APPENDIX A

RAW MATERIAL ANALYSIS

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Proximate Analysis

Proximate analysis is an assay of the moisture, ash, volatile matter, and fixed carbon as determined by prescribed test method. Others constituents such as sulfur and phosphorus are not included [81].

A.1 Ash content analysis [82]

1. Crucible porcelain was ignited in the muffle furnace at 650 ± 25°C for 1 hour.
2. Crucible porcelain was cooled in the desiccator until room temperature is reached and then weighed.
3. Procedure 1-2 were repeated until constant weight is reached (error = ± 0.1 mg).
4. Durian shell was dried at 150 ± 5°C until constant mass is reached (in general it was obtained at 3 hours).
5. One gram sample was put into the ignited crucible.
6. The crucible was placed in the muffle furnace at 650 ± 25°C for 3 hours.
7. Sample was placed in desiccator and cooled until room temperature.
8. Procedure 6-7 were repeated until constant weight is reached.
9. Ash content can be calculated with equation:

$$\%\,\text{ash} = \frac{\text{mass of ash}}{\text{initial mass of sample}} \times 100\%$$

Sample analysis

Mass of crucible porcelain = 14.0923 grams

Mass of crucible porcelain + initial mass of durian shells = 15.0925 grams

Initial mass of durian shells = 1.0002 grams

Mass of crucible porcelain + ash = 14.1476 grams

Mass of ash = 14.1476 grams – 14.0923 grams = 0.0553 grams

$$\begin{aligned}\%\ \text{ash} &= \frac{\text{mass of ash}}{\text{initial mass of sample}}\times 100\% \\ &= \frac{0.0553\ \text{grams}}{1.0002\ \text{grams}}\times 100\% \\ &= 5.53\ \%\end{aligned}$$

A.2 Moisture content analysis [83]

1. Crucible porcelain was ignited in the muffle furnace at 650 ± 25°C for 1 hour.
2. Crucible porcelain was cooled in the desiccator until room temperature is reached and then weighed.
3. Procedure 1-2 were repeated until constant weight is reached (error = ± 0.1 mg).
4. One gram of dried activated carbon sample from procedure A was put into the crucible porcelain.
5. Sample was heated in the oven at 145–155°C for 3 hours.
6. Sample was placed in the desiccator and cooled until room temperature.
7. Procedure 5-6 were repeated until constant weight is reached.

8. Moisture content can be calculated with equation:

$$\% \text{ moisture} = \frac{\text{mass of moisture}}{\text{initial mass of sample}} \times 100\%$$

Sample analysis

Mass of crucible porcelain = 15.6106 grams

Mass of crucible porcelain + initial mass of durian shells = 16.6719 grams

Initial mass of durian shells = 1.0613 grams

Mass of crucible porcelain + dried sample = 15.6373 grams

Mass of dried sample = 16.6452 grams – 15.6106 grams = 1.0346 grams

Mass of moisture = initial mass of durian shells – mass of dried sample
= 1.0613 grams – 1.0346 grams
= 0.0267 grams

$$\begin{aligned} \% \text{ moisture} &= \frac{\text{mass of moisture}}{\text{initial mass of sample}} \times 100\% \\ &= \frac{0.0267 \text{ grams}}{1.0613 \text{ grams}} \times 100\% \\ &= 2.52\ \% \end{aligned}$$

A.3 Volatile matter content analysis [84]

1. Crucible porcelain with its lid was ignited in the muffle furnace at ±950°C for 30 minutes.
2. Crucible porcelain with its lid was cooled in desiccator until room temperature is reached and then weighed.

3. Procedure 1-2 were repeated until constant weight is reached (error = ± 0.1 mg).
4. One gram of dried activated carbon sample from procedure A was put into crucible porcelain and covered it with its lid.
5. The covered crucible was placed in the muffle furnace at 950 ± 25°C for 7 minutes ±10 seconds.
6. The covered crucible was placed in desiccator and cooled until room temperature.
7. Volatile matter content can be calculated with equation:

$$\%\ \text{loss mass} = \frac{\text{mass of ignited sample}}{\text{initial mass of sample}} \times 100\%$$

$$\%\ \text{volatile matter} = \%\ \text{loss mass} - \%\ \text{moisture}$$

Sample analysis

Mass of crucible porcelain + lid = 23.0464 grams

Mass of crucible + lid + initial mass of sample = 24.1107 grams

Initial mass of sample = 1.0643 grams

Mass of crucible + lid + ignited sample = 23.3432 grams

Mass of ignited sample = 0.2968 grams

Loss mass = initial mass of sample – mass of ignited sample
= 1.0643 grams – 0.2968 grams
= 0.7675 grams

$$\% \text{ loss mass} = \frac{\text{loss mass}}{\text{initial mass of sample}} \times 100\%$$

$$= \frac{0.7675 \text{ grams}}{1.0643 \text{ grams}} \times 100\%$$

$$= 72.11\ \%$$

$$\% \text{ volatile matter} = \% \text{ loss mass} - \% \text{ moisture}$$

$$= 72.11\ \% - 2.52\ \%$$

$$= 69.59\ \%$$

A.4 Carbon content analysis [81]

The fixed carbon is a calculated value. It is the resultant of the summation of percentage moisture, ash, and volatile matter subtracted from 100. Carbon content can be calculated with equation:

$$\% \text{ carbon} = 100\ \% - (\% \text{ ash} + \% \text{ moisture} + \% \text{ volatile matter})$$

Sample analysis

$$\% \text{ carbon} = 100\ \% - (\% \text{ ash} + \% \text{ moisture} + \% \text{ volatile matter})$$

$$= 100\ \% - (5.53\ \% + 2.52\ \% + 69.59\ \%)$$

$$= 22.36\ \%$$

APPENDIX B

DETERMINATION OF MAXIMUM WAVELENGTH AND METHYLENE BLUE STANDARD CURVE

APPENDIX B

DETERMINATION OF MAXIMUM WAVELENGTH AND METHYLENE BLUE STANDARD CURVE

B.1 Solution preparation

1. Preparation of 250 mg/L methylene blue mother liquor as much as 1 L.

   250 mg/L × 1 L = 0.2500 g (±10%)

   0.2500 gram methylene blue was weighed using analytical balace, and dissolved with aquadest until its volume was accurately 1000 mL.

2. Preparation of 10 standard solutions for each methylene blue dyes.

   i. 10 mL of mother liquor was taken and put into measuring flask, and then diluted with aquadest until its volume was 50 mL.

   ii. 20 ml of mother liquor was taken and put into measuring flask, and then diluted with aquadest until its volume was 50 mL.

   iii. 30 ml of mother liquor was taken and put into measuring flask, and then diluted with aquadest until its volume was 50 mL.

   iv. 40 ml of mother liquor was taken and put into measuring flask, and then diluted with aquadest until its volume was 50 mL.

   v. 50 ml of mother liquor was taken and put into measuring flask, and then diluted with aquadest until its volume was 50 mL.

B.2 Determination of maximum wavelength

Maximum wavelength was determined by measuring the absorbance of the standard solution (iii) using spectrophotometer UV-VIS in the range of wavelength 600-700 nm.

Table B.1 Relationship between λ and absorbance of methylene blue solution

Wavelength (nm)	Absorbance
600	0.0621
610	0.0701
620	0.0826
630	0.0846
640	0.1104
650	0.1355
660	0.1553
661	0.1569
662	0.1578
663	0.1586
664	0.1583
665	0.1576
666	0.1567
667	0.1553
668	0.1531
669	0.1501

From figure B.1, it can be seen that the maximum wavelength for methylene blue analysis is 663 nm.

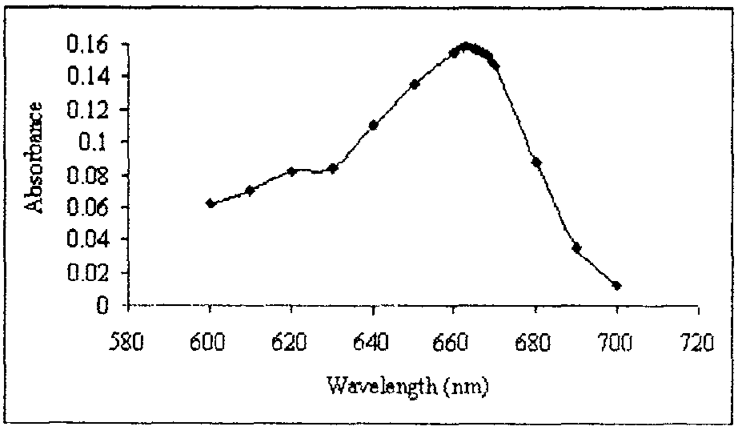

Figure B.1 Determination of maximum wavelength of methylene blue

From the figure above, it can be obtained the maximum wavelength of methylene blue, which is 663 nm.

B.3 Preparation of standard curve

1. Absorbance of each standard solution was measured using spectrophotometer UV-VIS at maximum wavelength.
2. Standard curve between absorbance and dyes concentration was prepared and then the linear regression was determined.

Table B.2 Relationship between concentration and absorbance of methylene blue

Concentration (mg/L)	Absorbance
0,5	0,0311
1,0	0,1002
1,5	0,1586
2,0	0,2345
2,5	0,3213

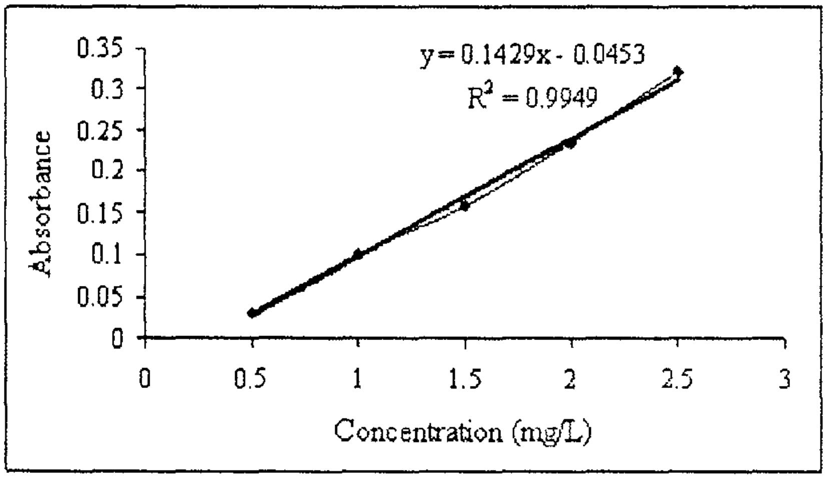

Figure B.2 Standard curve of methylene blue solution

The linear regression equation from figure B.2 determined using Sigma Plot 9.0 software is:

$$y = 0.1429\ x + 0.0453$$

where: y is the absorbance of methylene blue solution

x is the concentration of methylene blue solution

APPENDIX C

EXPERIMENTAL DATA

APPENDIX C

EXPERIMENTAL DATA

C.1 Calculation of % activated carbon yield

Original mass of the precursor on a dry basis = 25 grams

Table C.1 Yield data of activated carbon product

I.R.	T, K	Carbon code	Yield (Mass, g)
0.25	673.15	T_1I_1	10.55
	723.15	T_2I_1	9.14
	773.15	T_3I_1	7.79
	823.15	T_4I_1	7.14
	873.15	T_5I_1	6.62
	923.15	T_6I_1	6.17
0.50	673.15	T_1I_2	9.99
	723.15	T_2I_2	8.65
	773.15	T_3I_2	6.88
	823.15	T_4I_2	6.56
	873.15	T_5I_2	6.22
	923.15	T_6I_2	5.73
1.00	673.15	T_1I_3	9.30
	723.15	T_2I_3	7.62
	773.15	T_3I_3	6.29
	823.15	T_4I_3	5.82
	873.15	T_5I_3	5.72
	923.15	T_6I_3	5.49

C.2 Methylene blue adsorption

Table C.2 Experimental data of methylene blue adsorption

I.R.	T, K	Carbon code	M, g	A
0.25	673.15	T_1I_1	0.1345	0.178
			0.3322	0.097
			0.5347	0.070
			0.8187	0.062
			1.0274	0.056
			1.2374	0.054
	723.15	T_2I_1	0.0925	0.220
			0.1811	0.140
			0.2259	0.113
			0.2324	0.105
			0.6073	0.071
			0.8054	0.058
	773.15	T_3I_1	0.1175	0.263
			0.3254	0.184
			0.4760	0.123
			0.6531	0.109
			0.8435	0.098
			1.1220	0.093
	823.15	T_4I_1	0.1026	0.296
			0.2981	0.178
			0.4519	0.147
			0.6861	0.123
			0.9111	0.104
			1.1145	0.100
	873.15	T_5I_1	0.1131	0.232
			0.2513	0.135
			0.2879	0.108
			0.4831	0.094
			0.5183	0.090
			0.6188	0.084
	923.15	T_6I_1	0.1504	0.227
			0.3725	0.123
			0.6488	0.089
			0.8165	0.075
			1.0236	0.072
			1.2026	0.068

