Supporting Information

Combined methane energy recovery and toxic dye removal by porous carbon derived from anaerobically modified digestate

Zakaria Anfar, [†, ‡, ¥,*] Abdallah Amedlous, [§] Abdellah Ait El Fakir, [†] Hassan Ait Ahsaine, [†*] Mohamed Zbair, [+] Saaida lhanafi, [†] Rachid El Haouti, [†] Amane Jada, [‡, ¥,*] Noureddine El Alem, [†]

[†]Laboratory materials and environment, Ibn Zohr University, Agadir-8000, Morocco

[‡]Institute of materials science of Mulhouse, CNRS, Haute Alsace University, Mulhouse-F-68100, France

[¥]University of Strasbourg, Strasbourg-F-67081, France

[§]Laboratory of materials, catalysis and valorization of natural resources, Hassan II University, Casablanca-20650, Morocco.

[+]Laboratory of catalysis and corrosion of materials, Chouaïb Doukkali University, El Jadida-24000, Morocco.

2.1. Physicochemical parameters. The temperature, T, and the aqueous phase pH, were measured using a multimeter (ADWA-AD-1030 pH / mV). The conductivity, resistivity, TDS, and alkalinity were determined using a multi-parameter (CONSORT C864). Turbidity was determined by a standard digital turbidimeter (THERMO Scientific ORION AQ4500). Heavy metals concentrations were determined by an atomic absorption spectrophotometer (Shimadzu, AA-7000). BOD5 and COD were analyzed by COD photometer (MD 200) and BOD meter (oxy-direct). Other physicochemical parameters (Ca^{2+}, Mg^{2+}, NO_3^-, NH_4^+, TH, SV, SM, ST) were analyzed according to the new national and international standards using spectrophotometry method (JENWAY 6705) (1). The functional groups were determined by Fourier Transform Infrared spectroscopy operating in the frequency range 400-4000 cm^{-1} and using a Shimadzu 4800S.

2.2. Anaerobic Co-digestion experiments. The experimental device used at the laboratory scale to produce methane and the modified digestate by ACD, is a batch amber glass digester, having a volume capacity of 500 ml. The procedure consists to fill the digester with the mixture of wastes, then the inoculum, afterwards incubates at a temperature of 38 °C. The methane volume was measured using a gasometer based on CH_4 pressure (The volume of methane displaced was an equal measurable volume of water from the reservoirs) (2,3) (Figure S9). CO_2 was measured by the passage of biogas with an alkaline solution of NaOH (9N) (4,5) (Figure S8). Control tests were constructed under the same working conditions to determine the amount of endogenous gas in the inoculum that was subsequently sliced in all experiment (6). Different mathematical equations used to fit the experimental results are reported in Table S9.

2.3. Preparation of TDAW@alginate core-shell particles and characterization. The core-shell particles used in the adsorption of Methylene Blue during this work were prepared as follows: 1g of alginate powder and $CaCl_2$ were dissolved in 100 ml of distilled water for 6 hours of stirring to prepare two solutions A and B, respectively. Then, 1g of the biologically modified carbonaceous material named TDAW (The method of its preparation, as well as its characterization, were reported elsewhere (7)) was added to solution A and then stirred for 2 hours followed by 30 min sonication, this gives solution C. The Solution B was placed in a crystallizer and kept under low stirring (30 rpm). The preparation of core-shell particles was ensured by mixing solution C with solution B. Indeed when each droplet of the TDAW@alginate solution was brought into contact with the solution B, Ca^{2+} and carboxylic groups of alginate formed a capsule membrane instantly, then the TADW was immobilized inside the membrane (8). Finally, the core-shell particles were washed with distilled water and stored in a refrigerator in the aqueous medium until the adsorption experiments. In the following work, the abbreviation TDAW@Alginate was used to nominate the adsorbent.

The surface morphology of the TDAW@Alginate before and after adsorption were obtained from a scanning electron microscopy (SEM) coupled with EDS and EDS-Mapping analysis by FEI, Quanta 200-ESEM operated at 20 Kev. Pore size distribution and specific surface area were measured using an AUTOSORB-1 surface area and pore size analyzer at 77 K. The Fourier Transform Infrared spectra of TDAW@Alginat were obtained in the mid infrared region (400-4000cm^{-1}) using a Shimadzu 4800S.

2.4. CCD-RSM modelling. To optimize both processes (anaerobic co-digestion and adsorption), the parameters that influence the responses of these processes were modelled using Response Surface Methodology (RSM) coupled with Central Composite Design (CCD) (9). The CCD matrix was constructed by five levels (-1.68 (-α), -1, 0, +1, +1.68 (+ α)) for 3 independent variables (pH (X_1), Inoculum (X_2) and Load (X_3), for anaerobic co-digestion and TDAW@Alginate dose (X_1), time (X_2) and MB concentration (X_3) for adsorption process (Tables S7 and S10) (7). The results obtained from ACD and adsorption experiments were modelled using a quadratic polynomial equation. The different experimental domains of MB adsorption on TDAW@Alginate are determined from the individual effects of each parameter on MB removal efficiency (Table S10). The results of anaerobic co-digestion and adsorption are presented in Tables S7 and S10, respectively. The NEMRODW 2007 software (10) was used in this work to develop a quadratic polynomial equation.

