ISSN 2355-8776

Utilization of Fly Ash and Rice Husk as Chromium Metal Adsorbent in Batik Waste

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ARTICLE INFO

Article history
Received October 26, 2022
Revised March 3, 2023
Accepted March 6, 2023

Keywords
Adsorbent
Batik waste
Chromium metal
Fly ash boiler
Rice husk ash

ABSTRACT

Fly ash boiler as a waste of palm oil mill containing 63.4% of silica (SiO_2). Rice husk ash is a waste material from rice that has special properties, also containing about 94-96% of silica (SiO_2). Both of these wastes contain silica which can be used as an adsorbent. This study aims to produce adsorbents from fly ash boilers for palm oil mills and rice husk ash as adsorbents for batik waste. The research design used was Complete Block Design with 2 factors, namely the ratio of rice husk ash mass to fly ash boiler with 3 levels, namely A1 (25%:75%), A2 (50%:50%), A3 (75%:25%), and the concentration factor of HCl with 3 levels, namely B1 (1M); B2 (2M), B3 (3M), which is done 2 times repetition. The experimental stages include boiler fly ash pretreatment, rice husk ash pretreatment, synthesis and activation of adsorbents and adsorption tests on batik wastewater. Furthermore, analysis of COD, TSS and Chromium was carried out. The results showed that the A3B2 sample provided optimal adsorption capacity for the analysis of COD, TSS and Chromium metal with values of 57.62 mg/L, 1.43 mg/L and 3.24 ppm, respectively, where there was a decrease in COD of 74%, a decrease in TSS of 97.56% and a decrease in Chromium metal ion of 80.43%. This is due to the use of more rice husk ash with the use of HCl solution as an activator can increase the silica active group on the adsorbent thereby increasing the surface area of the adsorbent, where the surface area of the A3B2 sample is 118.24 m^2/g.

1. Introduction

Palm oil is one of the agribusiness commodities in Indonesia which is developing quite rapidly in the plantation sector. These abundant natural resources are scattered in various regions, especially in Sumatra and Kalimantan. The development of the palm oil industry that continues to increase will have an impact on solid waste generated from processing fresh fruit bunches (FFB). This waste is the rest of crude palm oil production, in the form of empty fruit bunches, coir, and palm shells. Solid waste in the form of fibers and shells is used as boiler fuel to produce mechanical energy and heat. As much as 5% of the boiler fuel is in the form of ash where the chemical elements contained in fly ash waste are silica (SiO_2) of 63.4%, Fe_2O_3 of 63.4%, calcium oxide (CaO) of 4.3%, magnesium oxide (MgO) of 3.7%, K_2O of 6.3%, SO_3 of 0.9%, Al_2O_3 of 5.5% and LOI of 6% [1], [2], [3]. The fly ash generated from biomass combustion contains a substantial number of elements, macronutrients (P, K, S, Ca, and Mg), and micronutrients (Mn, Cu, Zn, Co) considered as being essential for plant growth [4]. In form of oxides, the main chemical components contained in FA are silica (SiO_2), alumina oxide (Al_2O_3), and iron oxide (Fe_2O_3), the rest are carbon, calcium, magnesium, sulfur and other metals [5], [6], based on a statistical survey conducted by Cherian and Siddiqua (2019) [7].

Rice farming produces rice husk waste by 20%. Rice husk ash is a waste material from rice that has special properties, containing chemical compounds that can be pozzolanic, namely silica (SiO_2) [8]. The most common value of the silica content of husk ash is 94-96% and if the value is close to or below 90% it may be caused by husk samples that have been contaminated with other substances with low silica content so that proper rice husk waste treatment techniques are needed, namely by treating rice husk into synthetic zeolite [9], [10], [11].

The batik industry in its production process uses dyes. Meanwhile, the waste generated by the batik craft business is mostly in liquid form resulting from the rinsing/washing process. It is known in general that this batik craft business disposes of waste directly into the ditches around the house or batik location and is capable of causing adverse impacts on the environment, because the environment has a limited ability to degrade these dyes. Batik liquid waste contains hazardous heavy metals including Zn, Cd, Cu, Cr, and Pb. Sources of heavy metal chromium (Cr) come from dyes chromium chloride, potassium dichromate or from mordant substances, namely dye binders including $Cr(NO_3)_2$. Chromium metal is a chemical that is persistent, bioaccumulative, and highly toxic and cannot be decomposed in the environment and eventually accumulates in the human body through the food chain. As a heavy metal, chromium is a metal that has high toxicity [12].