0.50	673.15	T_1I_2	0.2883	0.072	18.91	80.15
			0.2081	0.087	29.34	106.054
			0.1670	0.103	40.55	125.44
			0.1078	0.144	68.74	168.12
			0.0980	0.158	79.08	174.32
			0.0427	0.269	156.88	218.283
	723.15	T_2I_2	0.0925	0.168	85.8455	177.464
			0.1811	0.104	41.1222	115.338
			0.2259	0.088	29.8905	97.4367
			0.2324	0.087	29.226	94.9974
			0.5812	0.057	8.1125	41.6186
			0.7522	0.053	5.1585	32.5501
	773.15	T_3I_2	0.1511	0.171	87.6557	107.442
			0.2891	0.112	46.4777	70.4104
			0.4019	0.088	30.112	54.7121
			0.5665	0.084	27.0969	39.3478
			0.7615	0.080	24.0922	29.6678
			1.0024	0.073	19.6927	22.9752
	823.15	T_4I_2	0.1121	0.187	99.2159	134.509
			0.1988	0.118	50.8029	100.2
			0.3559	0.105	41.736	58.5176
			0.4346	0.089	30.4194	50.5246
			0.4709	0.078	22.5591	48.2957
			0.5548	0.074	20.1058	41.4354
	873.15	T_5I_2	0.2261	0.253	145.5579	46.1929
			0.3191	0.215	118.9863	41.0573
			0.4234	0.186	98.1947	35.8539
			0.4961	0.174	90.0582	32.2398
			0.9496	0.110	45.6119	21.5236
			1.4916	0.087	29.4591	14.7855
	923.15	T_6I_2	0.1925	0.234	132.2114	61.1889
			0.2210	0.160	80.2544	76.808
			0.5123	0.143	68.2144	35.4842
			0.7711	0.103	40.4815	27.1714
			0.8235	0.085	27.6214	27.0041
			1.0561	0.074	20.4194	21.7385

1.00	673.15	T_1I_3	0.2566	0.182	95.9219	60.046
			0.4922	0.120	52.565	40.1128
			0.8565	0.091	32.3125	25.4159
			0.8956	0.074	20.2519	25.653
			0.9612	0.071	18.2694	24.1085
			1.1985	0.068	15.9156	19.5314
	723.15	T_2I_3	0.2416	0.160	80.0671	70.3365
			0.5009	0.080	24.0669	45.1054
			0.7891	0.075	21.0811	29.0101
			0.8022	0.074	20.0644	28.6631
			0.9064	0.071	18.0655	25.5885
			0.9566	0.068	16.0631	24.455
	773.15	T_3I_3	0.1064	0.269	156.8869	87.5123
			0.2816	0.150	72.9458	62.8744
			0.5077	0.105	42.0126	40.9666
			0.7018	0.092	32.9143	30.9327
			0.9160	0.083	26.6105	24.3875
			1.1106	0.074	20.1656	20.6946
	823.15	T_4I_3	0.1622	0.248	142.0546	66.5508
			0.2516	0.191	102.163	58.7587
			0.4416	0.124	55.0646	44.143
			0.6168	0.095	34.5164	34.9357
			1.4911	0.067	14.9821	15.7614
			1.5364	0.064	12.7642	15.441
	873.15	T_5I_3	0.1806	0.271	158.2161	50.8217
			0.2764	0.221	123.1564	45.8966
			0.3583	0.186	98.5465	42.2689
			0.7283	0.101	39.0645	28.9642
			0.9047	0.087	29.0546	24.4219
			1.2324	0.073	19.4591	18.7061
	923.15	T_6I_3	0.5411	0.156	77.6114	31.8589
			0.6223	0.132	60.4839	30.4541
			0.6352	0.127	57.2658	30.3423
			0.8451	0.082	25.8689	26.5213
			0.9521	0.067	14.9124	24.6915
			1.1569	0.059	9.8029	20.7621

C.3 Adsorption Equilibrium and Kinetics of T_1I_2

Table C.3 Experimental data of adsorption equilibrium of T_1I_2

$T_{adsorption}$, K	M, g	A
303.15	0.0427	0.269
	0.0577	0.229
	0.0829	0.182
	0.0980	0.158
	0.1078	0.144
	0.1375	0.116
	0.1670	0.103
	0.2081	0.087
	0.2883	0.072
	0.6086	0.057
313.15	0.0490	0.260
	0.0644	0.223
	0.0916	0.174
	0.1042	0.153
	0.1261	0.132
	0.1479	0.115
	0.1810	0.096
	0.2194	0.087
	0.3074	0.070
	0.8419	0.054
323.15	0.0472	0.275
	0.0607	0.244
	0.0719	0.219
	0.0898	0.187
	0.1076	0.163
	0.1175	0.145
	0.1517	0.119
	0.1802	0.102
	0.2229	0.086
	0.5249	0.060

Table C.4 Experimental data of adsorption kinetics of T_1I_2 at 303.15 K

C_0 mg/L	t, min	A
200	0	0.331
	30	0.317
	60	0.311
	90	0.307
	120	0.298
	150	0.287
	180	0.286
	240	0.270
	300	0.256
	360	0.241
	480	0.228
	720	0.188
	1440	0.106
	2880	0.068
250	0	0.403
	30	0.389
	60	0.385
	90	0.367
	120	0.360
	150	0.339
	180	0.336
	240	0.329
	300	0.306
	360	0.294
	480	0.259
	720	0.223
	1440	0.129
	2880	0.072
300	0	0.474
	30	0.457
	60	0.452
	90	0.435
	120	0.421
	150	0.403
	180	0.397
	240	0.382
	300	0.353
	360	0.336
	480	0.298
	720	0.253
	1440	0.143
	2880	0.076

Table C.5 Experimental data of adsorption kinetics of T_1I_2 at 313.15 K

C_0 mg/L	t, min	A
200	0	0.331
	30	0.310
	60	0.305
	90	0.301
	120	0.286
	150	0.268
	180	0.265
	240	0.244
	300	0.223
	360	0.210
	480	0.174
	720	0.140
	1440	0.080
	2880	0.056
250	0	0.403
	30	0.390
	60	0.362
	90	0.353
	120	0.345
	150	0.319
	180	0.310
	240	0.280
	300	0.262
	360	0.249
	480	0.204
	720	0.157
	1440	0.080
	2880	0.058
300	0	0.474
	30	0.446
	60	0.438
	90	0.405
	120	0.399
	150	0.378
	180	0.362
	240	0.326
	300	0.303
	360	0.274
	480	0.237
	720	0.176
	1440	0.090
	2880	0.062

Table C.6 Experimental data of adsorption kinetics of T_1I_2 at 323.15 K

C_0 mg/L	t, min	A	*Ce*, mg/L	*qe*, mg/g
200	0	0.331	200.0000	0.0000
	30	0.304	181.3216	3.1133
	60	0.300	178.1102	3.6483
	90	0.287	168.9159	5.1817
	120	0.260	150.3277	8.2800
	150	0.250	143.2060	9.4667
	180	0.233	131.5606	11.4067
	240	0.218	120.5820	13.2367
	300	0.194	103.7111	16.0483
	360	0.176	91.5808	18.0700
	480	0.149	72.7806	21.2033
	720	0.105	41.5671	26.4067
	1440	0.065	13.5808	31.0700
	2880	0.055	6.7075	32.2167
250	0	0.403	250.0000	0.0000
	30	0.374	230.1508	3.3083
	60	0.366	224.6108	4.2317
	90	0.336	203.1205	7.8133
	120	0.316	189.6508	10.0583
	150	0.290	171.5608	13.0733
	180	0.287	168.9471	13.5100
	240	0.248	141.7308	18.0450
	300	0.231	129.6808	20.0533
	360	0.204	110.7408	23.2100
	480	0.172	88.6808	26.8867
	720	0.115	48.9375	33.5117
	1440	0.069	16.8708	38.8550
	2880	0.058	8.6212	40.2300
300	0	0.474	300.0000	0.0000
	30	0.433	271.5940	4.7350
	60	0.423	264.5881	5.9033
	90	0.386	238.7442	10.2100
	120	0.372	228.9173	11.8483
	150	0.345	209.5410	15.0767
	180	0.319	191.4608	18.0900
	240	0.295	174.5205	20.9133
	300	0.255	147.0208	25.4967
	360	0.238	134.5604	27.5733
	480	0.179	93.4706	34.4217
	720	0.135	62.6110	39.5650
	1440	0.076	21.4716	46.4217
	2880	0.062	11.8316	48.0283

APPENDIX D

DATA ANALYSIS

APPENDIX D

DATA ANALYSIS

D.1 Calculation of % Activated Carbon Yield

The example calculation from table C.1 for impregnation ratio 0.25 and activation temperature 673.15 K:

Original mass of the precursor on a dry basis = 25 grams

Yield (mass) = 10.55 grams

$$\%\ \text{Yield} = \frac{\text{Yield (mass)}}{\text{Original mass of the precursor}} \times 100\%$$

$$= \frac{10.55\ \text{grams}}{25\ \text{grams}} \times 100\%$$

$$= 42.2\ \%$$

By the same way, table D.1 can be made.

Table D.1 Production yield of activated carbon

I.R.	T, K	Carbon code	Yield, %wt
0.25	673.15	T_1I_1	42.20
	723.15	T_2I_1	36.56
	773.15	T_3I_1	31.16
	823.15	T_4I_1	28.56
	873.15	T_5I_1	26.48
	923.15	T_6I_1	24.68
0.50	673.15	T_1I_2	39.96
	723.15	T_2I_2	34.60
	773.15	T_3I_2	27.52
	823.15	T_4I_2	26.24
	873.15	T_5I_2	24.88
	923.15	T_6I_2	22.92
1.00	673.15	T_1I_3	37.20
	723.15	T_2I_3	30.48
	773.15	T_3I_3	25.16
	823.15	T_4I_3	23.28
	873.15	T_5I_3	22.88
	923.15	T_6I_3	21.96

D.2 Methylene Blue Adsorption

The example calculation from table C.1 for impregnation ratio 0.25 and activation temperature 673.15 K:

Mass of activated carbon = 0.1342 grams

Absorbance = 0.178

$A = 0.1429\, C_1 + 0.0453$

$$C_1 = \frac{0.178 - 0.0453}{0.1429} = 0.928621 \text{ mg/L}$$

$$V_1 \times C_1 = Ve \times Ce$$

$$100 \text{ mL} \times 0.928621 \text{ mg/L} = 1 \text{ mL} \times Ce$$

$$Ce = 92.8621 \text{ mg/L}$$

$$qe = \frac{C_0 - C_e}{m} \times V$$

$$= \frac{250\ \text{mg/L} - 92.8621\ \text{mg/L}}{0.1342\ \text{g}} \times 0.1\ \text{L}$$

$$= 117.0923\ \text{mg/g}$$

By the same way, table D.2 – D.6 can be made.

Table D.2 Data calculation for methylene blue adsorption

I.R.	T, K	Carbon code	M, g	A	*Ce*, mg/L	*qe*, mg/g
0.25	673.15	T_1I_1	0.1345	0.178	92.5332	117.0494
			0.3322	0.097	36.1302	64.3802
			0.5347	0.070	17.1659	43.5453
			0.8187	0.062	11.5816	29.1209
			1.0274	0.056	7.1589	23.6359
			1.2374	0.054	6.3891	19.6876
	723.15	T_2I_1	0.0925	0.220	122.2388	138.1202
			0.1811	0.140	66.3661	101.3992
			0.2259	0.113	47.5444	89.6218
			0.2324	0.105	41.5811	89.6811
			0.6073	0.071	17.7891	38.2350
			0.8054	0.058	9.2285	29.8952
	773.15	T_3I_1	0.1175	0.263	152.3443	83.1112
			0.3254	0.184	97.3421	46.9139
			0.4760	0.123	54.2467	41.1246
			0.6531	0.109	44.6082	31.4488
			0.8435	0.098	36.5928	25.3002
			1.1220	0.093	33.3800	19.3066
	823.15	T_4I_1	0.1026	0.296	175.1076	72.9945
			0.2981	0.178	92.8098	52.7307
			0.4519	0.147	71.463	39.5081
			0.6861	0.123	54.1429	28.5464
			0.9111	0.104	41.181	22.9194
			1.1145	0.100	38.0649	19.0162
	873.15	T_5I_1	0.1131	0.232	130.8188	105.3768
			0.2513	0.135	62.8691	74.4651
			0.2879	0.108	43.8209	71.6148
			0.4831	0.094	34.3177	44.6455
			0.5183	0.090	31.1453	42.2255
			0.6188	0.084	27.2880	35.9910
	923.15	T_6I_1	0.1504	0.227	127.2577	81.6063
			0.3725	0.123	54.5276	52.4738
			0.6488	0.089	30.5514	33.822
			0.8165	0.075	20.6963	28.0831
			1.0236	0.072	18.6984	22.5967
			1.2026	0.068	16.1092	19.4482