Table S1. Characteristics of inoculums and substrates

	Substrate type			
	PCS	LDP	PW	LBS
pH	6.0.1	4.9	4.74	7.52
VS (g L^{-1})	28	198.19	50.19	10.48
	Proportion of the mixture			
Mixture used in this work	23.9 vol% PCS + 42.4 vol% of LBS + 27.6 vol% of PW + 6.1 vol% LDP			
IN_P	600g of primary treatment sludge by anaerobic decantation unit+ 10L distilled water			
IN_S	200g of primary treatment sludge by anaerobic decantation unit + 980mL of (Solution A + Solution B) + acetic acid 5ml L^{-1}, methanol 5 ml L^{-1} and micro-nutrient 10 ml L^{-1}			
Inoculum used in this work	55.5 vol% de IN_S + 44.5 vol% of IN_p			

IN_s: Synthesis inoculum, IN_p: Principal inoculum, PCS: physical-chemical sludge, LBS: liquid biological sludge, PW: pure whey, LDP: loss in dairy product

Solution A : KH_2PO_4: 0, 41 g ; Na_2HPO_4: 0,53g ; NH_4Cl: 0,03g ; NaCl : 20g : $CaCl_2$.$2H_2O$: 0,11g ; $MgCl_2.6H_2O$: 0,11g; $NaHCO_3$: 5g ; Cystéine : 0,3g ; Extrait of yeast : 1g ; $Na_2S.9H_2O$: 0,3g Oligo-element : 10ml.

Solution B (Oligo-element): $(NH_4)_6Mo_7O_{24}.4H_2O$: 10mg ; $COCl_{2.6}H_2O$: 100mg ; $MnC_{l2}.4H_2O$: 500mg.

Table S2. Different vibrations before and after ACD

Region	vibrations		characteristic
	Before ACD	After ACD	
(1)	3440 cm^{-1}	3000cm^{-1}	–O–H groups and N–H (amines and amides A) stretching
(2)	2510 cm^{-1}	2500 cm^{-1}	stretching of aromatic C-H
(3)	1793 cm^{-1}	1790 cm^{-1}	stretching of carboxylic acid C = O
(4)	1455 cm^{-1}	1450 cm^{-1}	–C–O– stretching or –O–H bending of carboxylic acid
(5)	-	1170 cm^{-1}	–C–O– stretching
(6)	1100 cm^{-1}	-	Symmetric and asymmetric stretching of phosphodiesters or polysaccharides and polysaccharide substances
(7)	860 – 700 cm^{-1}		C-O out of plane carbonate group
(8)	< 700 cm^{-1}		–C–H, C=C bending or some oxides

Table S3: Analysis of variance (ANOVA) for CCD.

Source	coefficients	P-value
Model	-	<0.0001
b_0	170.534	<0.0001
X_{pH}	-4.669	<0.0001
$X_{Inoculum}$	15.316	<0.0001
X_{Laod}	-15.676	<0.0001
$X_{pH\text{-}pH}$	-66.451	<0.0001
$X_{Inoculum\text{-}Inoculum}$	-21.519	<0.0001
$X_{Laod\text{-}Load}$	-19.743	<0.0001
$X_{pH\text{-}Inoculum}$	-2.083	0.00436
$X_{pH\text{-}Load}$	-0.337	0.46
$X_{Inoculum\text{-}Laod}$	-4.843	<0.0001
Lack of fit	-	<0.0001
R_2	-	0.900
R^2_{Adj}	-	0.806

Table S4. Optimum conditions for AD and ACD processes

Test	Conditions				BMP estimated by the Model
	pH	Inoculum	Load	IN/Load	
1	7.40	99.5	180	0.55	152.56 ± 1.24
2	8	90.60	199.7	0.45	151.92 ± 1.24
3	7.38	90	168.20	0.52	150.39 ± 1.25
The methane potential of single substrate digestion at optimum condition of test 1 ($L.CH_4/KgSV$)					
LDP		PCS		LBS	PW
15.33		25.65		60.09	36.66

Table S5. Characteristic isotherm adsorption parameters of MB adsorption.

T °C	Langmuir				Freundlich		
	q_{max} (mg g^{-1})	K_L (L mg^{-1})	R^2	R_L	K_F ($mg^{1-n}.L^n/g$)	n	R^2
40	26.178	1.179	0.9984	0.14-0.032	1.247	0.381	0.9512

Table S6. Characteristic thermodynamic parameters of MB adsorption

T°C	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J $k^{-1}mol^{-1}$)	E_a(kJ mol^{-1})
20	-41.04	-17.54	81.02	20.50
35	-42.67			
40	-42.92			

Table S7. Experimental domains of Factors and CCD-Matrix of MB adsorption

Variable	Name	Unit	-1.68	-1	0	+1	+1.68
X_1 (AD)	Adsorbent dose	mg	6.59	10	15	20	23.41
X_2 (T)	Time	min	46.36	60	80	100	113.64
X_3 (C)	MB concentration	mg/L	6.32	7	8	9	9.68

Run. No	Operating parameters			Rep. variable
	Adsorbent dose	Time	MB concentration	MB removal (%)
1	10.00	60.00	7.00	65.44
2	20.00	60.00	7.00	92.37
3	10.00	100.00	7.00	75.14
4	20.00	100.00	7.00	94.13
5	10.00	60.00	9.00	61.01
6	20.00	60.00	9.00	89.09
7	10.00	100.00	9.00	63.21
8	20.00	100.00	9.00	91.01
9	6.59	80.00	8.00	59.33
10	23.41	80.00	8.00	98.47
11	15.00	46.36	8.00	70.41
12	15.00	113.64	8.00	80.93
13	15.00	80.00	6.32	82.03
14	15.00	80.00	9.68	73.01
15	15.00	80.00	8.00	79.13
16	15.00	80.00	8.00	79.10
17	15.00	80.00	8.00	78.04
18	15.00	80.00	8.00	77.91
19	15.00	80.00	8.00	78.50
20	15.00	80.00	8.00	79.19

Table S8. Analysis of variance (ANOVA) for the adsorption of MB onto TDAW@Alginate.