This study aims to utilize fly ash boiler waste and rice husk ash as Cr metal adsorbent in batik waste, where it is expected that the adsorbent produced will produce synthetic zeolite because of the high silica content in rice husk ash and boiler fly ash. Besides adsorption on heavy metal Cr, COD and TSS were also tested.

2. Research Methodology

2.1. Materials

Research materials consist of fly ash from palm oil mill, rice husk ash, Hg_2SO_4, $K_2Cr_2O_7$, Ag_2SO_4, H_2SO_4, HCl, PP indicator and aquadest from Progo Mulyo Yogyakarta.

2.2. Procedures

The research design used is Complete Block Design with two factors, the first factor (A) is the ratio of the mass of rice husk ash and fly ash boiler with 3 levels, namely A1 (25%:75%), A2 (50%:50%), A3 (75%:25%), and the second factor (B) is the concentration of HCl solution with 3 levels, namely B1 (1M), B2 (2M) and B3 (3M). The experiment was repeated 2 times so that 18 experimental units would be obtained. The procedure in this study consisted of several stages, namely boiler fly ash pretreatment, rice husk ash pretreatment, adsorbent synthesis, and batik wastewater adsorption test.

1) Fly ash boiler pretreatment

Separation of magnetic components by inserting fly ash into a beaker glass filled with water and a magnetic stirrer, then stirred by heating. The ash attached to the magnet is discarded and the ash left in the glass beaker is taken as raw material. Then the fly ash was heated using an oven at a temperature of 105-110 ^oC for 6 h to remove the moisture content.

2) Rice husk ash pretreatment

Rice husk ash was dried in the sun then continued with drying using an oven at a temperature of 105 -110^oC to remove water until a constant moisture content was obtained.

3) Adsorbent synthesis

Adsorbent synthesis was shown as diagram in Fig. 1.

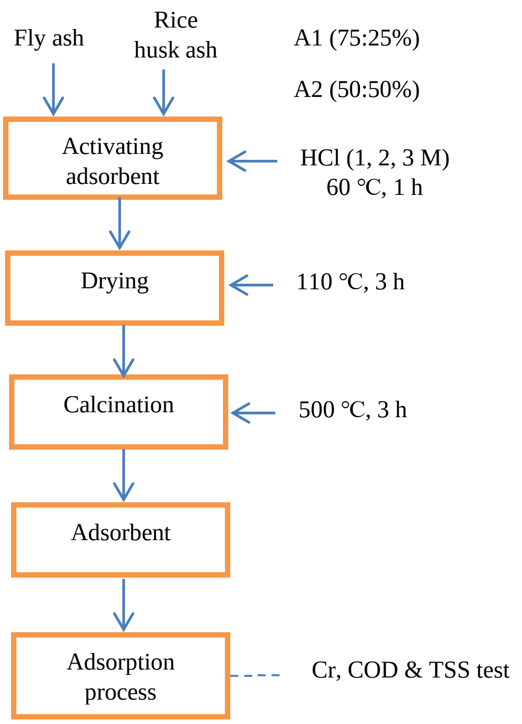

Fig. 1. Flowchart of adsorbent synthesis

3. Results and Discussion

3.1. Chrom Metal Test

One of the heavy metals that is dangerous and has the potential to pollute water is the heavy metal content of Cr. The results of the analysis of Cr metal after adsorption are shown in Table 1. From the results of the analysis that has been carried out, then a diversity analysis is carried out to determine whether or not there is a real influence on the mass ratio of rice husk ash and boiler fly ash and the addition of HCl concentration on the adsorbent on Cr analysis. The initial concentration of chrom in batik wastewater is 16.56 ppm.

