Potential of easily prepared low cost rice husk biochar and burnt clay composite for removal of Methylene Blue dye from contaminated water

Qudsia Ghzal[a1], Tariq Javed[a*] & Maryam Batool[a2]

a* is corresponding author.

[a1] qudsiaguzal@gmail.com, [a*] mtariq@uosahiwal.edu.pk, maryambatool6666@gmil.com[a2]

Department of Chemistry, University of Sahiwal, Sahiwal, Punjab, Pakistan[a, a*, a2]

Table S1. Chemical composition analysis of burnt clay, rice husk biochar and ideal RHBC/BC adsorbent.

Chemical composition

Compound	Burnt clay	Rice husk biochar	Ideal RHBC/BC
SiO_2	64.1	-	19.80
Al_2O_3	15.9	-	2.65
Fe_2O_3	4.2	-	1.55
ZrO_2	6.8	-	1.12
CaO	1.2	0.2	1.50
K_2O	2.2	-	0.70
SO_3	1.04	-	1.01
Nitrogen content	1.06	1.80	2.50
Ash content	1.045	47.9	48.07
Lignin and cellulose	-	39.1	13.1
Protein content	2.455	11.0	8.00

Table S2

Results of experiment to study the effect of pH Value (Experimental conditions; pH = variable (1-14), volume = 10 ml, C_o = 10 ppm, adsorbent dose = 0.25 g, contact time = 50 min, temperature = 20˚C)

pH	A_i	A_f	C_e	**% removal**
1	1.36	0.472	0.0561	65.2941
2	1.923	0.437	0.052	77.2751
3	2.09	0.466	0.0554	77.7033

4	1.965	0.332	0.0395	83.1043
5	1.784	0.278	0.0331	84.4170
6	1.972	0.113	0.1344	94.2698
7	2.012	0.023	0.0027	98.8568
8	1.772	0.055	0.0065	96.8962
9	1.64	0.07	0.0083	95.7317
10	1.733	0.1	0.0119	94.2296
11	1.709	0.15	0.0178	91.2229
12	1.634	0.16	0.0190	90.2080
13	1.881	0.406	0.0483	74.5131
14	0.643	0.213	0.0253	66.8740

Table S3

Results of experiment to determine the point of zero charge.

pH_i	**ΔpH**
2	0.6
3	1.11
4	1.54
5	1.62
6	1.78
7	-0.5
8	-0.89
9	-0.99
10	-1.97

Table S4

Results of experiment to study the effect of adsorbent dose (Experimental conditions; Adsorbent dose = variable (0.05- 0.5 g), volume = 10 ml, C_o = 10 ppm, contact time = 50 min, pH = 7, temperature = 20˚C)

Adsorbent dose (g)	A_i	A_f	C_e	**% Removal**
0.05	1.991	0.391	1.7209	80.3616
0.1	1.991	0.207	0.9111	89.6032
0.15	1.991	0.193	0.8495	90.3064
0.2	1.991	0.142	0.625	92.8679
0.25	1.991	0.058	0.2553	97.0868
0.3	1.991	0.057	0.2509	97.1371
0.35	1.991	0.045	0.1981	97.7398
0.4	1.991	0.009	0.0396	99.5479
0.45	1.991	0.009	0.0396	99.5479
0.5	1.991	0.009	0.0396	99.5479

Table S5

Results of experiment to study the effect of contact time (Experimental conditions; contact time = variable (5-70 min), volume = 10 ml, C_o = 10 ppm, adsorbent dose = 0.25 g, pH = 7 temperature = 20˚C)

Contact time (minutes)	A_i	A_f	C_e	**% Removal**
5	1.505	0.51	5.0295	66.1129
10	1.505	0.371	3.6588	75.3488
15	1.505	0.281	2.7712	81.3289
20	1.505	0.22	2.1696	85.3821
25	1.505	0.177	1.7456	88.2392
30	1.505	0.134	1.3215	91.0963
40	1.505	0.096	0.9467	93.6213
50	1.505	0.072	0.7101	95.2159
60	1.505	0.05	0.4931	96.6777

70	1.505	0.02	0.1972	98.6711

Table S6

Results of experiment to study the effect of initial dye concentration (Experimental conditions; C_o = variable (5-40 ppm), volume = 10 ml, adsorbent dose = 0.25 g, contact time = 50 min, pH = 7, temperature = 20˚C)