Source	coefficients	P-value
Model	-	<0.0001
b_0	78.592	<0.0001
X_{AD}	12.274	<0.0001
X_T	2.436	<0.0001
X_C	-2.777	<0.0001
X_{AD-AD}	0.436	0.0351
X_{T-T}	-0.706	0.00563
X_{C-C}	-0.052	0.0747
X_{AD-T}	-1.028	0.00399
X_{AD-C}	1.245	0.00171
X_{C-T}	-0.917	0.00643
Lack of fit	-	0.0051
R_2	-	0.987
R^2_{Adj}	-	0.97

Table S9. Different equations used in this work to fit the data of anaerobic co-digestion and adsorption experiments

Equations	Description	Utility	Ref.
$Y = a_0 + \sum_{i=1}^{n} a_i X_i + \sum_{i=1}^{n} a_{ii} X_i X_i + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} a_{ij} X_i X_j$	y is the predicted response variable; a_0 is the constant coefficient; a_i is the linear coefficients; a_{ii} is the quadratic coefficients; a_{ij} is the linear coefficients for the interaction between independent variables i and j; x_i and x_j are the coded independent parameters.	Second-order polynomial equation used for CCD-RSM modeling	(11)
$q_{e,t} = \frac{(C_0 - C_{e,t}) \times V}{m}$	C_0 (mg/L) and $C_{e,t}$ (mg/L) are the initial and equilibrium concentrations of MB, respectively. m (g) is the weight of adsorbent and V (L) is the volume of the adsorbate solution.	Calculate of adsorbent amount	(12)
$Removal\ \% = \left(\frac{C_0 - C_{e,t}}{C_0}\right) \times 100$	C_0 (mg/L) and $C_{e,t}$ (mg/L) are the initial and equilibrium concentrations of MB.	Calculate of MB removal	(12)
$\ln (q_e - q_t) = \ln q_e - K_1 t$	q_e and q_t are the adsorbed BPA amounts at equilibrium and at times t, respectively. K_1: the rate constant.	Pseudo-first-order equation	(13)
$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$	K_2: rate constant	Pseudo-second-order equation	(13)
$Q_t = K_{di}\sqrt{t} + C_i$	K_{di}= rate constant mg/g $min^{0.5}$ and Ci is a constant	Intraparticle Diffusion	(13)
$\frac{C_e}{Q_e} = \frac{1}{(K_L Q_{max})} + \frac{C_e}{Q_{max}}$	C_e and q_e are the concentration and amount at equilibrium; K_L: direct measure of the intensity of the adsorption process; q_{max}: maximum adsorption capacity.	Langmuir equation	(14)
$R_L = \frac{1}{1 + K_L C_0}$	The adsorption process can be de fined as irreversible (R_L = 0), favorable (R_L between 0 and 1), linear (RL = 1) or unfavorable (R_L<1).	Calculate of dimensionless constant separation factor	(15)
$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F$	K_F: adsorption capacity; n: intensity of adsorption; 1/n=0 irreversible; 1/n>1 unfavorable 0<1/n<1 favorable.	Frundliche equation	(16)
$\ln (k_2) = \frac{E_a}{RT} + C$	k_2 is the pseudo-second order rate constant; Ea is the activation energy (kJ·mol^{-1}). R is the ideal gas constant (8.314J·mol^{-1}·K^{-1}); T is the absolute temperature (K).C is the constant.	Calculate of activation energy	(15)
$\Delta G^{\circ} = -RT \ln K_d$	ΔG°: Gibbs free energy change; Kd: equilibrium constant; R: gas constant; T: temperature.	Thermodynamic study	(17)
$\ln K_d = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}$	ΔS°: entropy change; ΔH°: enthalpy change.	Van't Hoff	(17)
$BMP_{Sub/Cont} = BMP_{Average,\ Sub/Cont} \pm \sqrt[2]{(SD)^2_{blank} + (SD)^2_{Sub/Cont}}$	SD is the Standard deviation	Calculate of biomethane potential	(4)
$BMP_{Average,\ Sub/Cont} = \frac{1}{n} \sum_{i=1}^{n} (BMP_{i,\ Sub/Cont})$	n is the number of repetition	Calculate of average biomethane potential	(4)
$BMP_{i,\ Sub/Cont} = \frac{V^S_{STP} - V^B_{STP} \frac{m_{I,S}}{m_{I,B}}}{m_{S,S}}$	V^S_{STP} and V^B_{STP} is the actual volume of CH_4 vis-a-vis substrate and inoculum, respectively. $m_{I,S}$, $m_{I,S}$ and $m_{I,S}$ are the organics materials amount of inoculum in the substrate bottle, of inoculum in the blank bottle and of substrate in the substrate bottle.	Calculate of biomethane potential of experience i	(3)
$V^S_{STP} = V_{Cal} \times \frac{T_{STP}(K)}{760 mmHg \times T_{gas}(K)} \times (P_{gas})$	V_{Cal} is the accumulated volume of gas coming from the substrate. T_{gas} and P_{gas} are temperature and pressure of the measured gas.	Calculate of actual volume of CH_4 vis-a-vis substrate	(3)
$E_{AD} = \frac{1}{3600} q_i f_{SV} b_i g C_{CH4} Q_{CH4} \eta_e$	q_i annual available resource of biomass type i, (Mg y^{-1} dry matter), f_{SV}ratio of volatile solids to total solids, $b_i$volatile solids biodegradability for biomass type, g biogas yield ($m^3.kg^{-1}_{VS}$ destroyed), C_{CH4}volume concentration of methane in biogas ($m^3.m^{-3}$), Q_{CH4}volumetric heating value of methane ($MJ.m^{-3}$) and η_e engine-generator efficiency on biogas.	calculate annual electrical energy of ACD ($GW.h.y^{-1}$)	(18)