Table 1. Primary data analysis of Cr metal adsorption

Sample	Block		Total	Average
	I (ppm)	*II (ppm)*		
	B1			
A1	13.75	13.25	27.00	13.50
A2	10.93	10.25	21.18	10.59
A3	5.44	5.36	10.80	5.40
	B2			
A1	14.52	14.36	28.88	14.44
A2	4.48	4.69	9.17	4.58
A3	2.61	3.87	6.49	3.24
	B3			
A1	12.55	12.36	24.92	12.46
A2	9.45	9.36	18.81	9.40
A3	8.10	8.24	16.34	8.17
Total	81.86	81.76	163.63	81.81
Average	9.10	9.09	18.18	9.09

From Table 2 it can be seen that the diversity of A in this case with the comparison of the diversity of rice husk ash and boiler fly ash has a significant effect on the absorption of Cr metal in batik waste. Then for diversity B, in this case the concentration of HCl solution as an adsorbent activator also significantly affects the absorption of Cr metal, while the interaction of the ratio of rice husk ash and fly ash boiler and the concentration of HCl solution with a tolerance value of 5% is also very significantly different. Furthermore, Duncan's multiple distance test at 5% level was carried out to see the real difference between the two factors.

Table 2. Analysis of Cr metal adsorption diversity

Diversity	db	JK	RK	F Calc.	F Table	
					5%	*1%*
A	2	246.96	123.48	809.33**	4.46	8.65
B	2	11.88	5.94	38.96**	4.46	8.65
A x B	4	2.64	0.66	4.33*	3.84	7.01
Block	1	0.00	0.00			
Error	8	1.22	0.15			
Total	17	262.72	130.24			

[a.] **very different real

[b.] *real different

In Table 3, it is known that the addition of the ratio between fly ash and rice husk ash has a significant effect on the absorption of Cr metal, this is due to the high levels of silica and zeolite so that it accelerates the absorption of metal content in batik wastewater. Synthetic zeolites have the adsorption ability to reduce metal ion levels in water [13]. Rice husk ash can be used as an adsorbent because in addition to being a porous material, it also has active groups, namely Si-O-Si and Si-OH which can react with many polar organic compounds and can adsorb dyes [14].

Table 3. Cr metal adsorption multiple distance test results

Sample	A1	A2	A3	B average
B1	13.50^{x}	10.59^{y}	5.40^{z}	9.83^{p}
B2	14.44^{x}	9.40^{y}	4.58^{z}	9.47^{q}
B3	12.46^{x}	8.17^{y}	3.24^{z}	7.95^{r}
A average	13.47^{a}	9.39^{b}	4.41^{c}	

[c.] Description: The mean followed by the same letter (x,y,z) in the row or column shows a significant difference with the Duncan test at 5% level

Furthermore, the addition of HCl also has a significant effect on metal testing. This is related to the main function of HCl for the activation of adsorbent making materials and the formation of new content of adsorbents such as silica and zeolite content, where the silica and zeolite content is able to reduce and clean the metal content in liquid waste. To get the synthetic zeolite content in an adsorbent material, it must be activated first with a strong acid such as HCl [15].

The metal test on batik liquid waste resulted in an interaction. The best metal test average for batik liquid waste was obtained in the A3B2 treatment, which was 3.24 ppm. In terms of the lower the metal content of the liquid batik waste, the better the quality of the waste, and for the decrease in the metal content of the batik liquid waste by 11 ppm or 80.43%. However, in the study the results did not meet the SNI for the metal content of batik liquid waste, namely at 0.239 ppm.

3.2. COD Analysis

Chemical Oxygen Demand is the amount of oxygen needed to chemically oxidize organic matter in water [16]. The initial COD of batik wastewater is 221.43 mg/L, while the results of the COD analysis are shown in Table 4.

Table 4. COD analysis data

Sample	Block		Total	Average
	I	***II***		
	B1			
A1	148.17	131.71	279.88	139.94
A2	65.85	82.32	148.17	74.08
A3	49.39	65.85	115.25	57.63
	B2			
A1	131.71	115.24	246.96	123.48
A2	82.32	65.85	148.17	74.08
A3	65.85	49.39	115.24	57.62
	B3			
A1	164.64	148.17	312.81	156.40
A2	82.32	90.78	173.10	86.55
A3	82.32	65.85	148.17	74.08
Total	889.05	864.59	1753.64	876.82
Average	98.78	96.07	194.85	97.42

From the results of the analysis that has been carried out, then a diversity analysis is carried out to determine whether or not there is a significant effect on the ratio of the mass of rice husk ash and fly ash as well as the concentration of HCl.

