These results show that the mechanism of remazol blue and congo red adsorption onto silica was a physisorption mechanism through van der Walls forces or electrostatic attractions between the synthetic dyes and silica.

Adsorption Kinetics

Widely used two adsorption kinetics equations, pseudo-second-order and pseudo-first-order, were used to study the adsorption kinetics. The Lagergren rate equation for the pseudo-first-order is expressed as [19]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$

Where qt (mg/g) is the dye adsorbed onto silica at time t, q_e (mg/g) is the uptake equilibrium adsorption and k_1 (1/min) is the first-order rate constant for dyes adsorption. The linearized form pseudo-second-order kinetic model is written as follows [20]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

Where k_2 is the constant rate of pseudo-second-order adsorption. The value of q_e and k_2 were calculated from the slope and intercept of the plot of t/qt versus t, respectively. As seen from Table 3, with the pseudo-second-order and pseudo-first-order models, that were used to test the adsorption kinetically, the pseudo-second-order models showed the better fit of the empirical data with R^2 from 0.98 to 0.99.

Table-3: Adsorption Kinetics estimated by the Pseudo-second-order Model and Pseudo-first-order

Model	Parameter	Remazol Blue		Congo Red	
		50 (ppm)	100 (ppm)	50 (ppm)	100 (ppm)
Pseudo-first-order	k_1 (1/min)	0.001	0.001	0.001	0.004
	q_e (mg/g)	5.04	11.79	6.46	7.63
	R^2	0.27	0.12	0.79	0.26
Pseudo-second-order	k_2 (1/min)	1.148	0.612	0.011	0.156
	q_e (mg/g)	0.66	0.69	0.22	1.22
	R^2	0.96	0.99	0.98	0.98

Adsorption Thermodynamics

Studies of the adsorption thermodynamics consist of the changes of free energy (ΔG°), entropy (ΔS°) and enthalpy (ΔH°) that were calculated from batch procedures carried out at various temperatures. The equations below were used to calculate the thermodynamic parameters:

$$\Delta G° = -RT \ln K$$

$$\ln K = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT}$$

Table-4 shows the results of thermodynamic parameters. The dominant-negative value of free energy (ΔG°) for remazol blue and congo red indicates the spontaneous process. In contrast to the other reported values [21,22], the change of enthalpy (ΔH°) for both synthetic dyes in this study was negative or exothermic as shown on the less in adsorption percentage with increases in temperature. The positive values of entropy change (ΔS°) for both synthetic dyes maintain the elevated randomness at the solution - solid interface along with the adsorption of the dye on the surface of silica.[23]

Table-4: Adsorption Thermodynamics for Synthetic Dyes Adsorption onto Silica

Synthetic Dyes	ΔG° (kJ/mol)			ΔH° (kJ/mol)	ΔS° (J/mol.K)
	303 K	313 K	323 K		
Remazol Blue	-0.91	-0.73	-0.65	-4.726	0.019
Congo Red	-4.04	-1.69	2.19	-13.53	0.021

CONCLUSION

The extraction of silica from abundant natural resources of beach sand is reported here to remove hazardous dyes from the textile industry wastewater. The method has proven to be fast, simple and low-cost to adsorb synthetic dyes. Based on these adsorption experiments, we sum up that dyes adsorption mechanism onto silica mineral was attained by electrostatic attractions and van der Walls forces among the synthetic dyes and silica. At optimum conditions, more than 90% of dyes were adsorbed onto silica, with adsorption capacities for remazol blue and congo red were 133 and 131 mg/g, respectively. Based on the mechanism, we resolved that dyes adsorption was exothermic, spontaneous and increase the system's entropy. These results suggest that the use of silica as an adsorbent to reduce synthetic dyes from textile effluents is effective, and therefore can be used as a low-cost alternative to the expensive and complicated methods currently used.

ACKNOWLEDGMENT

The research was partially funded by the Ministry of Research, Technology and Higher Education, Indonesia (Grant number: 7/E/KPT/2019 and 053/SP2H/LT/DRPM/IV/2019).