Table S10. Experimental domains of Factors and CCD-Matrix of ACD process

Name of Variable	Unit	-1.68	-1	0	+1	+1.68
X_1 (pH)	-	6.32	7	8	9	9.68
X_2 (Inoculum)	mL	39.55	60	90	120	140.45
X_3 (Load)	mL	129.55	150	180	210	230.45

Run. No	Operating parameters			Rep. Variable		
	pH	Inoculum (mL)	Load-opt (mL)	IN-$_{opt}$ / Load-$_{opt}$	BMP sub/cont L CH_4 Kg SV^{-1}	Electric energy (GWh $year^{-1}$)
1	7	60	150	0.40	49.88	79.49
2	9	60	150	0.40	44.21	70.46
3	7	120	150	0.80	74.14	118.15
4	9	120	150	0.80	55.28	88.10
5	7	60	210	0.29	43.98	70.09
6	9	60	210	0.29	32.10	51.16
7	7	120	210	0.57	44.01	70.14
8	9	120	210	0.57	28.66	45.67
9	6.32	90	180	0.50	9.19	14.65
10	9.68	90	180	0.50	2.05	3.27
11	8	39.55	180	0.22	80.01	127.51
12	8	140.45	180	0.78	185.40	295.46
13	8	90	129.55	0.69	179.15	285.50
14	8	90	230.45	0.39	96.31	153.48
15	8	90	180	0.50	169.33	269.85
16	8	90	180	0.50	170.54	271.78
17	8	90	180	0.50	169.34	269.87
18	8	90	180	0.50	167.50	266.94

19	8	90	180	0.50	170.39	271.54
20	8	90	180	0.50	168.20	268.05

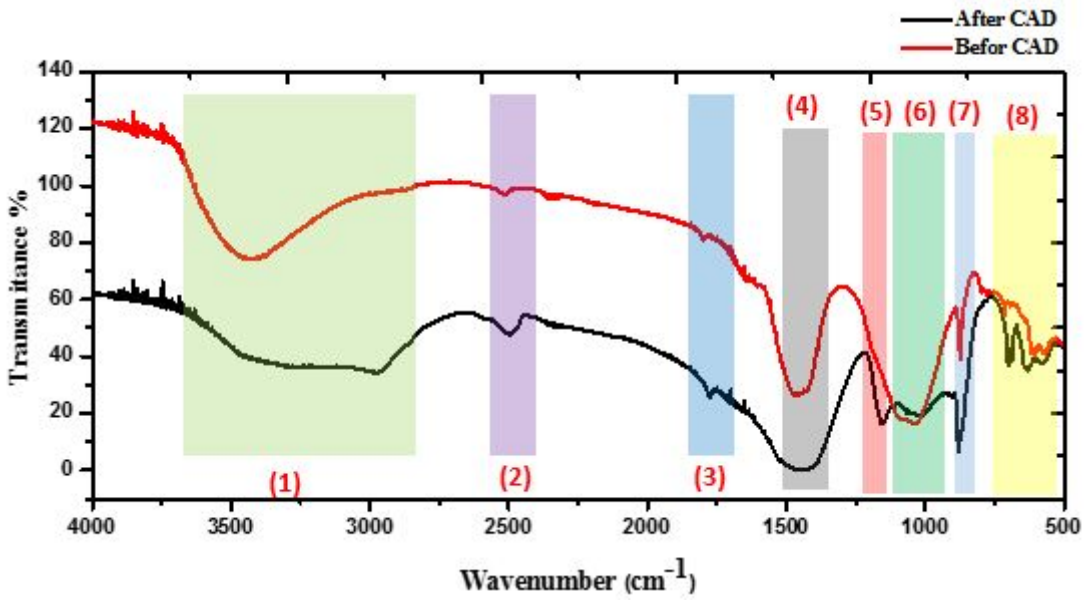

Figure S1. FTIR spectra before and after anaerobic co-digestion process for agri-food organic waste degradation