0.50	673.15	T_1I_2	0.0427	0.269	156.88	218.283
			0.0980	0.158	79.0801	174.324
			0.1078	0.144	68.7435	168.122
			0.1670	0.103	40.5515	125.44
			0.2081	0.087	29.3424	106.054
			0.2883	0.072	18.9111	80.1504
	723.15	T_2I_2	0.0925	0.168	85.8455	177.464
			0.1811	0.104	41.1222	115.338
			0.2259	0.088	29.8905	97.4367
			0.2324	0.087	29.226	94.9974
			0.5812	0.057	8.1125	41.6186
			0.7522	0.053	5.1585	32.5501
	773.15	T_3I_2	0.1511	0.171	87.6557	107.442
			0.2891	0.112	46.4777	70.4104
			0.4019	0.088	30.112	54.7121
			0.5665	0.084	27.0969	39.3478
			0.7615	0.080	24.0922	29.6678
			1.0024	0.073	19.6927	22.9752
	823.15	T_4I_2	0.1121	0.187	99.2159	134.509
			0.1988	0.118	50.8029	100.2
			0.3559	0.105	41.736	58.5176
			0.4346	0.089	30.4194	50.5246
			0.4709	0.078	22.5591	48.2957
			0.5548	0.074	20.1058	41.4354
	873.15	T_5I_2	0.2261	0.253	145.5579	46.1929
			0.3191	0.215	118.9863	41.0573
			0.4234	0.186	98.1947	35.8539
			0.4961	0.174	90.0582	32.2398
			0.9496	0.110	45.6119	21.5236
			1.4916	0.087	29.4591	14.7855
	923.15	T_6I_2	0.1925	0.234	132.2114	61.1889
			0.2210	0.160	80.2544	76.808
			0.5123	0.143	68.2144	35.4842
			0.7711	0.103	40.4815	27.1714
			0.8235	0.085	27.6214	27.0041
			1.0561	0.074	20.4194	21.7385

1.00	673.15	T_1I_3	0.2566	0.182	95.9219	60.046
			0.4922	0.120	52.565	40.1128
			0.8565	0.091	32.3125	25.4159
			0.8956	0.074	20.2519	25.653
			0.9612	0.071	18.2694	24.1085
			1.1985	0.068	15.9156	19.5314
	723.15	T_2I_3	0.2416	0.160	80.0671	70.3365
			0.5009	0.080	24.0669	45.1054
			0.7891	0.075	21.0811	29.0101
			0.8022	0.074	20.0644	28.6631
			0.9064	0.071	18.0655	25.5885
			0.9566	0.068	16.0631	24.455
	773.15	T_3I_3	0.1064	0.269	156.8869	87.5123
			0.2816	0.150	72.9458	62.8744
			0.5077	0.105	42.0126	40.9666
			0.7018	0.092	32.9143	30.9327
			0.9160	0.083	26.6105	24.3875
			1.1106	0.074	20.1656	20.6946
	823.15	T_4I_3	0.1622	0.248	142.0546	66.5508
			0.2516	0.191	102.163	58.7587
			0.4416	0.124	55.0646	44.143
			0.6168	0.095	34.5164	34.9357
			1.4911	0.067	14.9821	15.7614
			1.5364	0.064	12.7642	15.441
	873.15	T_5I_3	0.1806	0.271	158.2161	50.8217
			0.2764	0.221	123.1564	45.8966
			0.3583	0.186	98.5465	42.2689
			0.7283	0.101	39.0645	28.9642
			0.9047	0.087	29.0546	24.4219
			1.2324	0.073	19.4591	18.7061
	923.15	T_6I_3	0.5411	0.156	77.6114	31.8589
			0.6223	0.132	60.4839	30.4541
			0.6352	0.127	57.2658	30.3423
			0.8451	0.082	25.8689	26.5213
			0.9521	0.067	14.9124	24.6915
			1.1569	0.059	9.8029	20.7621

D.3 Adsorption Equilibrium and Kinetics of T_1I_2

Table D.3 Data calculation of adsorption equilibrium of T_1I_2

$T_{adsorption}$, K	M, g	A	*Ce*, mg/L	*qe*, mg/g
303.15	0.0427	0.269	156.8800	218.2828
	0.0577	0.229	128.7319	210.3089
	0.0829	0.182	95.9622	185.8824
	0.0980	0.158	79.0801	174.3243
	0.1078	0.144	68.7435	168.1221
	0.1375	0.116	49.8135	145.6134
	0.1670	0.103	40.5515	125.4400
	0.2081	0.087	29.3424	106.0539
	0.2883	0.072	18.9111	80.1504
	0.6086	0.057	8.1402	39.7421
313.15	0.0490	0.260	150.3265	203.2816
	0.0644	0.223	124.2622	195.2261
	0.0916	0.174	90.1108	174.6106
	0.1042	0.153	75.3188	167.6500
	0.1261	0.132	60.5503	150.2225
	0.1479	0.115	48.5111	136.2058
	0.1810	0.096	35.3592	118.5671
	0.2194	0.087	29.4368	100.5265
	0.3074	0.070	17.5322	75.6198
	0.8419	0.054	5.7592	29.0111
323.15	0.0472	0.275	160.7095	189.0101
	0.0607	0.244	138.9189	182.9627
	0.0719	0.219	121.5802	178.5066
	0.0898	0.187	99.0511	168.0026
	0.1076	0.163	82.5601	155.6326
	0.1175	0.145	69.7305	153.4386
	0.1517	0.119	51.5607	130.7882
	0.1802	0.102	39.4068	116.8397
	0.2229	0.086	28.2112	99.5211
	0.5249	0.060	10.5521	45.6200

Table D.4 Data calculation of adsorption kinetics of T_1I_2 at 303.15 K

C_0 mg/L	t, min	A	*Ce*, mg/L	*qe*, mg/g
200	0	0.331	200.0000	0.0000
	30	0.317	190.3102	1.6150
	60	0.311	185.6111	2.3983
	90	0.307	183.2421	2.7933
	120	0.298	176.9829	3.8367
	150	0.287	169.2200	5.1300
	180	0.286	168.1205	5.3133
	240	0.270	156.9816	7.1700
	300	0.256	147.2319	8.7950
	360	0.241	136.9826	10.5033
	480	0.228	127.5322	12.0783
	720	0.188	99.5109	16.7483
	1440	0.106	42.1424	26.3100
	2880	0.068	15.5968	30.7333
250	0	0.403	250.0000	0.0000
	30	0.389	240.5121	1.5817
	60	0.385	237.4102	2.0983
	90	0.367	225.2375	4.1267
	120	0.360	220.1887	4.9683
	150	0.339	205.6077	7.3983
	180	0.336	203.5799	7.7367
	240	0.329	198.7406	8.5433
	300	0.306	182.1126	11.3167
	360	0.294	174.2654	12.6667
	480	0.259	149.5824	16.7367
	720	0.223	124.6306	20.8950
	1440	0.129	58.6264	31.9000
	2880	0.072	18.7326	38.5450
300	0	0.474	300.0000	0.0000
	30	0.457	288.3109	1.9483
	60	0.452	284.5594	2.5733
	90	0.435	272.4516	4.5917
	120	0.421	263.1906	6.1350
	150	0.403	250.0640	8.3333
	180	0.397	246.0246	9.0000
	240	0.382	235.6431	10.7300
	300	0.353	214.9759	14.1700
	360	0.336	203.5281	16.0767
	480	0.298	176.9816	20.5033
	720	0.253	145.2316	25.7950
	1440	0.143	68.0594	38.6583
	2880	0.076	21.5906	46.4017

Table D.5 Data calculation of adsorption kinetics of T_1I_2 at 313.15 K

C_0 mg/L	t, min	A	*Ce*, mg/L	*qe*, mg/g
200	0	0.331	200.0000	0.0000
	30	0.310	185.3204	2.4467
	60	0.305	181.7450	3.0417
	90	0.301	179.0110	3.4983
	120	0.286	168.5424	5.2433
	150	0.268	155.6223	7.3967
	180	0.265	153.4401	7.7600
	240	0.244	139.2140	10.1317
	300	0.223	124.1457	12.6667
	360	0.210	115.3248	14.1133
	480	0.174	90.2443	18.2933
	720	0.140	66.4242	22.2633
	1440	0.080	24.1122	29.3167
	2880	0.056	7.5115	32.0817
250	0	0.403	250.0000	0.0000
	30	0.390	241.5606	1.4067
	60	0.362	221.5604	4.7400
	90	0.353	215.4104	5.7650
	120	0.345	209.6445	6.7267
	150	0.319	191.6853	9.7200
	180	0.310	185.4245	10.7633
	240	0.280	164.2325	14.2950
	300	0.262	151.4704	16.4217
	360	0.249	142.4276	17.9300
	480	0.204	111.2376	23.1283
	720	0.157	78.2114	28.6317
	1440	0.080	24.6243	37.5633
	2880	0.058	9.0215	40.1633
300	0	0.474	300.0000	0.0000
	30	0.446	280.1404	3.3186
	60	0.438	274.5112	4.2483
	90	0.405	251.4654	8.0900
	120	0.399	247.6348	8.7283
	150	0.378	232.5675	11.2400
	180	0.362	221.5675	13.0733
	240	0.326	196.5402	17.2433
	300	0.303	180.4547	19.9250
	360	0.274	160.2276	23.2967
	480	0.237	134.3245	27.6133
	720	0.176	91.5645	34.7404
	1440	0.090	31.5778	44.7383
	2880	0.062	11.7546	48.0417

Table D.6 Data calculation of adsorption kinetics of T_1I_2 at 323.15 K

C₀ mg/L	t, min	A	*Ce*, mg/L	*qe*, mg/g
200	0	0.331	200.0000	0.0000
	30	0.304	181.3216	3.1133
	60	0.300	178.1102	3.6483
	90	0.287	168.9159	5.1817
	120	0.260	150.3277	8.2800
	150	0.250	143.2060	9.4667
	180	0.233	131.5606	11.4067
	240	0.218	120.5820	13.2367
	300	0.194	103.7111	16.0483
	360	0.176	91.5808	18.0700
	480	0.149	72.7806	21.2033
	720	0.105	41.5671	26.4067
	1440	0.065	13.5808	31.0700
	2880	0.055	6.7075	32.2167
250	0	0.403	250.0000	0.0000
	30	0.374	230.1508	3.3083
	60	0.366	224.6108	4.2317
	90	0.336	203.1205	7.8133
	120	0.316	189.6508	10.0583
	150	0.290	171.5608	13.0733
	180	0.287	168.9471	13.5100
	240	0.248	141.7308	18.0450
	300	0.231	129.6808	20.0533
	360	0.204	110.7408	23.2100
	480	0.172	88.6808	26.8867
	720	0.115	48.9375	33.5117
	1440	0.069	16.8708	38.8550
	2880	0.058	8.6212	40.2300
300	0	0.474	300.0000	0.0000
	30	0.433	271.5940	4.7350
	60	0.423	264.5881	5.9033
	90	0.386	238.7442	10.2100
	120	0.372	228.9173	11.8483
	150	0.345	209.5410	15.0767
	180	0.319	191.4608	18.0900
	240	0.295	174.5205	20.9133
	300	0.255	147.0208	25.4967
	360	0.238	134.5604	27.5733
	480	0.179	93.4706	34.4217
	720	0.135	62.6110	39.5650
	1440	0.076	21.4716	46.4217
	2880	0.062	11.8316	48.0283

APPENDIX E

PUBLICATIONS

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dsorption of basic dye onto activated carbon prepared from durian shell: Studies of adsorption equilibrium and kinetics

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ctivated carbon was prepared from durian shell and used for the removal of methylene blue from aqueous solutions. The activated carbon epared using chemical activation method with potassium hydroxide as the activating agent. The activation was conducted at 673.15 K for h mass ratio of chemical activating agent to durian shell 1:2. Batch kinetics and isotherm studies were conducted to evaluate the adsorption or of the activated carbon from durian shell. The adsorption experiments were carried out isothermally at three different temperatures. The uir and Freundlich isotherm model were used to describe the equilibria data. The Langmuir model agrees with experimental data well. The uir surface kinetics, pseudo first order and pseudo second order models were used to evaluate the kinetics data and the rate constant were termined. The experimental data fitted very well with the Langmuir surface kinetics and pseudo first order model.

ds: Activated carbon; Adsorption; Durian shell

roduction

eral industries, such as textile, ceramic, paper, printing istic use dyes in order to color their product. In the coloring s, these industries also consume substantial volumes of and as a result, large amount of colored wastewater are ted. The present of dyes in water is undesirable since very small amount of these coloring agents is highly and may be toxic to aquatic environment [1–5]. Several ls are available for color removal from wastewater such as ane separation, aerobic and anaerobic degradation using microorganisms, chemical oxidation, coagulation and ation, adsorption using different kind of adsorbents and osmosis [1,3,5]. Among them, adsorption is a promising l technique that produces effluents containing very low of dissolved organic compounds.

siderable research has been conducted into the removal from water effluent using adsorption technique using it adsorbents such as activated carbon [2–5], fly ash [6], t [7–9], corncob [10], barley husk [10], orange peel [11], living biomass [12–17] and other low-cost adsorbents [1]. The most widely used adsorbent for this purpose is activated carbon, but commercially available activated carbons are expensive and so they may not be economical for wastewater treatment. Other untreated low-cost adsorbents often have low adsorption capacities; therefore their removal efficiencies are poor. If an activated carbon with high adsorption capacity for wastewater treatment purpose can be produced from low-cost or waste materials, then its use as an adsorbent should be economical.