REFERENCES

1. S. Ibrahim, I. Fatimah, H.M. Ang, S. Wang, *Water Science and Technology,* **62**, 1177(2010), **DOI:** 10.2166/wst.2010.388
2. M.L. Firdaus, E. Susanti, Ghufira, W. Alwi, E. Swistoro, *Rasayan Journal of Chemistry,* **11**, 1532(2018), **DOI:** 10.31788/RJC.2018.1144030
3. Erkurt, H. A. *Biodegradation of Azo Dyes*. Springer, 2010.
4. A. Niazi, A. Yazdanipour, J. Ghasemi, M. Kubista, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy,* **65**, 73(2006), **DOI:** 10.1016/j.saa.2005.09.030
5. M. Raziq, R. Kooh, L.B.L. Lim, L.H. Lim, *Desalination and Water Treatment,* **57**, 14632(2016), **DOI:**10.1080/19443994.2015.1065450
6. M.A. Ashraf, M. Hussain, K. Mahmood, A. Wajid, M. Yusof, Y. Alias, I. Yusoff, *Desalination and Water Treatment,* **51**, 4530(2013), **DOI:** 10.1080/19443994.2012.747187
7. B. Santos, F.J. Cervantes, J.B. van Lier, *Bioresource Technology*, **98**, 2369(2007), **DOI:** 10.1016/j.biortech.2006.11.013
8. M.A. Kamaruddin, M.S. Yusoff, H.A. Aziz, N.K. Basri, *Applied Water Science,* **3**, 359(2013), **DOI:** 10.1007/s13201-013-0086-1
9. K.C.A Bromley-Challenor, J.S Knapp, Z. Zhang, N.C.C. Gray, M.J. Hetheridge, M.R. Evans, *Water Research,* **34**, 4410(2000), **DOI:** 10.1016/S0043-1354(00)00212-8
10. M.L. Firdaus, N. Krisnanto, W. Alwi, R. Muhammad, M. Allan, *Aceh International Journal of Science and Technology,* **6**, 1(2017), **DOI:** 10.13170/aijst.6.1.5502
11. L. Wang, A. Wang, *Journal of Hazardous Materials,* **147**, 979(2007), **DOI:** 10.1016/j.jhazmat.2007.01.145
12. C. Huang, K. Chang, H. Ou, Y. Chiang, C. Wang, *Microporous and Mesoporous Materials,* **141**, 102(2011), **DOI:** 10.1016/j.micromeso.2010.11.002
13. D.R. Eddy, F.N. Puri, A.R. Noviyanti, *Procedia Chemistry,* **17**, 55(2015), **DOI:** 10.1016/j.proche.2015.12.132
14. T. Wulandari, Nirwana, M.L. Firdaus, *PENDIPA Journal of Science Education,* **3**, 66(2019), **DOI:**10.33369/pendipa.3.2.66-71
15. H. Mori, *Journal of materials science,* **8**, 3461(2003), **DOI:**10.1023/A:1025100901693
16. R.S.D. Farias, H.L.D.B. Buarque, M.R.D. Cruz, L.M.F. Cardoso, T.D.A. Gondim, V.R.D. Paulo, Adsorption of congo red dye from aqueous solution onto amino-functionalized silica gel. *Engenharia Sanitaria e Ambiental,* **23**, 1053(2018), **DOI:** 10.1590/S1413-41522018172982
17. H. Freundlich, *Zeitschrift für Physics Chemie,* **57**, 385(1907).
18. I. Langmuir, *Journal of the American Chemical Society,* **40**, 1361(1918).
19. Y.S. Ho, G. McKay, *Water Research,* **33**, 578(1999), **DOI:** 10.1016/S0043-1354(98)00207-3
20. Y.S. Ho, G. McKay, *Process Biochemistry,* **34**, 451(1999), **DOI:** 10.1016/S0032-9592(98)00112-5
21. S. Koner, B.K. Saha, R. Kumar, A. Adak, *International Journal of Current Research,* **3**, 128 (2011).
22. A.K. Hameed, N. Dewayanto, D. Dongyun, M.R. Nordin, M.H.A Rahim, *Bulletin of Chemical Reaction Engineering & Catalysis,* **11**, 250(2016), **DOI:** 10.9767/bcrec.11.2.443.250-261
23. A.M. Anshar, P. Taba, I. Raya, *Indonesian Journal of Science and Technology,* **1**, 47(2016), **DOI:** 10.17509/ijost.v1i1.2213

[RJC-5496/2019]