Table 5. COD diversity analysis

Diversity	db	JK	RK	F Calc.	F Table	
					5%	*1%*
A	2	18315.54	9157.77	67.40**	4.46	8.65
B	2	704.07	352.03	2.59tn	4.46	8.65
A x B	4	1847.18	461.79	3.39tn	3.84	7.01
Block	1	33.24	33.24			
Error	8	1086.82	135.85			
Total	17	21986.87	10140.70			

d. ** very different real

From Table 5 it can be seen that the diversity of A in this case the ratio of rice husk ash to fly ash obtained a calculated f value of 67.4095 this value is above the significance of 5% and 1%, so statistically there is a very significant difference between the ratio of rice husk ash and fly ash. ash produced so that statistically very significant effect on the decrease in COD. For the diversity of B in terms of the concentration of HCl as an adsorbent activator, it is obtained that f count is 2.5913 significantly, this value is above 5% and 1% so that statistically it is not significantly different, while the ratio of rice husk ash to fly ash and the concentration of HCl to the AxB value obtained f count of 3.3992 significantly then this value is above 5% so it is not significantly different. Furthermore, Duncan's multiple distance test at 5% level was carried out to see the real difference between the two factors.

In Table 6 it is known that there is a significant effect of adding rice husk ash with fly ash. This is due to the high silica content in the adsorbent derived from husk ash and fly ash. The more silica content in the adsorbent, the better the adsorption quality due to the high surface area and smaller pores so that it will reduce COD levels [8]. The best average COD levels in batik wastewater were obtained in the A3B2 treatment which was 57.624 mg/L, where the results obtained met the SNI, which was a maximum of 150 mg/L.

Table 6. COD multiple distance test results

Sample	A1	A2	A3	B average
B1	139.94^x	74.08^y	57.62^z	90.55
B2	123.48^x	107.01^y	57.62^z	96.04
B3	156.40^x	86.55^y	74.08^z	105.68
A average	139.94^a	89.21^b	63.11^c	

[e.] Description: The mean followed by the same letter (x,y,z) in the row or column shows a significant difference with the Duncan test at 5% level.

3.3. TSS Analysis

Liquid waste is generated from the washing, boiling, pressing and printing processes. The liquid waste contains high Total Suspended Solid (TSS). With the amount of pollutants in the wastewater, the oxygen levels will decrease. Thus it will cause life in the waters that need oxygen to be disturbed, and reduce its development and water acts as a carrier of disease [16], [17].

From the results of the analysis that has been carried out as shown in Table 7, then a diversity analysis is carried out to determine whether or not there is a significant effect on the percentage of adsorbent. From Table 8 it can be seen that the diversity of A in this case with the comparison of the diversity of rice husk ash with fly ash has a significant effect on the TSS test of batik liquid waste. The initial TSS for batik wastewater is 58.22 mg/L. For diversity B, in this case, the molarity of HCl was not significantly different, while the ratio of the mass of rice husk ash to fly ash and the concentration of HCl to the AxB value was very significantly different. Furthermore, Duncan's multiple distance test at 5% level was carried out to see the real difference between the two factors.

Table 7. TSS analysis data

Sample	Block		Total	Average
	I	*II*		
	B1			
A1	2.02	3.91	5.94	2.97
A2	4.70	4.50	9.20	4.60
A3	5.88	5.15	11.03	5.51
	B2			
A1	2.62	4.356	6.976	3.48
A2	4.71	5.348	10.048	5.02
A3	2.03	0.824	2.86	1.43
	B3			
A1	5.93	6.07	12.01	6.00
A2	2.66	3.38	6.04	3.02
A3	2	1.96	3.96	1.98
Total	32.56	35.52	68.08	34.04
Average	3.62	3.95	7.56	3.78

Table 8. TSS diversity analysis

Diversity	db	JK	RK	F. Calc.	F. Table	
					5%	*1%*
A	2	5.86	2.93	5.44*	4.46	8.65
B	2	3.41	1.70	3.17tn	4.46	8.65
A x B	4	31.23	7.80	14.51**	3.84	7.01
Block	1	0.48	0.48			
Error	8	4.30	0.53			
Total	17	45.30	13.47			

[f.] ** very different real

[g.] *real different

In Table 9 it can be seen that the addition of fly ash and rice husk ash had a significant effect on the TSS test on batik wastewater, but had no significant effect on the addition of HCl, the effect of adding strong acid to activate rice husk ash and fly ash as adsorbents and in this process resulted in an increase in the amount of silica zeolite in rice husk ash and fly ash, so as to reduce the level of solids or impurities of the adsorbent, as well as increase the active group so as to increase the absorption of the adsorbent [18].