Activated carbon is the most popular adsorbent for the adsorption process since it has high adsorption capacity. The adsorption capacity of activated carbon depends not only on its surface area, but also on its internal pore structure, surface characteristic and the presence of functional group on pore surface. Internal pore structure and surface characteristic play an important role in adsorption processes and depend both on the precursor used and method of preparation [18]. Different methods are available for characterizing the pore structure (surface area, pore volume, pore size distribution, etc.) of activated carbon such as small angle X-ray, mercury porosimetry, scanning electron microscopy and gas as well as liquid phase adsorption [19]. The characteristics of adsorption behavior of activated carbon are generally inferred in terms of both adsorption kinetics and equilibrium isotherm [20]. Therefore, to study both the adsorption kinetics and equilibrium, it is important to understand the adsorption mechanism

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enclature

equilibrium concentration (mg/L)
initial concentration (mg/L)
solute concentration at the liquid phase at any time t (mg/L)
activation energy of adsorption (kJ/mol)
activation energy of desorption (kJ/mol)
the rate constant of adsorption (g/mg min)
desorption constant (min^{-1})
desorption rate constant at infinite temperature (min^{-1})
the rate constant for the first order (min^{-1})
rate constant of pseudo second order (g/mg min)
Freundlich adsorption constant (mg/g)
Langmuir equilibrium constant (L/mg)
adsorption equilibrium coefficient
mass of activated carbon (g)
parameter characterizes the heterogeneity of the system
equilibrium adsorption capacity (mg/g)
maximum adsorption capacity (mg/g)
the amount of solute adsorbed on the activated carbon at any time t (mg/g)
gas constant equal to 8.314 J/mol K
rate of adsorption
rate of desorption
time (min)
temperature (K)
volume of dye solution (L)

theoretical evaluation and interpretation of thermody-
·arameters [20–22].
preparation of activated carbon can be carried out in
erent processes: physical activation and chemical activa-
ysical activation involves carbonization of carbonaceous
.s followed by activation of the resulting char using
vating agents, while in chemical activation both of car-
on and activation takes place in the same process in
ence of chemical agents. The chemical activation takes
a temperature lower than that used in physical activa-
refore it can improve the pore development in the carbon
: because of the effect of chemicals. Furthermore, the
yields of chemical activation are higher than physical
.

ın is one of the famous fruit commodities in Indone-
durian production every year is 600,000 tonnes, and the
of durian shell generated approximately 350,000 tonnes,
ct discharge of this solid wastes will cause the envi-
al problems. Although there are many studies in the
: concerning to the preparation of activated carbon and
:ation for liquid phase adsorption, there is no informa-
.he production and utilization of activated carbon from
ıell for color removal.

In this article, we report our study of the preparation of activated carbon from durian shell and the adsorption equilibrium and kinetics of methylene blue on this carbon. We also compared the applicability several well-known adsorption isotherm and kinetics models to describe the equilibria and dynamic.

2. Experimental technique

2.1. Preparation of activated carbon

Durian shells collected from local fruit stores in Surabaya were repeatedly washed with distilled water to remove dirt and other impurities and then dried at 393.15 K for 24 h to reduce the moisture content. The durian shell was grounded in micro hammer mill JANKE & KUNKEL. The proximate analysis of the precursor used in this study were 2.52, 5.53, 69.59 and 22.36% for moisture, ash, volatile matter and fixed carbon, respectively.

The preparation of activated carbon from durian shell was performed by chemical activation. Potassium hydroxide was used as chemical activating agent. The procedure of preparation of activated carbon using chemical activation method is as follows: 25 g of dried durian shell was mixed with 100 mL KOH solution, and then stirred at 303.15 K for about 5 h. The amount of KOH in the solution was adjusted to give mass ratio of chemical activating agent to durian shell 1:2. The resulting homogeneous slurry was dried at 383.15 K for at least 24 h.

The resulting samples were placed in a horizontal tubular reactor and then heated (at heating rate (10 K min^{-1}) at a carbonization temperature of 673.15 K. The carbonization and activation was performed under nitrogen flow of 150 cm^3 min^{-1} STP. Since carbonization time does not have much effect on the pore characteristic of activated carbon product [23,24], samples were held at final temperature for 1 h before cooling down under nitrogen flow. The activated carbon products were washed sequentially with a 0.5N HCl solution. Subsequently, the samples were repeatedly washed with hot distilled water until the pH of the solution reach 6.5 and finally washed with cold distilled water. After that, the samples were dried at 383.15 K for 24 h and stored in desiccator.

2.2. Activated carbon characterization

The pore structure characteristics of the resulting carbon were determined by nitrogen adsorption at 77.15 K using an automatic Micromeritics ASAP-2010 volumetric sorption analyzer. Prior to gas adsorption measurements, the carbon was degassed at 573.15 K in a vacuum condition for a period of at least 24 h. Nitrogen adsorption isotherms were measured over a relative pressure (P/P_0) range from approximately 10^{-5}–0.995. The Brunauer–Emmett–Teller (BET) surface area, micropore volume and micropore surface area of the activated carbons were determined by application of the Brunauer–Emmett–Teller and Dubinin–Asthakov (DA) analysis software available with the instrument, respectively. The BET surface area was determined

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eans of the standard BET equation applied in the relative ure range from 0.06 to 0.3.

Adsorption procedure

isic dye used in this study was methylene blue purchased Sigma–Aldrich and it was used as received without fur-urification. The maximum wavelength of this dye is 663. solutions were prepared by dissolving accurately 0.250 g ethylene blue in 1 L of distilled water. To prevent decol-tion by direct sunlight, the stock solutions were stored in bottle and kept in dark place before being used.

dsorption equilibrium and kinetics studies were conducted static technique. Equilibrium data were obtained by adding .1 g of activated carbons into a series of 250 mL conical s each filled with 100 mL of dye solution with initial con-ation of 250 mg/L. The conical flasks then covered with inum foil and were then placed in a thermostatic shaker (Memmert Type WB-14 equipped with an SV 1422 tem-ure controller) and shaken at 120 rpm for 96 h. During the rption the temperatures of system were kept constant at three rent temperatures (303.15, 313.15 and 323.15 K). Product sis showed that equilibrium conditions were reached after

fter equilibrium time had reached, the solutions were ifuged (MLW T.51.1) at 2500 rpm for 5 min, and the ied supernatant solutions were carefully decanted to be zed using a UV/VIS spectrophotometer (Shimadzu UV-). If the reading of absorbance in the spectrophotometer eded 0.7, the dye solutions were diluted. The final con-ation of the solution was then determined from calibration e.

ne amount of dye adsorbed is calculated based on the fol-ng equation

$$\frac{C_0 - C_e}{m} V \qquad (1)$$

e q_e is the amount of dye adsorbed in activated carbon, C_0 e the initial and equilibrium concentration of dye solutions, ctively, m the amount of adsorbent and V is the volume of on.

the adsorption experiments the dye solutions were pre-by mixing weighed amount of dye with distilled water to concentration 200, 250 and 300 mg/L. The solutions were up in a series of 0.25 L of conical flasks. The experiments conducted in thermostatic shaker bath operating at 303.15, 5 and 323.15 K and 120 rpm. Prior the addition of carbon, isks containing 100 mL of dye solutions were placed in ostatic bath for 30 min so that they could heat up to the ting temperature of experiment. At different time inter-sample was taken from a flask (1 mL using micropipette). imples were diluted with distilled water and analyzed diately.

re we also compare the adsorption capacity of activated n produced from durian shell with Filtrasorb-400 (F-400), mercially available coal based activated carbon, produced lgon Carbon.

Table 1
Pore characteristics of DSAC and F-400

Pore characteristic	DSAC	F-400
BET surface area (m^2/g)	991.82	877.82
Micropore surface area (m^2/g)	849.31	761.80
Micropore volume (cm^3/g)	0.368	0.343
Total pore volume (cm^3/g)	0.471	0.468

3. Results and discussions

3.1. Pore characteristic of activated carbon

The pore characteristic of the activated carbon prepared from durian shell with chemical activation (DSAC) and Filtrasorb-400 are given in Table 1. The nitrogen adsorption of DSAC and F-400 are depicted in Fig. 1. From pore characteristic (given in Table 1) and nitrogen adsorption isotherm (Fig. 1) it can be seen that the activated carbon from durian shell (DSAC) has higher capacity than F-400, indicating that DSAC is promising candidate for adsorption application. The nitrogen gas adsorption isotherm of DSAC clearly shows that the nature of carbon is a combination of microporous and mesoporous.

The internal structures of microporous and mesoporous carbons are usually characterized in terms of the pore size distribution. The pore size distribution is a function of the assumed shape of the model pores used in the analysis. Here we used the DFT model to interpret the pore size distribution based on nitrogen adsorption. Fig. 2 shows that the DSAC has a microporous and mesoporous structure. The presence of mesopores together with micropores in the activated carbons enhances their adsorption capacities, especially for large molecules of adsorbates such as dye molecules [3].

3.2. Adsorption equilibrium studies

The analysis and design of adsorption separation processes requires the relevant adsorption equilibria, which is the most important piece of information in understanding an adsorption process [25]. The adsorption equilibrium data of methylene blue

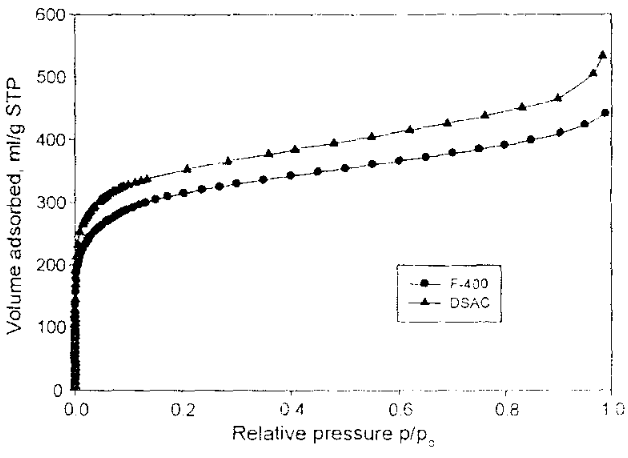


Fig. 1. Nitrogen adsorption isotherm of F-400 and DSAC.

e cite this article in press as: T.C. Chandra et al., Adsorption of basic dye onto activated carbon prepared from durian shell: Studies of ption equilibrium and kinetics, Chem. Eng. J. (2006), doi:10.1016/j.cej.2006.09.011

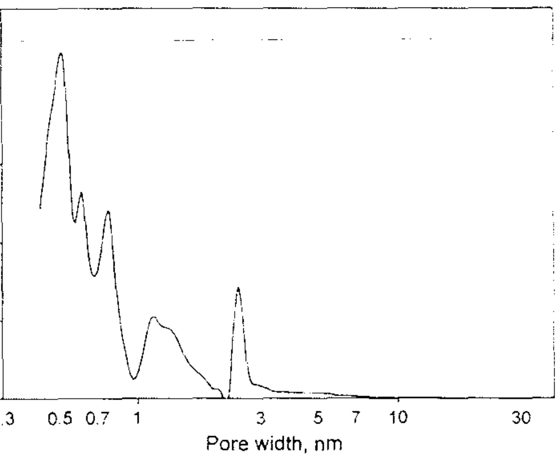
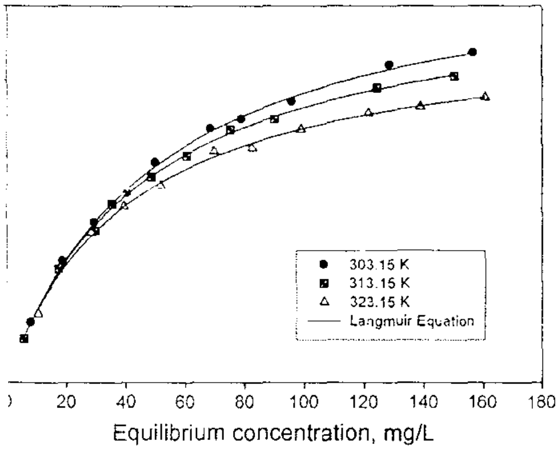


Fig. 2. Pore size distribution of DSAC.

ated carbon derived from durian shell was fitted by sev-
ll-known isotherm models to assess their utility. These
Langmuir and Freundlich models.
gmuir model is the most widely used isotherm equation,
as the form as follows

$$\frac{K_\mathrm{L}C_\mathrm{e}}{1+K_\mathrm{L}C_\mathrm{e}} \quad (2)$$

$_\mathrm{o}$ and K_L are Langmuir isotherm parameters, represent-
naximum adsorption capacity for the solid phase loading
Langmuir equilibrium constant related to the heat of
ion, respectively. Fig. 3 depicts the adsorption isotherm
ylene blue on activated carbon from durian shell. In this
the experimental data are represented as symbols and
gmuir model as solid lines. This figure clearly shows
Langmuir equation can describe the experimental data
ell. The optimal parameters from the fitting of Langmuir
n with the experimental data are given in Table 2. Tem-
is well known to play an important role in adsorption in
d carbons, generally having a negative influence on the
adsorbed [25]. The adsorption of organic compounds



lsorption isotherm of methylene blue on DSAC and fits of Langmuir

Table 2
Parameters of Langmuir equation

Temperature (K)	q_o (mg/g)	K_L (L/mg)	R^2
303.15	289.26	0.0197	0.998
313.15	265.72	0.0219	0.998
323.15	237.13	0.0245	0.997

(including dye) is an exothermic process and the physical bonding between the organic compounds and the active sites of the carbon will weaken with increasing temperature. Also with the increase of temperature, the solubility of methylene blue also increases, the interaction forces between the solute and the solvent become stronger than solute and adsorbent, consequently the solute is more difficult to adsorb. Both of these features are consistent with the order of Langmuir adsorption capacity as seen in Table 2.

