

Surface characterization and dye adsorptive capacities of char obtained from pyrolysis/gasification of sewage sludge

Charothon Jindarom^a, Vissanu Meeyoo^{b,*}, Boonyarach Kitiyanan^a,
Thirasak Rirksomboon^a, Pramoch Rangsunvigit^a

^a *The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330, Thailand*

^b *Center for Advanced Materials and Environmental Research, Mahanakorn University of Technology, Bangkok 10530, Thailand*

Received 19 June 2006; received in revised form 25 October 2006; accepted 4 February 2007

Abstract

Sewage sludge was used to develop a potential adsorbent for dye removal by pyrolysis under either N₂ or CO₂ atmospheres. The results showed that the surface area of the char increases as the pyrolysis temperature increase under the CO₂ atmosphere. The maximum surface area of the char is achieved with pyrolysis at 750 °C under the CO₂ atmosphere, 60.7 m² g⁻¹ with mainly mesopores. The FT-IR spectra of the char prepared under both N₂ and CO₂ atmospheres indicate a decrease in –OH, –NH and C=O functionalities with increasing the pyrolysis temperature, corresponding to a decrease in the acidity of the char. The maximum adsorption capacities of acid and basic dyes were found to increase with an increase in the pyrolysis temperature while that of the reactive dye possessed no correlation. The adsorption mechanism is governed by the combination of the electrostatic interactions and dispersive interactions. The equilibrium data fit well with the Langmuir model of adsorption suggesting a monolayer coverage of dye molecules at the outer surface of sewage sludge derived chars. The maximum adsorption capacities of acid yellow 49, basic blue 41 and reactive red 198 dyes are reported at 116, 588 and 25 mg g⁻¹ of char, respectively.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Azo dye adsorption; Adsorbent; CO₂ pyrolysis; Surface chemistry

1. Introduction

Sewage sludge is a by-product from wastewater treatment plants, and contains significant amounts of heavy metals, organic toxins and pathogenic microorganisms, which are considered to be harmful to the environment and all living organisms [1]. Agricultural use, land filling and incineration are commonly used as disposal methods. It was, however, reported that sewage sludge applications in agriculture gives rise to an accumulation of harmful components (heavy metals and organic compounds) in soil [2,3]. The problems encountered with the land filling are the leachate and the landfill gas. The major gas released from the land filling is methane, which is a significant contributor to the climate change [4]. Since hazardous air pollutants (HAPs) are usually present during incineration, an expensive pollutant reduction unit has to be implemented in the incineration.

Pyrolysis can be considered as a promising technique to treat the sewage sludge including the production of fuels [5]. Generally, pyrolysis products are divided into a volatile fraction consisting of gasses; vapours and tar components; and a carbon rich solid residue. The processing conditions can be optimized to maximize the production of these products [6–8]. The solid residue usually has a porous structure and surface area that is appropriate for use as an adsorbent. Typically, pyrolysis utilizes an inert gas, e.g. nitrogen or helium. In commercial-scale, a pyrolysis plant, however, has been operated under low oxygen atmosphere. Therefore, a recycle of gas product stream, CO₂ rich stream [9], seems to be the economical way. CO₂ is an unreactive molecule at ambient temperature. If the temperature is high enough, CO₂ is turned to be the reactive molecule and can be used as an activating agent in gasification. Under such a reactive atmosphere, it may significantly influence the yield and the quality of the products [10]. However, a few literatures have been found on the effect of CO₂ on pyrolysis.

In general, activated carbon productions involve in high temperatures (900–1200 °C) and also in the presence of an activating agent such as CO₂. It was reported that CO₂ can enhance the

* Corresponding author. Tel.: +66 2988 3655x108; fax: +66 2988 4039.
E-mail address: vissanu@mut.ac.th (V. Meeyoo).

porosity of materials by the gasification of C atoms in the interior of the particle [11,12]. However, in contrast to the bio-oil productions, they require lower temperatures (400–600 °C) to maximize a bio-oil yield. The different solids formed during the bio-oil production are “char”, for which they have the potential utilization as substituted activated carbons. Therefore, this work explores the utilization of sewage sludge char obtained from both N₂ and CO₂ atmospheric pyrolyses in the temperature range of 350–750 °C by evaluating the dye adsorption capacities. Three classes of monoazo dyes; acid, basic, and reactive, were evaluated for their adsorption capacities. Isothermal adsorption equilibrium data on sewage sludge char were determined and mathematically modeled. The adsorption characteristics were discussed in terms of surface chemistry.