As for the best average value in the TSS or solids test, it was obtained in the A3B2 sample of 1.430 mg/L or 97% where there was a significant decrease in the TSS content of batik liquid waste, namely a decrease of around 56 mg/L, and the reason for choosing the A3B2 sample even though all samples entered into SNI this is because the higher the decrease in solids content, the clearer the waste produced, so that the TSS test still meets the SNI for batik liquid waste, which is a maximum of 50 mg/L.

Table 9. TSS multiple distance test results

Sample	A1	A2	A3	B average
B1	2.97^{x}	4.60^{y}	5.51^{z}	4.36
B2	3.48^{x}	5.02^{y}	1.43^{z}	3.31
B3	6.00^{x}	3.02^{y}	1.98^{z}	3.66
A average	4.15^{b}	4.21^{a}	2.97^{c}	

[h.] Description: The mean followed by the same letter (x,y,z) in the row or column shows a significant difference with the Duncan test at 5% level.

3.4. BET Test

The BET test was only carried out on the best sample, namely A3B2, where the surface area was 118.214 m^2/g, and the surface area of the adsorbent that had not been activated was 62.068 m^2/g, where there was an increase in surface area after activation thereby increasing the active site on the adsorbent and reducing impurities present before activation. This causes the adsorbent produced to have a higher absorption capacity before activation using HCl solution [19], [20]. Although the adsorbent produced has a relatively high adsorption capacity, its surface area is still below that of the silica adsorbent, which is below 460 m^2/g [21].

4. Conclusion

The best adsorbent was produced at the ratio of rice husk ash and fly ash of 75%: 25% or 3:1 and the use of HCl solution as an activator of 2M, where the adsorption of heavy metal Cr was 80.43%, decreased COD was 74% and decreased TSS of 97.56%. This is due to the use of more rice husk ash with the use of HCl solution as an activator can increase the silica active group on the adsorbent thereby increasing the surface area of the adsorbent, where the surface area of the A3B2 sample is 118.24 m^2/g.

Acknowledgment

Authors want to thank to Department of Agricultural Products Technology for facilities and supports.

References

[1] A.A. Ayoola, O.S I. Fayomi, and I.F. Usoro, "Data on PKO biodiesel production using CaO catalyst from Turkey bones," Data in Brief, vol. 19, pp. 789–797, August 2018 https://doi.org/10.1016/j.dib.2018.05.103.

[2] B.L. Suparma, T.W. Panggabean, and S. Mude "Potensi penggunaan limbah kelapa sawit sebagai agregat pengisi pada campuran *hot rolled sheet-base*," Jurnal Transportasi, vol. 14(2), pp. 87-96 August 2014.

[3] P.S. Utama, R. Yamsaensung, and C. Sangwichien, "Silica gel derived from palm oil mill fly ash," Songklanakarin Journal of Science and Technology, vol. 40(1), pp. 121–126, February 2018. https://doi.org/10.14456/sjst-psu.2018.27.

[4] E. Jarosz-Krzeminska, and J. Poluszynska, "Repurposing fly ash derived from biomass combustion in fluidized bed boilers in large energy power plants as a mineral soil amendment," Energies (Basel), vol. 13(18), pp. 4805, September 2020. https://doi.org/10.3390/en13184805.

[5] A. Haile, G.G. Gelebo, T. Tesfaye, W. Mengie et al, "Pulp and paper mill wastes: utilizations and prospects for high value-added biomaterials," Bioresources and Bioprocessing, vol. 8(35), pp. 1-22, April 2021. https://doi.org/10.1186/s40643-021-00385- 3.

[6] X. Hu, T. Jarnerud, A. Karasev, P.G. Jonsson, and C. Wang, "Utilization of fly ash and waste lime from pulp and paper mills in the argon oxygen decarburization process," Journal of. Cleaner Production, vol. 261, pp. 121182, July 2010. https://doi.org/10.1016/j.jclepro.2020.121182.

[7] C. Cherian, S. Siddiqua, "Pulp and paper mill fly ash: a review," Sustainability (Switzerland) vol.11, pp. 1–16, August 2019. https://doi.org/10.3390/su11164394.