The heat of adsorption can be estimated from integrated van't Hoff equation, which relates the Langmuir equilibrium constant K to the temperature

$$K_\mathrm{L} = K_\mathrm{o} \exp\left[\frac{-E_\mathrm{a}}{RT}\right] \quad (3)$$

here E_a is the activation energy of adsorption and K_o is the adsorption equilibrium coefficient. The gas constant R is equal to 8.314 J/mol K and T is the temperature of the solution. The magnitude of activation energy gives a type of adsorption, which is mainly physical or chemical. The range of 5–40 kJ/mol of activation energies correspond a physisorption mechanism or the range of 40–800 kJ/mol suggests a chemisorption mechanism [20]. The relation between the Langmuir equilibrium constant and $1/T$ is given in Fig. 4. The values of K_o and E_a obtained from Eq. (3) are 0.6883 L/g and 8.967 kJ/mol, respectively. The value of E_a obtained in this study indicating that the adsorption has low potential barrier and assigned to a physisorption.

The Freundlich isotherm is an empirical equation that is also often used to correlate adsorption experimental data. The Freundlich isotherm equation has the following form

$$q_\mathrm{e} = K_\mathrm{f}C_\mathrm{e}^{1/n} \quad (4)$$

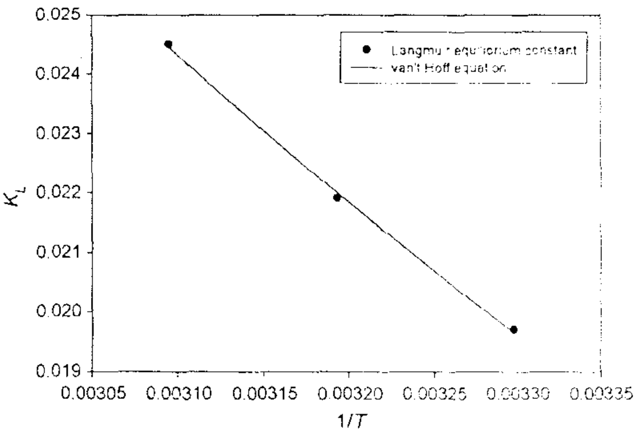


Fig. 4. Plot K_L vs. $1/T$ for methylene blue.

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3
eters of Freundlich equation

erature (K)	K_f (mg/g)	n	R^2
5	21.85	2.1422	0.973
5	21.93	2.1910	0.968
5	25.27	2.4601	0.958

e K_f is a parameter related to the adsorption capacity and
meter n characterizes the heterogeneity of the system. The
meters of Freundlich equation for system studied are given
ble 3, while the adsorption isotherm and model fit by Fre-
ch equation is depicted in Fig. 5. From this figure it is
ous that Freundlich equation fails to represent the adsorp-
data at low (because this equation does not incorporates
y's law) and high concentration.

Adsorption kinetics studies

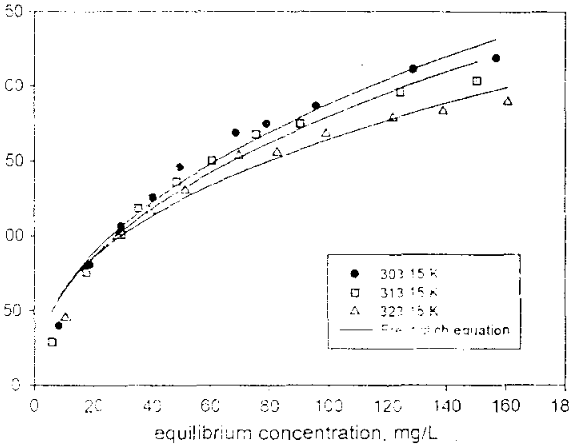
he studies of adsorption equilibria are important in deter-
ng the effectives of adsorption; however, it is also necessary
entify the types of adsorption mechanism in a given system.
is study we used three different models to predict the adsorp-
kinetic of methylene blue on activated carbon prepared from
.

n approach to modeling both equilibrium and kinetics
lsorption is the Langmuir surface kinetics approach. The
mptions of this approach [26] are:

- rface is homogeneous, that is adsorption energy is constant
er all sites;
- sorption on surface is localized, that is adsorbed atoms or
olecules are adsorbed at definite, localized sites;
- ch site can accommodate only one molecule or atom.

ased on this approach, the rate of adsorption, R_a, can be
ed as

$$= k_a C_t (q_e - q_t) \quad (5)$$



Adsorption isotherm of methylene blue on DSAC and fits of Freundlich

where k_a is the rate constant of adsorption, C_t the solute concentration at the liquid phase at any time t and q_t the amount of solute adsorbed on the activated carbon at any time t. The rate of desorption of solute, R_d, from the adsorbent surface to liquid phase can be written as

$$R_d = k_d q_t \quad (6)$$

where k_d is the desorption constant. Therefore, the rate of change of amount adsorbed at any time

$$\frac{dq_t}{dt} = R_a - R_d = k_a C_t (q_e - q_t) - k_d q_t \quad (7)$$

At equilibrium this equation become a well-known Langmuir equation (Eq. (2)). Rearrangement of Eq. (7) by combining the equilibrium condition (Eq. (2)) gives

$$\frac{dq_t}{dt} = \frac{k_a(1 + K_L C_e)(q_e - q_t)}{K} \quad (8)$$

since

$$K_L = \frac{k_a}{k_d} \quad (9)$$

Therefore, Eq. (8) can be written as

$$\frac{dq_t}{dt} = k_d(1 + K_L C_e)(q_e - q_t) \quad (10)$$

Integrating Eq. (10) yields

$$q_t = q_e(1 - \exp(-k_d(1 + K_L C_e)t)) \quad (11)$$

Eqs. (2) and (11) were used to model the kinetics of the adsorption process, and parameter k_d and q_e obtained at different initial concentrations and temperatures are summarized in Table 4. Figs. 6–8 depict the applicability of this model on the prediction of adsorption kinetics of methylene blue on durian shell activated carbon at different initial concentrations and temperatures. From Figs. 6–8 it is obvious that the Langmuir surface kinetics model can represent the data well. Also the fitted equilibrium adsorption capacities are in agreement with those experimental data as indicated in Table 4.

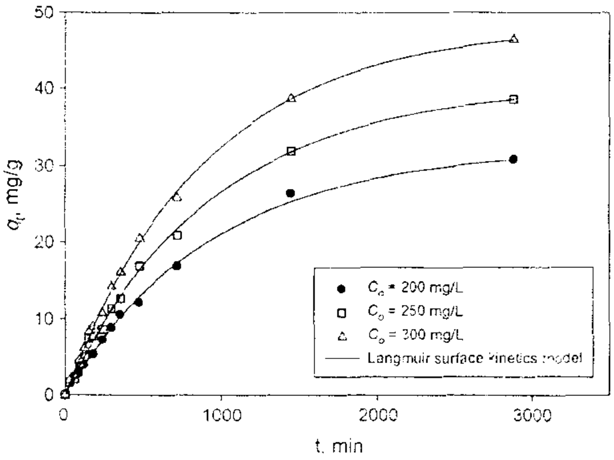


Fig. 6. Langmuir surface kinetic model for the adsorption of methylene blue on DSAC at 303.15 K.

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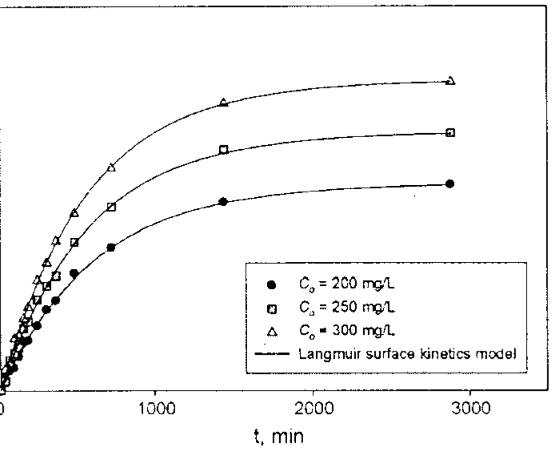
orption equilibrium and kinetics, Chem. Eng. J. (2006), doi:10.1016/j.cej.2006.09.011

ameters values using Langmuir surface kinetics model

	303.15 K			313.15 K			323.15 K		
	$k_d \times 10^3$ (min^{-1})	q_e (mg/g)	q_e (exp) (mg/g)	$k_d \times 10^3$ (min^{-1})	q_e (mg/g)	q_e (exp) (mg/g)	$k_d \times 10^3$ (min^{-1})	q_e (mg/g)	q_e (exp) (mg/g)
	0.9204	32.74	32.27	1.419	32.48	32.28	1.974	32.31	32.26
	0.9315	40.25	41.30	1.456	40.64	40.31	1.973	40.28	42.27
	0.9314	48.24	47.30	1.461	48.33	48.31	1.989	47.88	49.05

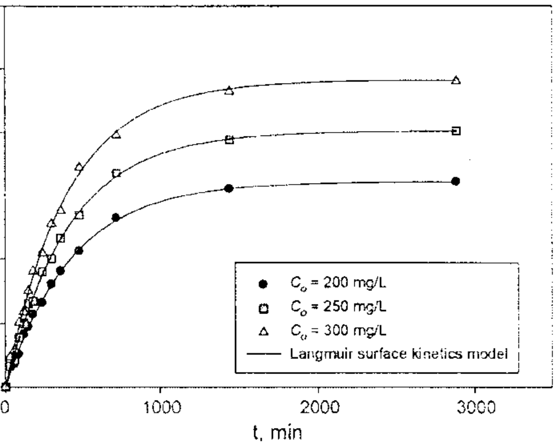


ngmuir surface kinetic model for the adsorption of methylene blue on 313.15 K.

desorption energy can be calculated also from integrated off equation

$$_0 \exp\left[\frac{-E_d}{RT}\right] \qquad (12)$$

$_{do}$ and E_d are desorption rate constant at infinite tem- and activation energy of desorption, respectively. The of desorption can be obtained by plotting k_d versus $1/T$ n in Fig. 9. The value of k_{do} and E_d obtained by Eq. (12) .68 min^{-1} and 29.28 kJ/mol, respectively.



ngmuir surface kinetic model for the adsorption of methylene blue on 323.15 K.

Even this model can predict the adsorption kinetics data well as seen in Figs. 6–8, the energy of desorption (E_d) is larger than the heat of adsorption (E_a) that was calculated from the equilibrium data to be 8.967 kJ/mol. However, both of adsorption and desorption energies still correspond a physisorption mechanism. This discrepancy could be due to the fact that this model has ignored the energetic heterogeneity of the carbon surface and the distribution of pore sizes.

Another model widely used to describe the adsorption kinetics is pseudo first order model which is also known as Lagergren equation. This equation has the form as follows

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (13)$$

where k_1 is the rate constant for the first order (min^{-1}). Integrating Eq. (13) for the boundary conditions $t = 0$–t and $q_t = 0$–q_t gives

$$q_t = q_e(1 - \exp(-k_1 t)) \qquad (14)$$

The rate constant for the pseudo first order model (k_1) and equilibrium adsorption capacity (q_e) were determined using Sigma Plot software. The first order kinetics constant for the adsorption of methylene blue on DSAC at different initial concentrations and temperatures is given in Table 5. For the adsorption of methylene blue on DSAC, the pseudo first order kinetics is applicable for the system studied as shown in Figs. 10–12, furthermore the value of q_e obtained from the plot also agree with experimental values. Similar result was also obtained by Garg et al. for removal methylene blue using Indian Rosewood sawdust [27].