Concentration (ppm)	A_i	A_f	C_e	**% Removal**
5	0.884	0.045	0.8806	94.9095
10	1.808	0.0904	1.7691	95
15	1.829	0.169	3.3072	90.76
20	1.868	0.312	6.1056	83.2976
25	2.106	0.455	8.9041	78.3951
30	2.399	0.636	12.4461	73.4891
35	2.666	0.782	15.3033	70.6676
40	2.897	0.999	19.5499	65.5161

Table S7

Results of experiment to study the effect of temperature (Experimental conditions; temperature = variable (10-70˚C), volume = 10 ml, C_o = 10 ppm, adsorbent dose = 0.25 g, contact time = 50 min, pH = 7)

Temperature (C°)	A_i	A_f	**Ce**	**% Removal**
10	1.452	0.042	0.2241	97.11
20	1.59	0.071	0.3789	95.53
30	1.793	0.1	0.5336	94.42
40	1.802	0.162	0.8645	91.01
50	1.903	0.237	1.2647	87.54
60	1.908	0.3	1.6008	84.27
70	1.942	0.473	2.5240	75.64

Table S8

Statistical data for Pseudo first order kinetics

Time (min)	$C_e(\frac{mg}{L})$	$Q_t(\frac{mg}{L})$	$\log Q_e - Q_t$
5	5.0296	0.1988	-0.7137
10	3.6588	0.2536	-0.8587
15	2.7712	0.2891	-0.9873
20	2.1696	0.3132	-1.1029
25	1.7456	0.3301	-1.2081
30	1.3215	0.3471	-1.3471
40	0.9467	0.3621	-1.5231
50	0.7101	0.3716	-1.6880
60	0.4931	0.3803	-1.9268
70	0.1972	0.3921	---------

Table S9

Statistical data for Pseudo second order kinetics

Time (min)	$C_e(\frac{mg}{L})$	$Q_t(\frac{mg}{L})$	$\frac{t}{Q_t}$
5	5.0296	0.1988	25.1488
10	3.6588	0.2536	39.4245
15	2.7712	0.2891	51.8758
20	2.1696	0.3132	63.8539
25	1.7455	0.3301	75.7168
30	1.3215	0.3471	86.4205
40	0.9467	0.3621	110.4575
50	0.7101	0.3716	134.5541
60	0.4931	0.3803	157.7801
70	0.1972	0.3921	178.5211

Table S10

Statistical data for intraparticle diffusion model

Time (min)	$\mathbf{t^{1/2}}$	$C_e(\frac{mg}{L})$	$Q_t(\frac{mg}{L})$
5	2.236	5.0295	0.1988
10	3.162	3.6587	0.2536
15	3.872	2.7712	0.2891
20	4.472	2.1696	0.3132
25	5	1.7456	0.3302

30	5.477	1.3215	0.3471
40	6.324	0.9467	0.3621
50	7.071	0.7101	0.3716
60	7.745	0.4931	0.3803
70	8.366	0.1972	0.3921

Table S11

Statistical data for Liquid film mode.

Time (min)	$C_e(\frac{mg}{L})$	$Q_t(\frac{mg}{L})$	$Q_e(\frac{mol}{L})$	$\frac{Q_t}{Q_e}$	$1-\frac{Q_t}{Q_e}$	**ln (** $1-\frac{Q_t}{Q_e}$**)**	**Bt = -0.4977- ln (** $1-\frac{Q_t}{Q_e}$**)**
5	5.03	0.2	0.39	0.51	0.4929	-0.7073	0.2096
10	3.66	0.25	0.39	0.65	0.3531	-1.0409	0.5432
15	2.77	0.29	0.39	0.74	0.2626	-1.3372	0.8395
20	2.17	0.31	0.39	0.8	0.2012	-1.6034	1.1057
25	1.74	0.33	0.39	0.84	0.1579	-1.8455	1.3478
30	1.32	0.35	0.39	0.88	0.1147	-2.1655	1.6678
40	0.95	0.36	0.39	0.92	0.0764	-2.5710	2.0733
50	0.71	0.37	0.39	0.95	0.0523	-2.9505	2.4528
60	0.49	0.38	0.39	0.97	0.0301	-3.5005	3.0028
70	0.2	0.39	0.39	1	0	-----	------

Table S12.

Correlation of the MB adsorption on RHBC/BC kinetics model.