2. Materials and methods

2.1. Production of the sewage sludge derived char

Sewage sludge obtained from Bangkok Municipal Wastewater treatment plants with about 5 wt% water content was used for the preparation of the char. The detailed chemical composition of this sludge was reported elsewhere [13]. It contains around 35 wt% inorganic matters, mainly in the forms of iron, alumina, silica oxides, and carbonates as well as up to 50 wt% of organic matters. The adsorbents used in this study were prepared by pyrolysis of sewage sludge in a fixed bed reactor at the temperature between 350 and 750 °C in a nitrogen atmosphere. The pyrolyzed heating rate was employed at 20 °C min⁻¹. When the temperature was reached a set point, it was held for 30 min. Finally, samples were ground and sieved, the particle size of 20/50 mesh was used for conducting the adsorption tests. The samples are referred to as N350, N450, N550, N650 and N750 where N indicates the sample prepared under nitrogen atmosphere and the numbers represent the pyrolysis temperature in Celsius. In some experiments, carbon dioxide was introduced as a gasifying agent, and hence the designated N is altered to C, indicating the sample prepared under the carbon dioxide atmosphere.

2.2. Characterization of the sewage sludge derived char

2.2.1. BET surface area and SEM

The BET surface area and pore structure of char were obtained from N₂ adsorption isotherms at 77 K using a QUANTACHROME AutoSorb-1 analyzer. The specific surface area was calculated by the Bruanauer–Emmet–Teller (BET) equation. The micropore surface area and volume were calculated by the *t*-method. Prior to the analysis, the samples were outgassed at 250 °C for 4 h. The surface morphology of the char samples was examined using a scanning electron microscope (JOEL 631).

2.2.2. FT-IR and total surface acidity/basicity

Fourier transform infrared spectroscopy (FT-IR) spectra of the char samples were scanned in the range of 400–4000 cm⁻¹ using Thermo Nicolet FT-IR spectroscope modeled Nexus 670 using potassium bromide (KBr) disks at the ratio of 1:50 (char

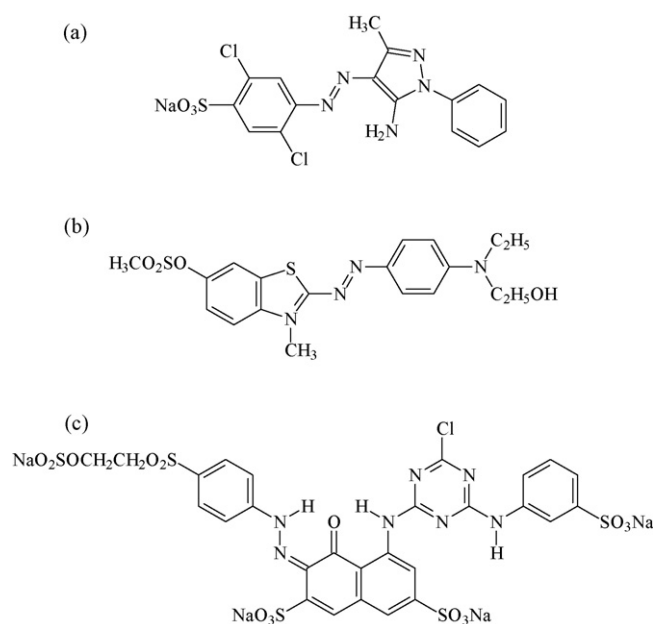


Fig. 1. Molecular structures of acid yellow 49, basic blue 41 and reactive red 198.

sample/KBr). The total surface acidity/basicity was determined by the conventional back titration methods. To determine the total acidity (basicity) of a sample, about 0.200 g of sewage sludge char was soaked into 25 ml of 0.025N NaOH (0.025N HCl) solution in a closed flask and agitated for 48 h at room temperature. While the suspension was decanted, the supernatant was titrated with 0.025N HCl (0.025N NaOH) solution to determine the remaining of NaOH (HCl) in the solution.

2.3. Dye adsorption experiments

Three dyes from different classes namely, acid yellow 49, basic blue 41, and reactive red 198, were selected for evaluating the adsorptive capacities of sewage sludge derived char. Dye structures and their characteristics are presented in Fig. 1 and Table 1, respectively. For adsorption experiments, ca. 0.150 g of each char sample was mixed with a 50 cm³ dye solution of a concentration range between 10 and 750 mg l⁻¹ in a closed Erlenmeyer flask without further pH adjustment. The flask containing suspension was then shaken for 48 h using a horizontal shaker operated at 150 rpm. Preliminary adsorption tests indicated that the holding time of 48 h is enough for the suspension to reach its equilibrium. For each set of experiments, a blank test (without adsorbent) was always carried out. After 48 h, the suspension was filtered and the remaining dye in the supernatant

Table 1
Dye characteristics

Class ^a	Commercial name	Generic name	λ_{\max} ^b
Acid	Telon light yellow FG	C.I. acid yellow 49	402
Basic	Astrazon blue FGGL	C.I. basic blue 41	606
Reactive	Remazol red RB	C.I. reactive red 198	518

^a Monoazo in chemical class.