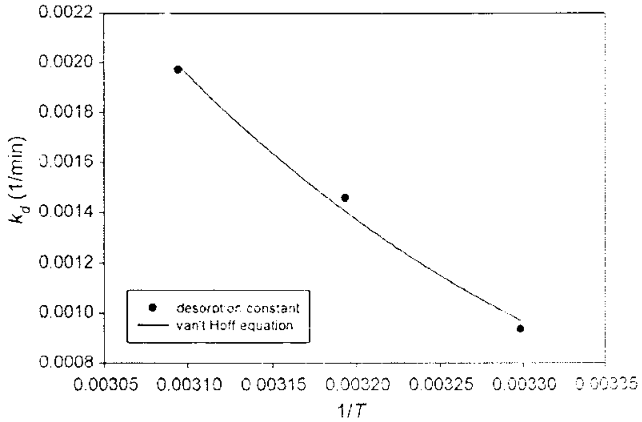


Fig. 9. Determination of energy of desorption.

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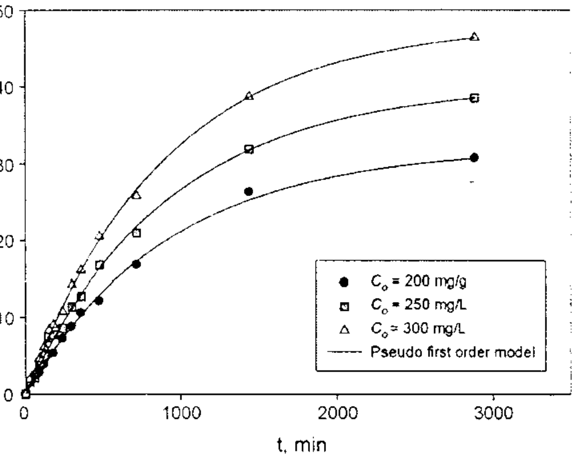
parameters values using pseudo first order kinetics model

/L)	303.15 K			313.15 K			323.15 K		
	$k_1 \times 10^3$ (min^{-1})	q_e (mg/g)	q_e (exp) (mg/g)	$k_1 \times 10^3$ (min^{-1})	q_e (mg/g)	q_e (exp) (mg/g)	$k_1 \times 10^3$ (min^{-1})	q_e (mg/g)	q_e (exp) (mg/g)
	1.036	32.74	32.27	1.615	32.48	32.28	2.284	32.30	32.26
	1.082	40.25	41.30	1.716	40.64	40.31	2.377	40.28	42.27
	1.118	48.24	47.30	1.785	48.33	48.31	2.498	47.87	49.05

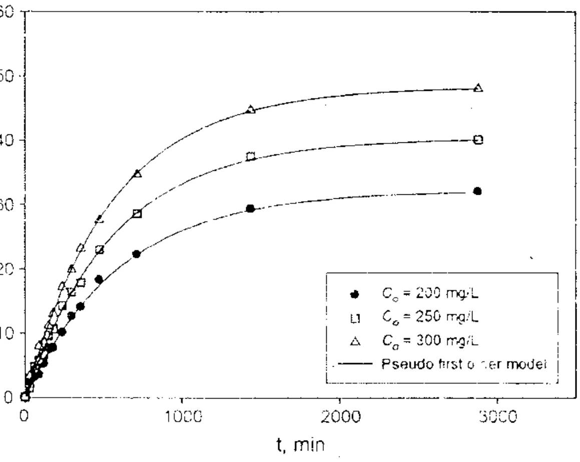


. Pseudo first order model for the adsorption of methylene blue on DSAC 15 K.

netics data were further treated with the pseudo second kinetics model. The differential equation of this model is en as follows

$$= k_2(q_e - q_t)^2 \qquad (15)$$

k_2 is the rate constant of pseudo second order (g/mg min). rating Eq. (15) for the boundary condition $t = 0$–t and



. Pseudo first order model for the adsorption of methylene blue on DSAC 15 K.

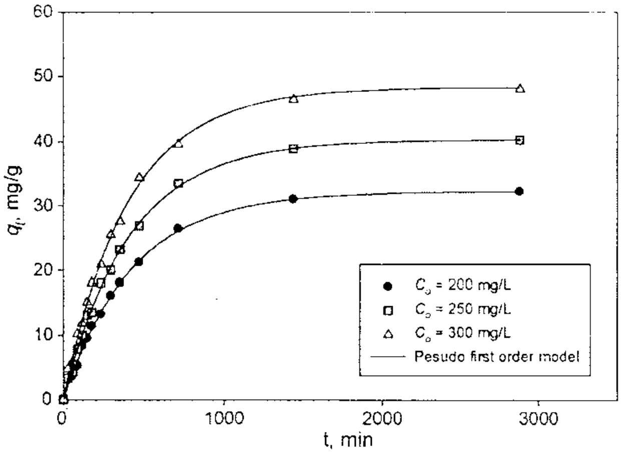


Fig. 12. Pseudo first order model for the adsorption of methylene blue on DSAC at 323.15 K.

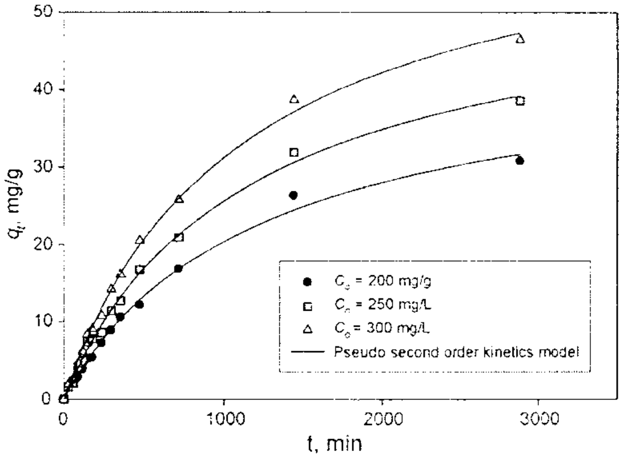


Fig. 13. Pseudo second order model for the adsorption of methylene blue on DSAC at 303.15 K.

$q_t = 0$–q_t gives

$$q_t = q_e\left(\frac{q_e k_2 t}{1 + q_e k_2 t}\right) \qquad (16)$$

which is the integrated rate law for a pseudo second order reaction. In this model q_e and k_2 are the fitted parameters. The fitted parameter q_e and k_2 obtained from optimization using Sigma Plot software are listed in Table 6 and the model curves are plotted in Figs. 13–15. As can be seen in these figures that this model can adequately represent the adsorption kinetics data of methy-

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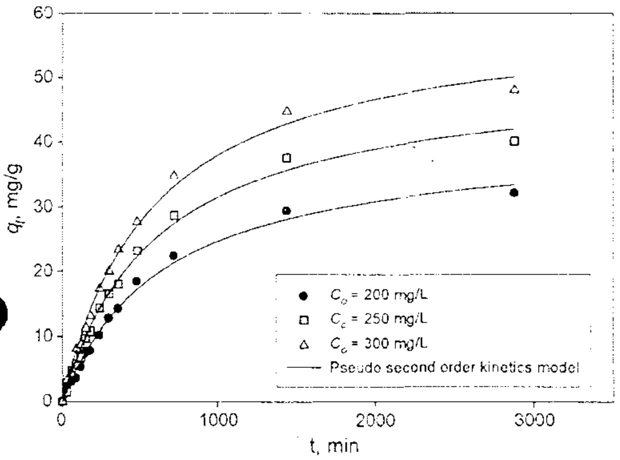
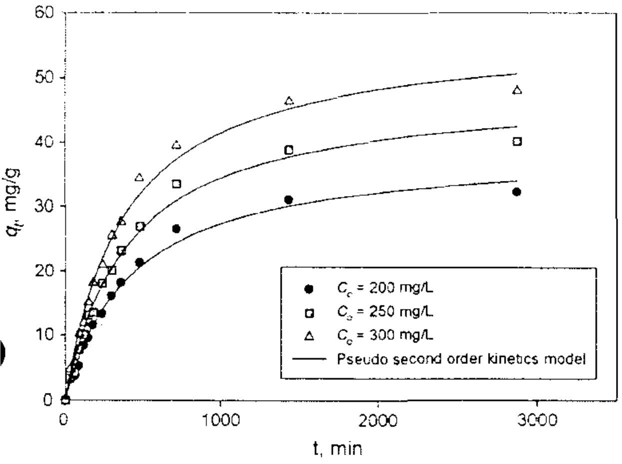
ıble 6
itted parameters values using pseudo second order kinetics model

$_0$ (mg/L)	303.15 K			313.15 K			323.15 K		
	$k_2 \times 10^5$ (g/mg min)	q_e (mg/g)	q_e (exp) (mg/g)	$k_2 \times 10^5$ (g/mg min)	q_e (mg/g)	q_e (exp) (mg/g)	$k_2 \times 10^5$ (g/mg min)	q_e (mg/g)	q_e (exp) (mg/g)
)0	1.85	44.89	32.27	3.57	41.30	32.28	5.92	39.12	32.26
50	1.63	54.52	41.30	3.14	51.08	40.31	5.61	48.56	42.27
)0	1.42	65.07	47.30	2.79	60.41	48.31	4.51	57.43	49.05



ig. 14. Pseudo second order model for the adsorption of methylene blue on SAC at 313.15 K.



ig. 15. Pseudo second order model for the adsorption of methylene blue on SAC at 323.15 K.

ene blue on DSAC. However, the values of q_e from the pseudo econd order kinetics are not in agreement with experimental ata (see Table 6). This confirms that the chemisorption is not ie controlling mechanism for the adsorption of methylene blue n activated carbon prepared from durian shell.

. Conclusions

This study shows that the activated carbon prepared from urian shell with chemical activation is a potential adsorbent for methylene blue removal. The batch adsorption experiments were conducted isothermally at three different temperatures (303.15, 313.15 and 323.15 K). For the adsorption equilibrium, it was found that Langmuir model can represent the data well compared with Freundlich isotherm. The adsorption kinetics of methylene blue can be well described by both of the pseudo first model equation and Langmuir surface kinetics model.

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Kesetimbangan dan Kinetika Adsorpsi Methylene Biru Pada Karbon Aktif Yang Terbuat Dari Kulit Durian

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ABSTRAK

Industri tekstil, keramik, kertas, cat dan lain-lain dalam proses produksinya menggunakan zat warna untuk mewarnai produk yang dihasilkan. Zat warna yang digunakan tidak semuanya terpakai, sebagian akan terbuang sebagai limbah. Limbah zat warna jika dibuang ke lingkungan akan menimbulkan pencemaran. Meskipun dalam jumlah kecil, keberadaan zat warna dalam lingkungan terutama perairan akan menimbulkan masalah yang cukup serius. Saat ini berbagai macam metode telah tersedia untuk pengolahan limbah zat warna, salah satunya adalah dengan menggunakan proses adsorpsi.

Keberhasilan proses adsorpsi untuk menghilangkan zat warna dalam air sangat dipengaruhi oleh jenis bahan penyerap/adsorbent yang digunakan, salah satu bahan penyerap yang paling sering digunakan adalah karbon aktif, karena kemampuan penyerapan dari bahan penyerap ini sangat bagus. Kendala utama yang dihadapi pada proses pengolahan limbah dengan menggunakan karbon aktif ini adalah masalah ekonomi karena harga karbon aktif yang ada di pasaran cukup mahal. Pengolahan limbah zat warna dengan proses adsorpsi menggunakan karbon aktif akan menjadi ekonomis jika bahan baku pembuatan karbon aktif tidak mahal dan banyak terdapat di sekitar kita. Pada penelitian ini limbah kulit durian dimanfaatkan sebagai bahan baku pembuatan karbon aktif.

Karbon aktif yang digunakan pada penelitian ini diperoleh dengan cara aktivasi kimia kulit durian menggunakan KOH. Aktivasi dilakukan pada suhu 400°C selama 1 jam dengan perbandingan zat activator/kulit durian 1:2. Karbon aktif yang dihasilkan digunakan untuk mengadsorpsi zat warna methylene biru dari limbah cair sintetis. Proses adsorpsi methylene biru dilakukan secara isoterm pada variasi suhu 30-50°C. Persamaan Langmuir digunakan untuk menggambarkan isoterm adsorpsi dan kinetika adsorpsi digambarkan dengan menggunakan persamaan kinetika permukaan Langmuir. Harga konstanta Langmuir yang diperoleh adalah berkisar 0,0197-0,0245 L/mg untuk konstanta kesetimbangan Langmuir dan 237,15-289,26 mg/g untuk konstanta kapasitas penyerapan pada kesetimbangan. Sedangkan konstanta reaksi Langmuir adalah $9{,}204.10^{-4}$-$1{,}989.10^{-3}$ (1/menit).

1. Pendahuluan

Beberapa industri seperti tekstil, keramik, kertas, plastik dan lain-lain menggunakan zat warna dalam proses pembuatan produk mereka. Pada proses pewarnaan, industri-industri tersebut mengkonsumsi sejumlah besar air sehingga menghasilkan limbah pewarna yang luar biasa banyak. Meskipun hanya sebagian kecil zat warna yang terdapat dalam limbah tersebut, namun kehadirannya tidak diinginkan karena dapat membahayakan lingkungan perairan [1-5]. Beberapa metode telah digunakan untuk menghilangkan zat warna yang terdapat dalam limbah seperti metode pemisahan dengan menggunakan membran, degradasi aerobik maupun anaerobik dengan menggunakan mikroorganisme, oksidasi secara kimia, koagulasi dan flokulasi, adsorpsi dengan menggunakan berbagai macam jenis adsorben, maupun dengan *reverse osmosis* [1, 3, 5]. Dari berbagai macam metode yang telah disebutkan di atas, adsorpsi merupakan teknik yang paling menjanjikan dalam memperkecil konsentrasi organik terlarut dalam limbah.