Kinetic model	Parameter	Value
Pseudo-first order	K_1	0.0492842 min^{-1}
	Q_{eq}(exp)	0.392110454 mg g^{-1}

	Q_{eq}(cal) R^2	0.221 mg g^{-1} 0.9941
Pseudo-second order	K_2 Q_{eq}(exp) Q_{eq}(cal) R^2	0.3483393245 g $mg^{-1}min^{-1}$ 0.392110454 mg g^{-1} 0.4249532551 mg g^{-1} 0.9994
Intraparticle diffusion model Liquid film model	K_{id} R^2 K_{fd} R^2	0.0293 $min^{0.5}$ 0.9169 0.0493min^{-1} 0.9941

Table S13

Experimental data for Langmuir isotherm model

Initial conc. (ppm)	**Initial Conc. (mol/L)**	$C_e(\frac{mol}{L})$	$C_e(\frac{mg}{L})$	$C_{ads} = C_o - C_e\frac{V}{M}(^{mol}/_{g}$ **)**
5	1.56E-05	2.75E-06	0.8806	5.15E-07
10	3.13E-05	5.53E-06	1.7691	1.03E-06
15	4.69E-05	1.03E-05	3.3072	1.46E-06
20	6.25E-05	1.91E-05	6.1057	1.74E-06
25	7.82E-05	2.78E-05	8.9041	2.01E-06
30	9.38E-05	3.89E-05	12.4461	2.2E-06
35	1.09E-04	4.78E-05	15.3033	2.46E-06
40	1.25E-04	6.11E-05	19.5499	2.56E-06

Table S14

Calculation for R_L value

$b = \frac{L}{mol}$	Initial dye concentration (mol/L)	R_L
7.80E-04	1.563E-05	1
7.80E-04	3.126E-05	1
7.80E-04	4.690E-05	1
7.80E-04	6.253E-05	1
7.80E-04	7.816E-05	1
7.80E-04	9.379E-05	1
7.80E-04	1.094E-04	1
7.80E-04	1.251E-04	1

Table S15

Experimental data for Freundlich isotherm model

Initial conc. (ppm)	**Initial Conc. (mol/L)**	$C_e(ppm)$	$C_e(^{mol}/_{L})$	$C_{ads} = C_o - C_e\frac{V}{M}$)	$\log C_e$	$\log C_{ads}$
5	1.56E-05	0.8806	2.75E-06	5.15E-07	-5.5601	-6.2881
10	3.13E-05	1.7691	5.53E-06	1.03E-06	-5.2572	-5.9874
15	4.69E-05	3.3072	1.03E-05	1.46E-06	-4.9855	-5.8349
20	6.25E-05	6.1056	1.91E-05	1.74E-06	-4.7192	-5.7600
25	7.82E-05	8.9041	2.78E-05	2.01E-06	-4.5553	-5.6961
30	9.38E-05	12.4461	3.89E-05	2.19E-06	-4.4099	-5.6585
35	1.09E-04	15.3033	4.78E-05	2.46E-06	-4.3202	-5.6084
40	1.25E-04	19.5499	6.11E-05	2.56E-06	-4.2138	-5.5921

Table S16

Experimental data for Dubinin-Radushkevich model

Initial conc. (ppm) or mg/L	$C_e(ppm)$	$C_{ads} = C_o - C_e\frac{V}{M}($	$\ln C_{ads}$	$\varepsilon = RT\{1 + (1 +$	ε^2
5	0.8806	5.15E-07	-14.4787	2.1288	4.5319
10	1.7690	1.03E-06	-13.7866	2.0128	4.0515
15	3.3072	1.46E-06	-13.4355	1.9088	3.6436
20	6.1057	1.74E-06	-13.2630	1.8069	3.2648
25	8.9041	2.01E-06	-13.1159	1.7441	3.0419
30	12.4461	2.19E-06	-13.0292	1.6884	2.8508
35	15.3033	2.46E-06	-12.9140	1.6541	2.7359
40	19.5499	2.56E-06	-12.8765	1.6134	2.6029

Table S17

Comparison of all isotherm models.