[8] A. Fadhilla, K.N. Hafni and A.H. Simamora, "Pengaruh limbah abu pembakaran biomassa kelapa sawit terhadap sifat-sifat fisika dan mekanik high impact polystyrene," Jurnal Teknik Kimia USU, vol. 4(3), pp. 23–28, September 2015. https://doi.org/10.32734/jtk.v4i3.1477.

[9] Houston, and D.F. Yahya, "Rice Chemistry and Technology," *American Association on of Cereal Chemist*, 2012.

[10] S.N. Azizi, and M. Yousefpour, "Synthesis of zeolite NaA and analcime using rice husk as silica source without using organic template," Journal of Materials Science, vol. 45, pp. 5692-5697, June 2010.

[11] T. Ningsih, R. Chairunnisa, and S. Miskah, "Pemanfaatan abu kerak boiler hasil pembakaran limbah kelapa sawit sebagai pengganti parsila pasir pada pembuatan beton," Positron, vol. 5(1), pp. 26-29, 2015. https://doi.org/10.26418/positron.v5il.9744.

[12] E. Prianti, M.B. Malino, and B.P. Lapanporo, "Pemanfaatan abu kerak boiler hasil pembakaran limbah kelapa sawit sebagai pengganti parsial pasir pada pembuatan beton," Positron, vol. 5(1), pp. 26–29, 2015. https://doi.org/10.26418/positron.v5i1.9744.

[13] V.H Putranto, E. Kusumastuti, and Jumaeri, "Pemanfaatan zeolit dari abu sekam padi dengan aktivasi asam untuk penurunan kesadahan air," Indonesian Journal of Mathematics and Natural Sciences, vol. 32(2), pp.164-174, 2015.

[14] T. Ahmad, M. Rafatullah, A. Ghazali et al, "Oil palm biomass–based adsorbents for the removal of water pollutants-a review," Journal of Environmental Science and Health, vol. 29(3), pp. 177-222, September 2011.

[15] H. Oktavianty, S. Sunardi, and R.M.A.A.S. Wardani, "Sintesis zeolit dari ekstrak sekam padi dan kaleng bekas sebagai adsorben penurunan kesadahan air," Jurnal Ilmiah Rekayasa Pertanian dan Biosistem, vol. 9(2), pp. 185–192, September 2021. https://doi.org/10.29303/jrpb.v9i2.293.

[16] A.K. Lumaela, B.W. Otok, and Sutikno, "Pemodelan chemical oxygen demand (cod) sungai di Surabaya dengan metode mixed geographically weighted regression," Jurnal Sains dan Seni, vol. 2(1), pp. 100-105, March 2013. https://doi.org/10.12962/j23373520.v2i1.3204.

[17] Y.S. Dewi, and Y. uchori, "Penurunan COD, TSS pada penyaringan air limbah tahu menggunakan media kombinasi pasir kuarsa, karbon aktif, sekam padi dan zeolite," Jurnal Universitas Satya Negara Indonesia, vol. 9(1), pp. 74-80, June 2016.

[18] D.L. Novianti, and A. Tuhu, "Penurunan TSS dan warna limbah industri batik secara elektro koagulasi," Envirotek: Jurnal Ilmiah Teknik Lingkungan, vol. 6(1), pp. 37-44, 2014.

[19] H. Oktavianty, "Sintesis zeolit x dari *fly ash* boiler pabrik kelapa sawit sebagai adsorben pemurnian biodiesel," Sang Pencerah, vol. 8(2), pp. 430-443, May 2022. https://doi.org/10.35326/pencerah.v8i2.1938.

[20] H. Oktavianty, S. Sunardi, and R.M.A.A.S. Wardani, “Sintesis zeolit dari ekstrak sekam padi dan kaleng bekas sebagai adsorben penurunan kesadahan air,” Jurnal Ilmiah Rekayasa Pertanian dan Biosistem, vol. 9(2), pp.185–192, September 2021. https://doi.org/10.29303/jrpb.v9i2.293.

[21] B. Ounphikul, N. Chantarasombat, A.J. Hunt, Y. Ngernyen, “A new low-cost carbon–silica composite adsorbent from a by-product of the sugar industry,” Materials Today: Proceedings, vol. 51, pp. 1884-1887, 2022. https://doi.org/10.1016/j.matpr.2021.10.113.