Beberapa penelitian telah dilakukan untuk memisahkan zat warna dari limbah dengan metode adsorpsi menggunakan berbagai jenis adsorben seperti karbon aktif [2-5], *fly ash* [6], serbuk gergaji [7-9], tongkol jagung [10], *barley husk* [10], kulit jeruk [11], biomassa (baik yang hidup ataupun yang telah mati) [12-17], dan adsorben lainnya [1]. Adsorben yang paling banyak digunakan untuk tujuan ini adalah karbon aktif, akan tetapi karbon aktif yang tersedia biasanya mahal dan tidak ekonomis untuk pengolahan limbah. Adsorben dengan harga yang lebih murah seringkali memiliki kapasitas adsorpsi yang rendah; karena itu efisiensinya juga rendah. Apabila karbon aktif dengan kapasitas adsorpsi tinggi untuk pengolahan limbah dapat dihasilkan dari bahan baku yang murah, maka adsorben tersebut juga bernilai ekonomis.

Karbon aktif merupakan adsorben yang paling umum digunakan untuk proses adsorpsi karena kapasitas adsorpsinya yang tinggi. Kapasitas adsorpsi dari karbon aktif tidak hanya bergantung pada luas permukaan, tetapi juga pada struktur pori internal, karakteristik permukaan, dan adanya gugus fungsi pada permukaan pori. Struktur pori internal dan karakteristik permukaan memiliki peran penting dalam proses adsorpsi dan bergantung pada bahan baku yang digunakan serta metode persiapan [18]. Metode-metode yang berbeda dapat digunakan untuk mengkarakterisasi struktur pori (luas permukaan, volume pori, distribusi ukuran pori, dan lain-lain) dari karbon aktif seperti *small angle X-ray, mercury porosimetry, SEM (Scanning Electron Microscopy),* dan gas, serta adsorpsi pada fasa liquid [19]. Karakteristik dari kemampuan adsorpsi karbon aktif biasanya ditunjukkan dari kinetika adsorpsi dan isoterm kesetimbangan [20]. Oleh karena itu, untuk memperlajari kinetika adsorpsi dan kesetimbangan, sangatlah penting untuk memahami mekanisme adsorpsi untuk evaluasi secara teori dan interpretasi parameter termodinamika [20-22].

Ada dua cara berbeda yang dapat dilakukan dalam proses pembuatan karbon aktif, yaitu aktivasi fisika dan aktivasi kimia. Aktivasi fisika meliputi karbonisasi bahan berkarbon yang diikuti oleh aktivasi *char* yang dihasilkan dengan menggunakan agen pengaktivasi yang berupa gas. Pada aktivasi secara kimia, proses karbonisasi dan aktivasi dilakukan dalam satu tahap dengan adanya zat kimia. Aktivasi kimia dilakukan pada suhu yang lebih rendah dibandingkan aktivasi fisika, karenanya dapat meningkatkan perkembangan pori pada struktur karbon akibat efek dari zat kimia tersebut. Oleh karena itu, hasil karbon dari aktivasi kimia lebih besar daripada aktivasi fisika [23].

Durian merupakan salah satu komoditas buah yang terkenal di Indonesia. Produksi durian tiap tahunnya adalah 600.000 ton, dan jumlah kulit durian yang dihasilkan kira-kira 350.000 ton dan pembuangan langsung dari limbah padat ini dapat menyebabkan masalah lingkungan. Meskipun telah banyak penelitian mengenai pembuatan karbon aktif dan aplikasinya untuk adsorpsi pada fasa liquid, ternyata masih tidak ada informasi tentang produksi dan penggunaan karbon aktif dari kulit durian untuk menghilangkan zat warna dalam limbah.

Pada artikel ini, kami melaporkan penelitian kami tentang pembuatan karbon aktif dari kulit durian dan kesetimbangan adsorpsi serta kinetika *methylene blue* (MB) pada karbon ini. Kami juga membandingkan dengan beberapa isoterm adsorpsi yang telah ada dan model kinetika untuk menggambarkan kesetimbangan dan dinamikanya.

2. Metode Percobaan

2.1. Pembuatan Karbon Aktif

Kulit durian yang diperoleh dari toko buah lokal di Surabaya dicuci berulang kali dengan menggunakan air suling untuk menghilangkan pengotor-pengotor yang ada dan kemudian dikeringkan pada suhu 393.15 K selama 24 jam untuk mengurangi kadar air. Kulit durian dihancurkan dengan menggunakan *micro hammer mill* JANKE & KUNKEL. Analisa proksimat bahan baku kulit durian adalah 2.52%, 5.53%, 69.59%, dan 22.36% berturut-turut untuk kadar air, abu, *volatile matter*, dan karbon tetap.

Pembuatan karbon aktif dari kulit durian dilakukan dengan metode aktivasi kimia. KOH digunakan sebagai agen pengaktivasi kimia. Prosedur pembuatan karbon aktif menggunakan metode aktivasi kimia adalah sebagai berikut: 25 gram kulit durian dicampur dengan larutan 100 mL KOH, dan kemudian diaduk pada suhu 303.15 K selama 5 jam. Jumlah KOH pada larutan disesuaikan untuk memberi perbandingan massa zat aktivator terhadap kulit durian 1:2. *Slurry* homogen yang dihasilkan kemudian dikeringkan pada suhu 383.15 K selama minimal 24 jam.

Sampel yang dihasilkan ditempatkan dalam reaktor tubular horisontal dan kemudian dipanaskan (dengan laju pemanasan 10 K min^{-1}) pada suhu karbonisasi 673.15 K. Karbonisasi dan aktivasi dilakukan di bawah aliran nitrogen 150 $cm^3 min^{-1}$ STP. Karena waktu karbonisasi tidak banyak berpengaruh pada karakteristik pori dari karbon aktif [23, 24], sampel ditempatkan pada suhu akhir selama 1 jam sebelum pendinginan di bawah aliran nitrogen. Produk karbon aktif dicuci dengan menggunakan larutan 0.5 N HCl. Selanjutnya, sampel dicuci berulang-ulang dengan air suling hangat sampai pH larutan mencapai 6.5 dan akhirnya dicuci dengan air suling dingin. Setelah itu, sampel dikeringkan pada suhu 383.15 K selama 24 jam dan selanjutnya disimpan dalam desikator.

2.2. Prosedur Adsorpsi

Zat warna yang digunakan pada analisa ini adalah *methylene blue* (MB) yang diperoleh dari Sigma Aldrich dan langsung digunakan tanpa pemurnian lebih lanjut. Panjang gelombang maksimum MB adalah

663. Larutan MB disiapkan dengan cara melarutkan 0,250 gram MB secara akurat dalam 1 L air suling. Untuk mencegah degradasi warna akibat sinar matahari langsung, larutan MB tersebut disimpan di dalam botol gelap dan diletakkan di ruangan yang gelap sebelum digunakan.

Penelitian mengenai kesetimbangan dan kinetika adsorpsi dilakukan dengan teknik yang sama dengan literatur lainnya. Data kesetimbangan diperoleh dengan menambahkan 0,1-1,1 gram karbon aktif ke dalam beberapa erlenmeyer berukuran 250 mL yang masing-masing telah diisi larutan MB sebanyak 100 mL dengan konsentrasi mula-mula adalah 250 mg/L. Erlenmeyer-erlenmeyer tersebut lalu ditutup dengan aluminium foil yang kemudian diletakkan dalam *thermostatic shaker bath* (Memmert Type WB-14 yang dilengkapi dengan SV 1422 *temperatur controller*) dan dikocok pada 120 rpm selama 96 jam. Suhu sistem dijaga konstan selama adsorpsi pada tiga suhu yang berbeda (303,15, 313,15 dan 323,15 K). Analisa produk menunjukkan bahwa kesetimbangan dicapai setelah 96 jam. Setelah waktu kesetimbangan tercapai, larutan tersebut kemudian disentrifugasi (MLW T.51.1) selama 5 menit dengan kecepatan 2500 rpm, dan setelah itu larutan yang jernih didekantasi untuk kemudian dianalisa menggunakan UV/VIS *spectrophotometer* (Shimadzu UV-1201). Apabila absorbansi yang terbaca di spektrofotometer lebih dari 0,7, larutan tersebut diencerkan. Konsentrasi akhir larutan kemudian ditentukan dari kurva kalibrasi.

Jumlah zat warna yang terserap dihitung berdasarkan persamaan berikut:

$$q_e = \frac{(C_o - C_e)}{m} V \tag{1}$$

Di mana q_e adalah jumlah zat warna yang terserap pada karbon aktif, C_o adalah konsentrasi awal larutan, C_e adalah konsentrasi larutan pada saat setimbang, m adalah jumlah adsorben, dan V adalah volume larutan.

Pada percobaan adsorpsi, larutan zat warna dibuat dengan cara mencampur sejumlah zat warna dengan air suling untuk menghasilkan konsentrasi 200, 250, dan 300 mg/L. Larutan dibuat di dalam erlenmeyer berukuran 0,25 L. Percobaan dilakukan di dalam *thermostatic shaker bath* yang beroperasi pada suhu 303,15 K, 313,15 K, dan 323,15 K pada kecepatan 120 rpm. Sebelum penambahan karbon, erlenmeyer yang berisi 100 mL larutan zat warna diletakkan dalam *thermostatic bath* selama 30 menit sehingga larutan tersebut mencapai suhu operasi yang diinginkan. Pada interval suhu yang berbeda, sebuah sampel diambil sebanyak 1 mL dari erlenmeyer (menggunakan mikropipet). Semua sampel kemudian diencerkan dengan air suling lalu dianalisa.

3. Hasil dan Pembahasan

3.1. Kesetimbangan Adsorpsi

Analisa dan desain proses pemisahan adsorpsi membutuhkan kesetimbangan adsorpsi yang relevan, yang merupakan salah satu informasi penting dalam memahami proses adsorpsi [25]. Data kesetimbangan adsorpsi MB pada karbon aktif dari kulit durian disesuaikan dengan beberapa model isoterm untuk mengukur kemampuannya. Langmuir dan freundlich model termasuk di dalamnya.

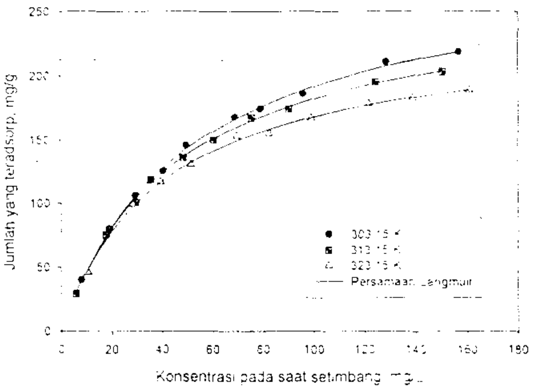
Langmuir model adalah persamaan isoterm yang paling banyak digunakan, dengan rumus sebagai berikut:

$$q_e = q_o \frac{K_L C_e}{1 + K_L C_e} \tag{2}$$

Dimana q_o dan K_L adalah parameter isoterm Langmuir, mewakili kapasitas adsorpsi maksimum untuk adsorbat dan konstanta kesetimbangan Langmuir yang berkaitan dengan panas adsorpsi. Gambar 1 menggambarkan isoterm adsorpsi MB pada karbon aktif dari kulit durian. Pada gambar ini, data percobaan diwakili dengan simbol dan model Langmuir dengan garis. Gambar ini menunjukkan dengan jelas bahwa persamaan Langmuir dapat menggambarkan data percobaan dengan cukup baik. Parameter optimum dari persamaan Langmuir dengan data percobaan ditunjukkan pada Tabel 1.

Tabel 1. Parameter-parameter persamaan Langmuir

Suhu, K	q_o, mg/g	K_L, L/mg	R^2
303.15	289.26	0.0197	0.998
313.15	265.72	0.0219	0.998
323.15	237.13	0.0245	0.997



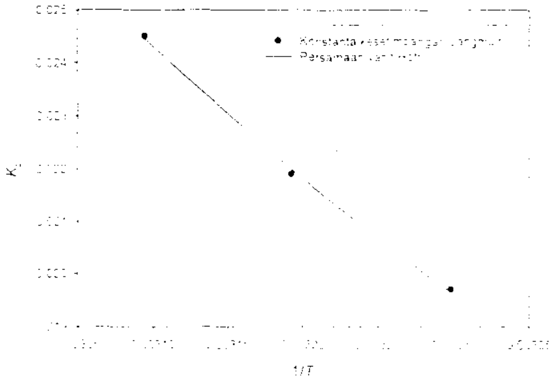
Gambar 1. Isoterm adsorpsi *methylene blue* pada DSAC dan mengikuti model Langmuir

Suhu memainkan peranan penting dalam adsorpsi pada karbon aktif, umumnya memiliki pengaruh negatif pada jumlah yang terserap [25]. Adsorpsi komponen organik (termasuk zat warna) merupakan proses eksotermis dan ikatan fisika antara komponen organik dan daerah aktif dari karbon aktif akan melemah seiring dengan naiknya suhu. Seiring dengan naiknya suhu, kelarutan MB juga naik, gaya tarik antara larutan dengan pelarut menjadi lebih kuat daripada larutan dan adsorben, akibatnya zat terlarut lebih sulit untuk diserap. Kedua fitur tersebut cocok dengan kapasitas adsorpsi Langmuir seperti terlihat pada Tabel 1.