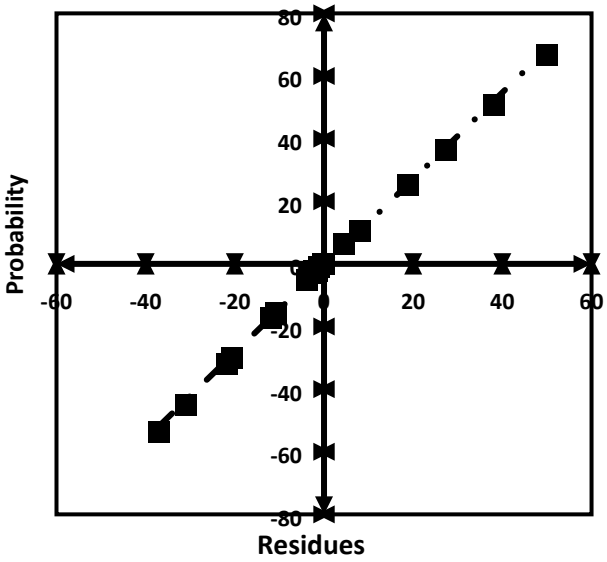

Figure S2. Normal probability plot of studentized residuals of ACD

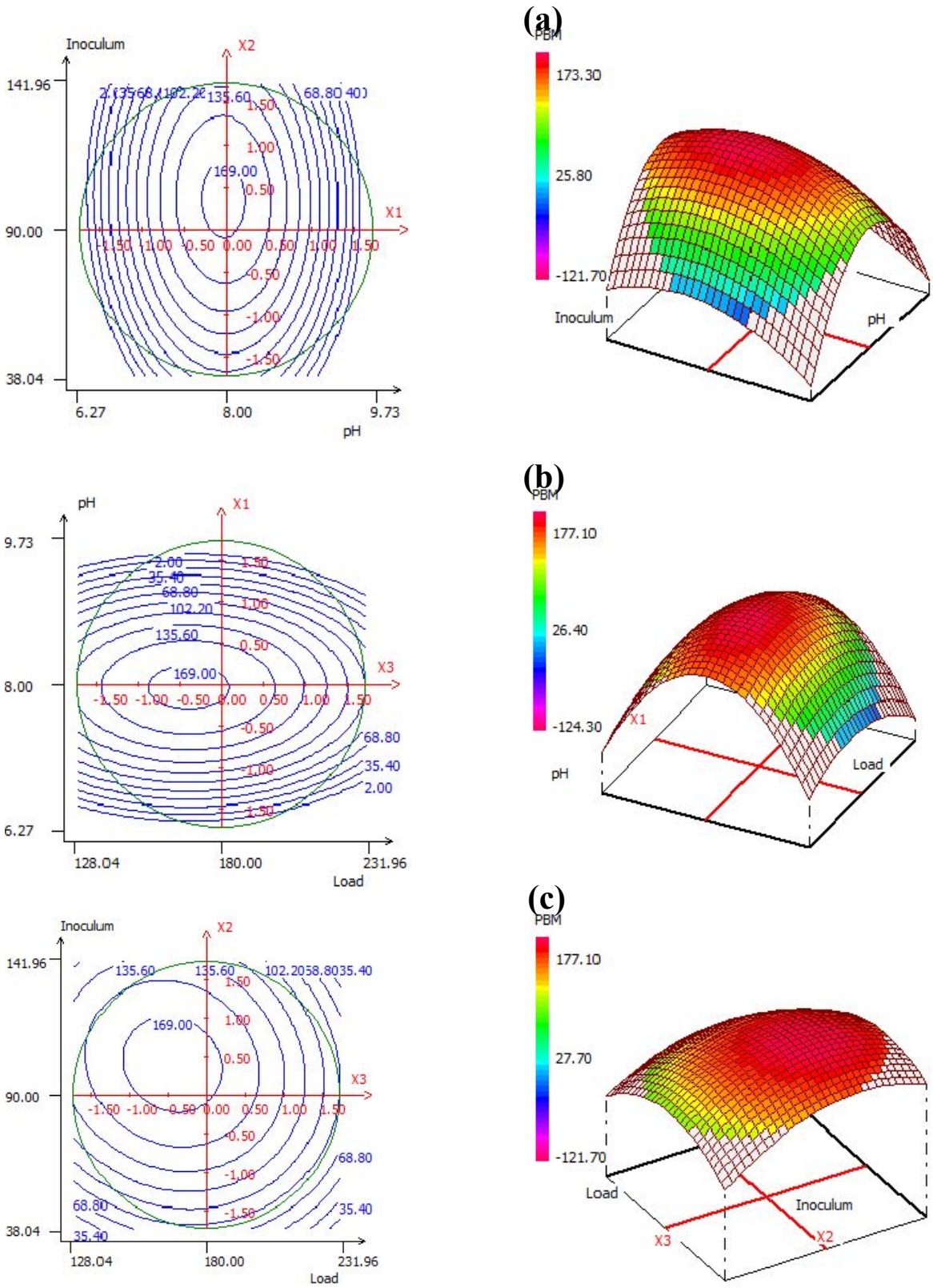

Figure S3 : RSM and Contour plot presentations of ACD process a) plan Inoculum-pH b) plan Load-pH and c) plan Inoculum-Load