^b Maximum adsorption wavelength.

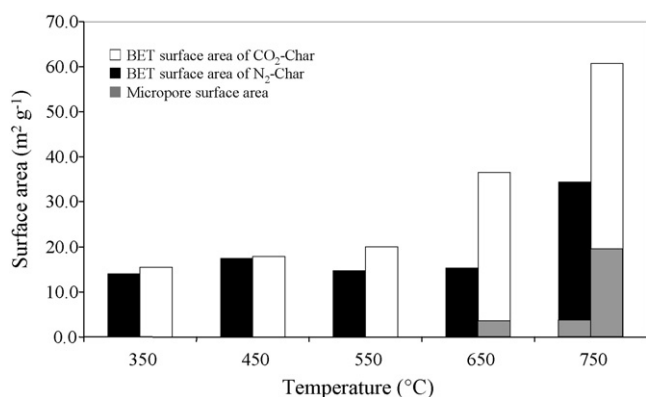


Fig. 2. BET surface area of the N₂-char and CO₂-char as a function of temperature.

was analyzed using a Shimadzu UV–vis spectrophotometer Model UV-2550 at its maximum absorption wavelength as indicated in Table 1. The pH values of initial and final solution were measured. For instances, the initial pH values of 500 mg l⁻¹ dye solution were 5.98 for acid dye, 5.45 for basic dye and 5.36 for

reactive dye. After the contact with the sewage sludge char, the final pH values of these solutions were slightly increased within the range between 6.0 and 7.0. The final pH values of the solutions were still in this range although the dye concentration of dye was increased to 750 mg l⁻¹.

3. Results and discussion

3.1. BET surface area and SEM

BET surface areas and micropore surface areas of sewage sludge derived char are shown in Fig. 2. The BET surface areas of the as-received sludge are considerably low, ca. 3.4 m² g⁻¹. Under either N₂ or CO₂ atmosphere, the porosity of the materials was found to increase due to the removal of volatile matters during pyrolysis [14]. Under the N₂ atmosphere, the BET surface area of char slightly increases with increasing the pyrolysis temperature from 14.0 m² g⁻¹ (at 350 °C) to 15.3 m² g⁻¹ (at 650 °C) and the mesopore characteristics are dominant. At 750 °C, the BET surface areas of char increases substantially, up to 34.3 m² g⁻¹ and some micropores are evidently yielded.