Panas adsorpsi dapat diukur dari persamaan van't Hoff, yang menghubungkan konstanta kesetimbangan Langmuir K dengan suhu.

$$K_L = K_o \exp\left[\frac{-E_a}{RT}\right] \tag{3}$$

E_a adalah energi aktivasi adsorpsi dan K_o adalah koefisien kesetimbangan adsorpsi. Konstanta gas R setara dengan 8.314 J/mol.K, dan T adalah suhu larutan. Besarnya energi aktivasi menentukan tipe adsorpsinya, yang umumnya fisika atau kimia. Range energi aktivasi sebesar 5-40 kJ mol merupakan mekanisme adsorpsi fisikan (*physisorption*) dan *range* antara 40-800 kJ/mol menunjukkan mekanisme adsorpsi kimia (*chemisorption*) [20]. Hubungan antara konstanta kesetimbangan Langmuir dan $1/T$ ditunjukkan pada Gambar 2. Nilai K_o and E_a yang diperoleh dari persamaan (3) adalah 0.6883 L/g and 8.967 kJ/mol. Nilai E_a yang diperoleh pada penelitian ini menunjukkan bahwa adsorpsi memiliki hambatan yang kecil dan cenderung ke adsorpsi fisika.



Gambar 2. Grafik K_L vs $1/T$ untuk *methylene blue*

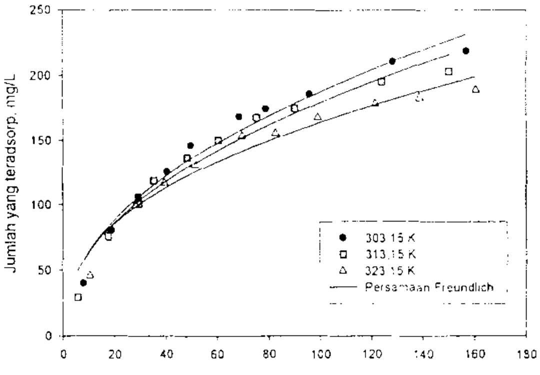
Isoterm Freundlich merupakan persamaan empiris yang juga sering digunakan untuk menghubungkan data percobaan adsorpsi. Persamaan isoterm Freundlich mempunyai bentuk sebagai berikut:

$$q_e = K_f C_e^{1/n} \tag{4}$$

di mana K_f merupakan suatu parameter yang berhubungan dengan kapasitas adsorpsi dan parameter n mengkarakterisasi heterogenitas sistem. Parameter pada persamaan Freundlich pada sistem yang dipelajari dapat dilihat pada Tabel 2, sedangkan isoterm adsorpsi dan kesesuaian model dengan persamaan Freundlich dapat dilihat pada Gambar 3. Dari gambar tersebut dapat dengan jelas terlihat bahwa persamaan Freundlich tidak dapat mewakili data adsorpsi pada konsentrasi tinggi dan rendah (karena persamaan ini tidak mengikuti hukum Henry).

Tabel 2. Parameter-parameter persamaan Freundlich

Suhu, K	K_F, mg/g	n	R^2
303.15	21.85	2.1422	0.973
313.15	21.93	2.1910	0.968
323.15	25.27	2.4601	0.958



Gambar 3. Isoterm adsorpsi *methylene blue* pada DSAC dan mengikuti model Freundlich

3.2. Kinetika Adsorpsi

Percobaan mengenai kesetimbangan adsorpsi sangat penting dalam menentukan efektivitas adsorpsi; hal tersebut juga penting dalam mengidentifikasi macam mekanisme adsorpsi pada sistem. Pendekatan yang dapat digunakan untuk memodelkan kesetimbangan dan kinetika adsorpsi MB pada karbon aktif dari kulit durian adalah pendekatan kinetika permukaan Langmuir.

Asumsi-asumsi yang digunakan pada pendekatan ini adalah [26]:

- Permukaan homogen, karena itu energi adsorpsi tiap daerah konstan.
- Adsorpsi pada permukaan dibatasi, sehingga atom atau molekul yang terserap adalah tertentu.
- Tiap daerah hanya dapat menyerap 1 molekul atau atom.

Berdasarkan pendekatan-pendekatan tersebut, laju adsorpsi, R_a, dapat ditentukan dengan:

$$R_a = k_a C_t (q_e - q_t) \tag{5}$$

di mana k_a adalah konstanta kecepatan adsorpsi, C_t adalah konsentrasi zat terlarut fasa liquid pada waktu t, dan q_t adalah jumlah zat terlarut yang teradsorp oleh karbon aktif pada waktu t. Laju desorpsi zat terlarut, R_d, dari permukaan adsorbent ke fasa liquid dapat ditulis sebagai berikut:

$$R_d = k_d q_t \tag{6}$$

di mana k_d adalah konstanta desorpsi. Oleh karena itu, laju perubahan jumlah zat terlarut yang teradsorp pada waktu t adalah:

$$\frac{dq_t}{dt} = R_a - R_d = k_a C_t (q_e - q_t) - k_d q_t \tag{7}$$

Pada saat setimbang persamaan tersebut menjadi persamaan Langmuir (persamaan (2)). Persamaan (7) dikombinasi dengan kondisi kesetimbangan (persamaan (2)) menghasilkan:

$$\frac{dq_t}{dt} = \frac{k_a (1 + K_L C_e)(q_e - q_t)}{K} \tag{8}$$

di mana

$$K_L = \frac{k_a}{k_d} \tag{9}$$

Sehingga persamaan (8) dapat ditulis sebagai berikut:

$$\frac{dq_t}{dt} = k_d(1 + K_L C_e)(q_e - q_t) \qquad (10)$$

Persamaan (10) diintegralkan menjadi

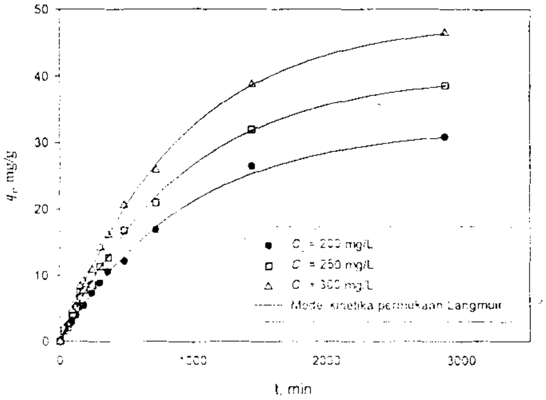
$$q_t = q_e(1 - \exp(-k_d(1 + K_L C_e)t)) \qquad (11)$$

Persamaan (2) dan (11) digunakan untuk memodelkan kinetika proses adsorpsi. dan parameter k_d dan q_e didapatkan pada konsentrasi dan suhu awal dirangkum pada Tabel 3.

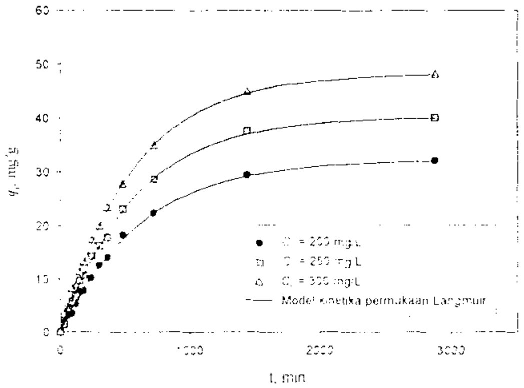
Tabel 3. Harga parameter-parameter yang diperoleh dari model kinetika permukaan Langmuir

C_o, mg/L	303.15 K			313.15 K			323.15 K		
	$k_d \times 10^3$ (1/min)	q_e , (mg/g)	q_e exp (mg/g)	$k_d \times 10^3$ (1/min)	q_e , (mg/g)	q_e exp (mg/g)	$k_d \times 10^3$ (1/min)	q_e , (mg/g)	q_e exp (mg/g)
200	0.9204	32.74	32.27	1.419	32.48	32.28	1.974	32.31	32.26
250	0.9315	40.25	41.30	1.456	40.64	40.31	1.973	40.28	42.27
300	0.9314	48.24	47.30	1.461	48.33	48.31	1.989	47.88	49.05

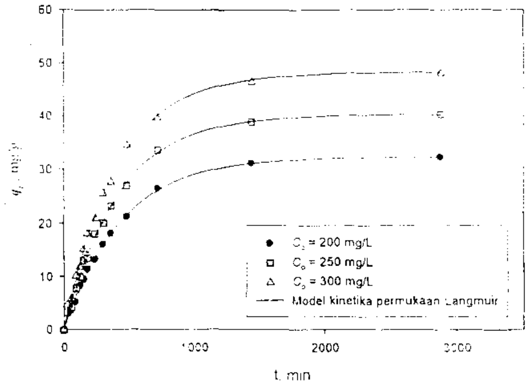
Gambar 4-6 menggambarkan penerapan model ini pada prediksi kinetika adsorsi dari MB pada DSAC pada konsentrasi awal dan suhu yang berbeda. Dari Gambar 4-6 jelas terlihat bahwa model kinetika permukaan Langmuir dapat mewakili data percobaan dengan baik. Kapasitas adsorpsi kesetimbangan yang disesuaikan juga sesuai dengan data percobaan pada Tabel 3.



Gambar 4. Model kinetika permukaan Langmuir untuk adsorpsi *methylene blue* pada DSAC pada suhu 303.15 K



Gambar 5. Model kinetika permukaan Langmuir untuk adsorpsi *methylene blue* pada DSAC pada suhu 313.15 K

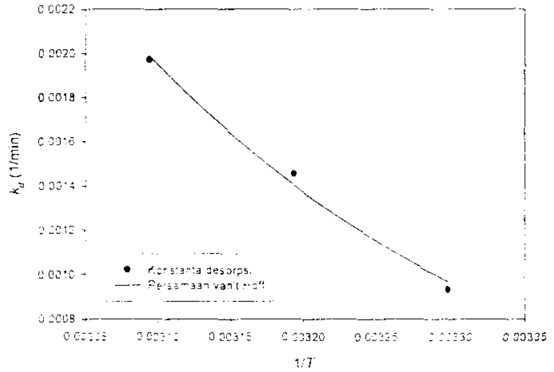


Gambar 6. Model kinetika permukaan Langmuir untuk adsorpsi *methylene blue* pada DSAC pada suhu 323,15 K

Energi desorpsi dapat juga dihitung dengan mengintegralkan persamaan van't Hoff

$$k_d = k_{do} \exp\left[\frac{-E_d}{RT}\right] \tag{12}$$

di mana k_{do} dan E_d merupakan konstanta laju desorpsi pada suhu tak terhingga dan energi aktivasi desorpsi. Energi desorpsi dapat diperoleh dengan menggambarkan k_d vs $1/T$ seperti ditunjukkan pada Gambar 7. Harga k_{do} dan E_d yang diperoleh dari persamaan (12) berturut-turut adalah 107.68 1/min dan 29.28 kJ/mol.



Gambar 7. Penentuan energi desorpsi

Meskipun model ini dapat memprediksi data kinetika adsorpsi dengan baik seperti terlihat pada Gambar 4-6, bagaimanapun juga energi desorpsi (E_d) lebih besar daripada panas adsorpsi (E_a) yang dihitung dari data kesetimbangan yaitu 8.967 kJ/mol. Bagaimanapun, energi adsorpsi dan desorpsi masih sesuai dengan mekanisme adsorpsi fisika. Ketidaksesuaian dapat disebabkan karena model tersebut mengabaikan heterogenitas energi dari permukaan karbon dan distribusi ukuran pori.

4. Kesimpulan

Hasil percobaan menunjukkan bahwa karbon aktif yang berasal dari kulit durian dengan metode aktivasi secara kimia merupakan adsorben yang sangat potensial untuk menghilangkan zat warna (MB). Adsorpsi secara *batch* dilakukan secara isotermal pada tiga suhu yang berbeda (303.15 K, 313.15 K, dan 323.15 K). Untuk kesetimbangan adsorpsi, persamaan isoterm Langmuir mewakili data yang ada lebih baik dibandingkan dengan persamaan Freundlich. Kinetika adsorpsi MB dapat diketahui dari persamaan model kinetika permukaan Langmuir.

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