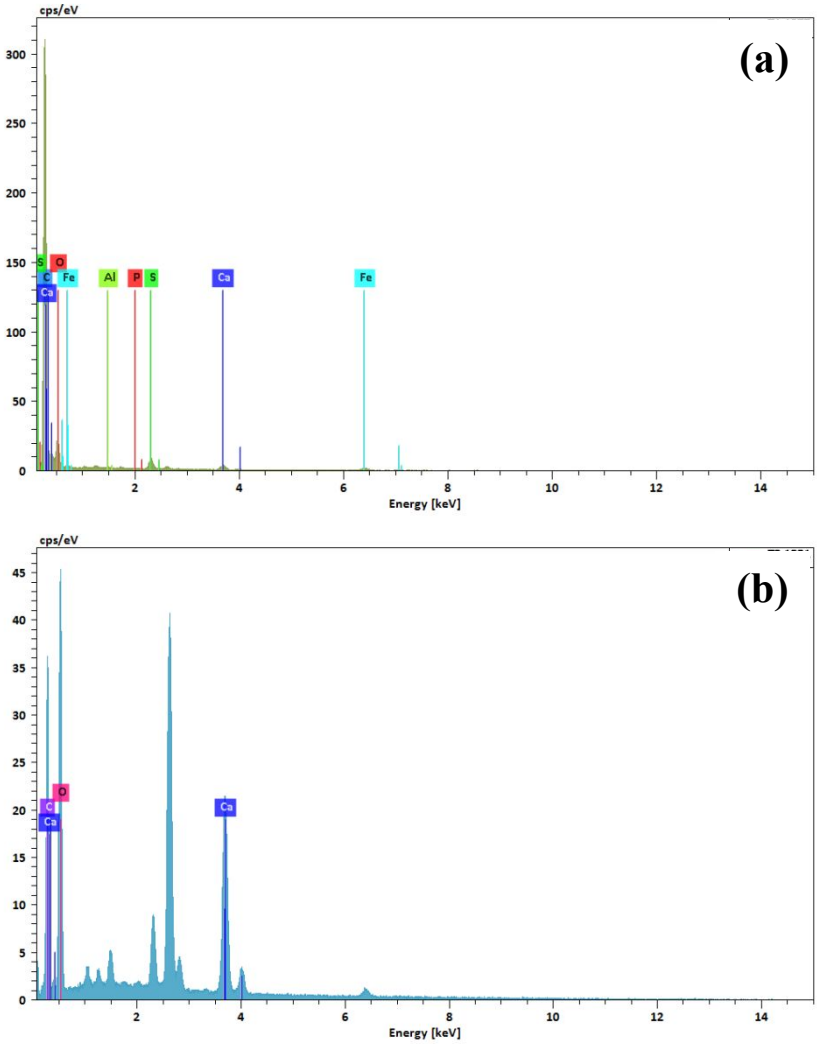

Figure S4. Energy-dispersive X-ray spectroscopy analysis of core-shell particles a) in the core of particles and b) in the shell of particles.

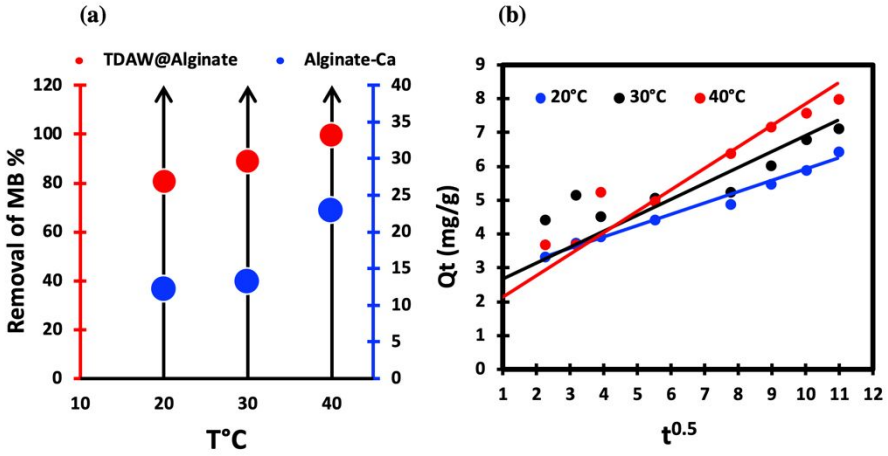

Figure 5S. a) MB removal efficiency using TDAW@Alginate and Alginate-Ca adsorbent, b) Intraparticle Diffusion analysis