Isotherm Models	Parameter	Value
Langmuir isotherm	Q_o	0.974902768 mg g^{-1}
	b	7.804462635*10^{-4} dm^3 mol^{-1}
	R^2	0.9936
D-R isotherm	β	1.2327 KJ^2 mol^{-2}
	E_s	0.6368780837Kjmol^{-1}
	R^2	0.9555
Freundlich isotherm	n	2.094240838
	K_f	1.093805198 *10^9 mg g^{-1}

	R^2	0.9407

Table S18

Error analysis for Kinetic and Isotherm models

	Models	ERRSQ	ARE	HYBRID	EABS	MPSD
KINETIC MODELS	1. Pseudo First Order	1.398E-01	32.117	5.314	1.032	23.053
	2. Pseudo Second Order	**1.363E-01**	**-32.00**	**5.012**	**-1.004**	**22.387**
	3. Intraparticle Diffusion	1.355E+00	90.58	29.776	2.945	54.568
	4. Liquid Film	7.602E-01	87.037	27.6	2.835	52.542
ISOTHERM	**1. Langmuir isotherm**	**7.603E+00**	**-6.5E+07**	**8.04E+07**	**-7.7992**	**8.9664E+04**
	2. Freundlich isotherm	9.571E+18	-8.1E+16	1.01E+26	-8.7E+09	1.006E+14
	3. D-R isotherm	1.216E+01	-9.12E+7	1.29E+08	-9.8620	1.134E+05

Table S19

Statistical data for thermodynamics parameters

$C_e(\frac{mol}{L})$	$C_a = C_e - C_i$ **(mol/L)**	**T (C^0)**	**T (K)**	$\frac{1}{T}$	$K_c = \frac{C_a}{C_e}$	$\ln K_c$
7.007E-07	3.06E-05	10	283	0.0035	43.6190	3.7754

1.184E-06	3.01E-05	20	293	0.0034	25.3943	3.2345
1.668E-06	2.96E-05	30	303	0.0033	17.74	2.8758
2.702E-06	2.86E-05	40	313	0.0032	10.5679	2.3578
3.953E-06	2.73E-05	50	323	0.0031	6.9072	1.9326
5.01E-06	2.63E-05	60	333	0.0030	5.2495	1.6581
7.89E-06	2.34E-05	70	343	0.0029	2.9658	1.0871

Table S20

Calculation of thermodynamic parameters.

T(C^o)	T(K)	ΔG($kJmol^{-1}$)	ΔH($kJmol^{-1}$)	ΔS ($Jmol^{-1}K^{-1}$)
10	283	-0.6278	-35.0601	-0.1217
20	293	-0.5378	-35.0601	-0.1178
30	303	-0.4782	-35.0601	-0.1141
40	313	-0.3921	-35.0601	-0.1108
50	323	-0.3213	-35.0601	-0.1076
60	333	-0.2757	-35.0601	-0.1044
70	343	-0.1808	-35.0601	-0.1017

Table S21. Key parameters of bed depth service time (BDST) model.

C_t/ Co	a	b	R^2

0.4	87.596	62.565	0.9954
0.6	102.99	46.499	0.9928
0.8	186.20	68.413	0.9793

Table S22

Result of experiment to study the effect of tap water (Experimental conditions; Adsorbent dose = (0.25 g), Volume = 10 ml, C_o = 10 ppm, Contact time = 50 min, pH = 7, Temperature = 10˚C).

C_i (ppm)	**A_i**	**A_f**	**C_e**	**% Removal**
10	1.585	0.122	0.5760151	92.302

Table S23

Result of experiment to study the effect of well water (Experimental conditions; Adsorbent dose = (0.25 g), Volume = 10 ml, C_o = 10 ppm, Contact time = 50 min, pH = 7, Temperature = 10˚C).

C_i (ppm)	**A_i**	**A_f**	**C_e**	**% Removal**
10	1.248	0.058	0.6872	95.352

Table S24

Result of experiment to study the effect of river water (Experimental conditions; Adsorbent dose = (0.25 g), Volume = 10 ml, C_o = 10 ppm, Contact time = 50 min, pH = 7, Temperature = 10˚C).

C_i (ppm)	**A_i**	**A_f**	**C_e**	**% Removal**
10	2.347	0.183	0.6016	92.203

Table S25

Effect of various ions on adsorption capacity of adsorbent.

Cations	Adsorption %	Anions	Adsorption %
No cation	97.11	No anion	97.11
Potassium	96.35	Sulphate	91.36
Zinc	96.78	Iodide	94.78

Sodium	96.22	Chromate	85.83
Copper	95.99	Chloride	96.35
Barium	92.66	Bromide	91.83
Magnesium	95.69	Oxalate	83.52
Ammonium	94.49	Dihydrogen phosphate	86.41

Table S26

Result of desorption study.

Adsorbent	Rice husk biochar and burnt clay composite
Adsorbate (Dye)	Methylene blue
Chemical used for desorption	1 M HNO_3
Contact time	50 min
% desorption	90 %