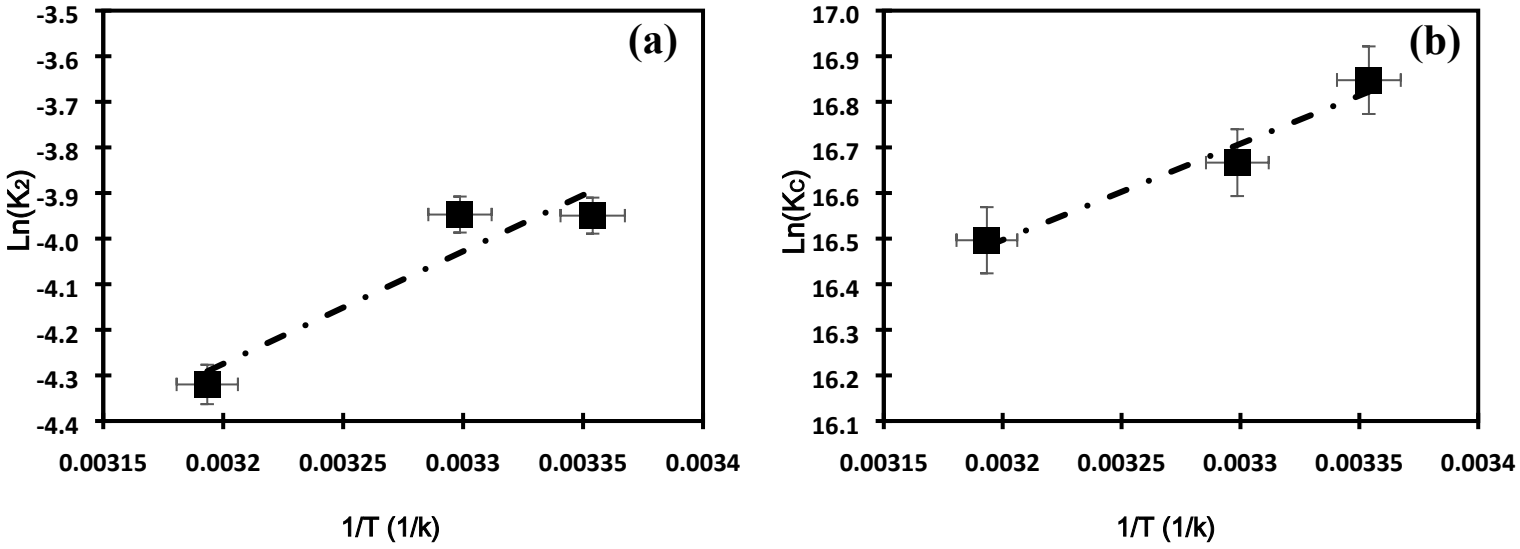

Figure S6: a) Activation energy and b) Van't Hoff plot

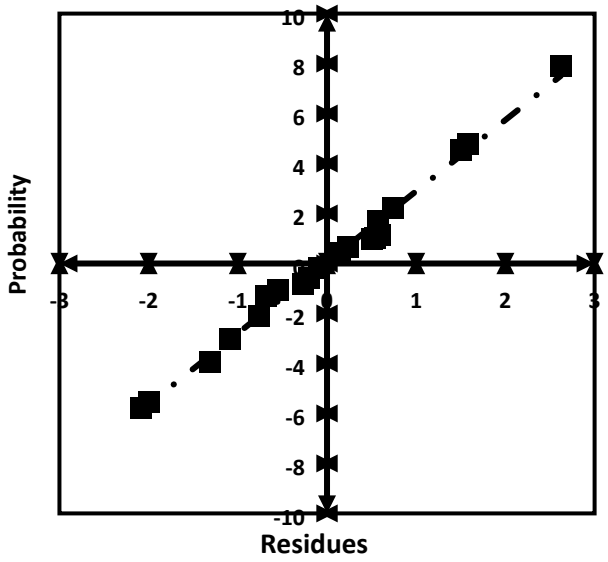

Figure S7. Normal probability vs studentized residual of MB adsorption onto TDAW@alginate

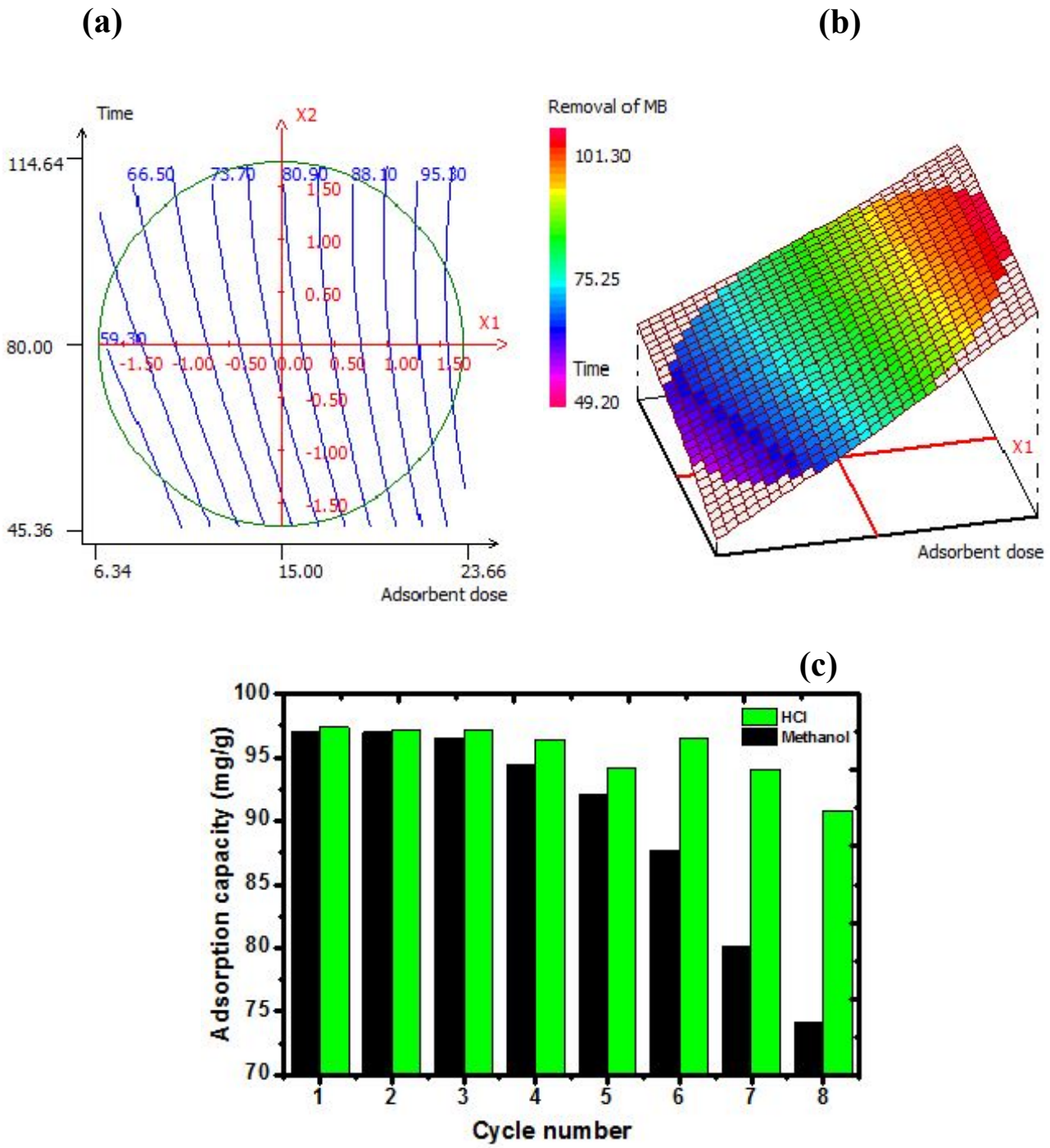

Figure S8. a) RSM and b) contour plot presentations c) regeneration cycle of MB-loaded TDAW@Alginate using HCl and methanol

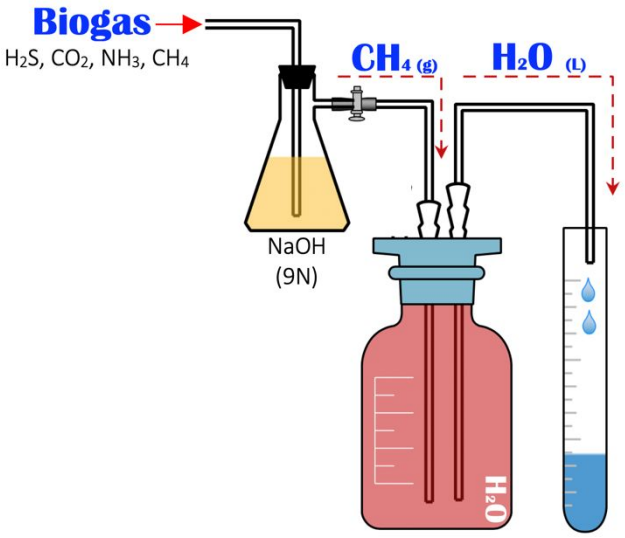

Figure S9. Schematic of gasometer based on volume of methane displaced

References

1. Rodier J, Legube B, Merlet N. Analyse de l'eau Rodier. 9ème edition. 9th ed. Jean Rodier, editor. Paris; 2009. 1579 p.
2. Walker M, Zhang Y, Heaven S, Banks C. Potential errors in the quantitative evaluation of biogas production in anaerobic digestion processes. Bioresour Technol. 2009;100(24):6339–46.
3. Strömberg S, Nistor M, Liu J. Towards eliminating systematic errors caused by the experimental conditions in Biochemical Methane Potential (BMP) tests. Waste Manag. 2014;34(11):1939–48.
4. Holliger C, Alves M, Andrade D, Angelidaki I, Astals S, Baier U, et al. Towards a standardization of biomethane potential tests. Water Sci Technol. 2016;74(11):2515–22.
5. Serrano A, Ángel Siles López J, Chica AF, Martin M, Karouach F, Mesfioui A, et al. Mesophilic anaerobic co-digestion of sewage sludge and orange peel waste. Environ Technol. 2014;35(7):898–906.
6. Hansen TL, Schmidt JE, Angelidaki I, Marca E, Jansen JLC, Mosbæk H, et al. Method for determination of methane potentials of solid organic waste. Waste Manag. 2004;24(4):393–400.
7. Anfar Z, El Haouti R, Lhanafi S, Benafqir M, Azougarh Y, El Alem N. Treated digested residue during anaerobic co-digestion of Agri-food organic waste: Methylene blue adsorption, mechanism and CCD-RSM design. J Environ Chem Eng. 2017;5(6):5857–67.
8. Do XH, Lee BK. Removal of Pb2+ using a biochar-alginate capsule in aqueous solution and capsule regeneration. J Environ Manage. 2013;131:375–82.
9. Zbair M, Anfar Z, Ait Ahsaine H, El Alem N, Ezahri M. Acridine orange adsorption by zinc oxide/almond shell activated carbon composite: Operational factors, mechanism and performance optimization using central composite design and surface modeling. J Environ Manage [Internet]. 2018 Jan;206:383–97.
10. MATHIEU, D. et LUU, R. Phan Tan. Software Nemrod. Université d'Aix-Marseille III, France, 1980.
11. Hassani A, Soltani RDC, Karaca S, Khataee A. Preparation of montmorillonite-alginate

nanobiocomposite for adsorption of a textile dye in aqueous phase: Isotherm, kinetic and experimental design approaches. J Ind Eng Chem. 2015;21:1197–207.
12. Zbair M, Ainassaari K, Drif A, Ojala S, Pirilä M, Keiski RL, et al. Toward new benchmark adsorbents: preparation and characterization of activated carbon from argan nut shell for bisphenol A removal. Environ Sci Pollut Res. 2018;25(2):1869–82.
13. Ahsaine HA, Zbair M, El Haouti R. Mesoporous treated sewage sludge as outstanding low-cost adsorbent for cadmium removal. Desalin Water Treat. 2017;85:330–8.
14. Langmuir I. The constitution and fundamental properties of solids and liquids. Part I. Solids. J Am Chem Soc. 1916;38(11):2221–95.
15. Fan S, Wang Y, Wang Z, Tang J, Tang J, Li X. Removal of methylene blue from aqueous solution by sewage sludge-derived biochar: Adsorption kinetics, equilibrium, thermodynamics and mechanism. J Environ Chem Eng. 2017;5(1).
16. Freundlich H. Über die Adsorption in Lösungen. Zeitschrift für Phys Chemie. 1907;57U(1).
17. Hayeeye F, Sattar M, Chinpa W, Sirichote O. Kinetics and thermodynamics of Rhodamine B adsorption by gelatin/activated carbon composite beads. Colloids Surfaces A Physicochem Eng Asp. 2017;513(Supplement C):259–66.
18. Matteson GC, Jenkins BM. Food and processing residues in California: Resource assessment and potential for power generation. Bioresour Technol. 2007;98(16):3098–105.