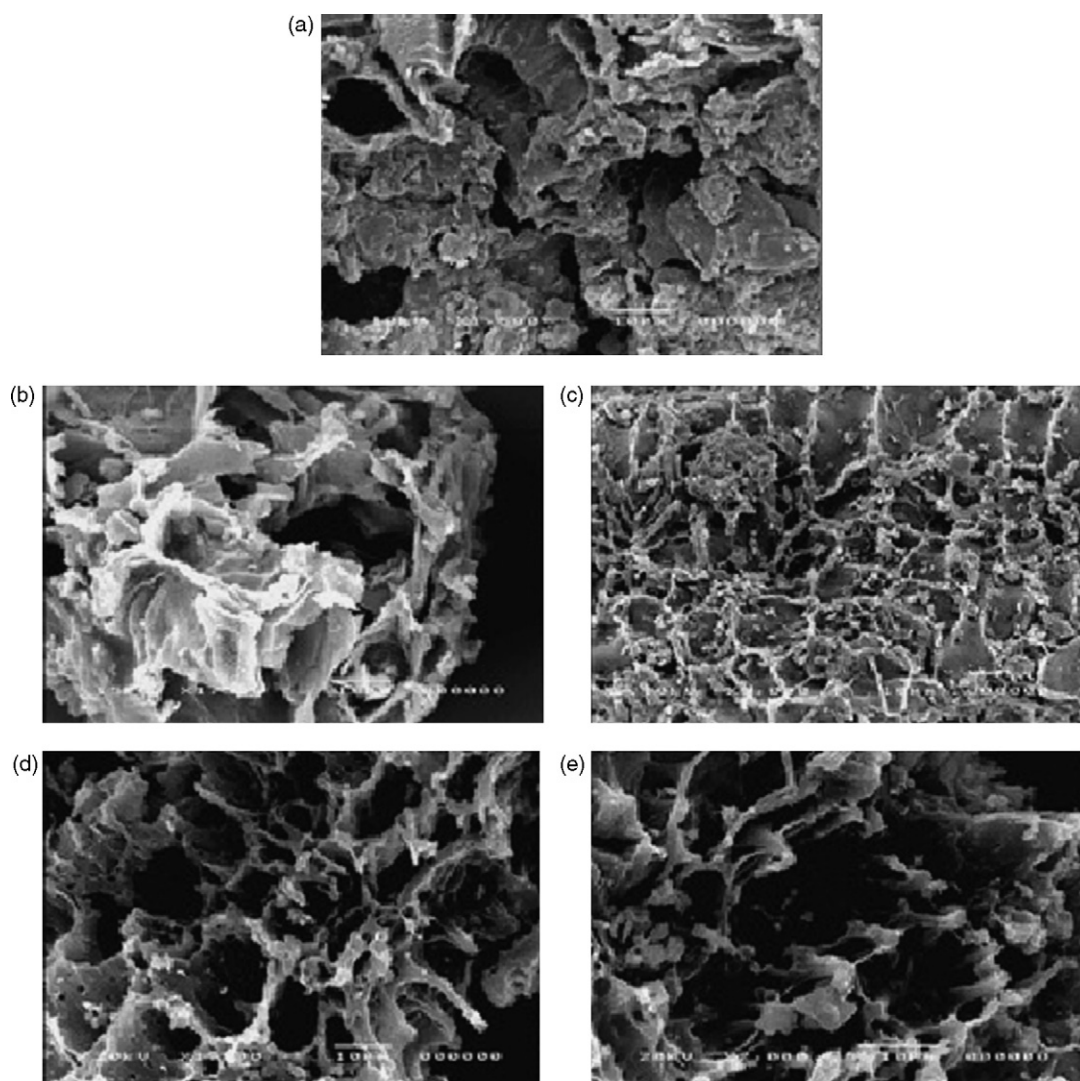


Fig. 3. SEM micrographs of sewage sludge derived chars (a) as-received sludge, (b) N350, (c) C350, (d) N750 and (e) C750.

As CO₂ was introduced, the BET surface areas of the char prepared at medium temperatures (350–550 °C) are quite similar to those of the char derived under nitrogen atmosphere. However, above 550 °C, the surface area improves dramatically from 20.0 m² g⁻¹ (550 °C) to 60.7 m² g⁻¹ (750 °C) owing to the CO₂ gasification effect. It was reported that the gasification removes carbon atoms from the interior of the particle, resulting in the enlargement of opened micropores and the opening up the closed micropores [15]. The presence of CO₂ was found to enhance the formation of micropore of sewage sludge char. The micropore was found at lower temperature, 650 °C, in the case of the char prepared by CO₂ pyrolysis while the micropore in the char prepared by N₂ pyrolysis was found at 750 °C. The scanning electron microscopy (SEM) technique was employed to observe the surface morphology of the as-received sewage sludge and char. The irregular shape solids containing pores with different sizes were observed as depicted in Fig. 3. When the pyrolysis temperature increases, an increase in the solid porosity can be found. This results support the increase in the BET surface area as a function of temperature.

3.2. FT-IR and total acidity/basicity

The FT-IR spectra of chars are shown in Fig. 4. It should be noted that the information obtained from the FT-IR is limited by the concentration of the functional groups present on the surface. Thus, the absorption bands and peaks could only provide the evidence of the presence of some surface functional groups. The major absorption band of the char is 1040 cm⁻¹ assigned to either Si–O–Si or Si–O–C structures, which is associated with the silicon content in sewage sludge and char [16]. The fingerprint spectra beyond this band, which is quite identical in all samples, might be due to the mineral content in the sludge. Possible surface functional groups present on the surface of the char are the –OH and –NH of either alcohols or phenols, and nitrogen containing surface group; and the C=O of carbonyl groups, indicated by the peaks at the bands of 3650–3200 and 1760–1650 cm⁻¹, respectively. These oxygenated functional groups are normally related to the acidity of the carbon [17,18]. The evidence of the C=C bond of aromatic rings polarized by oxygen atoms bound near one of the C atoms is observed at the band of 1450–1428 cm⁻¹ suggesting the presence of basic oxygen-containing functionalities such as chromene structures, diketones or quinone groups and pyrone-like groups [18–20]. Generally, the effect of pyrolysis temperature on the FT-IR profiles is not pronounced. However, if one closely looks at the spectra, one might find an increasingly upward drift in the baseline of the spectrum from low to high wavenumbers at the high pyrolysis temperature, probably due to the increase in aromatics content of char during pyrolysis [21]. The results also indicates a slight decrease in the –OH, –NH and C=O functionalities with increasing pyrolysis temperature, resulting in a decreasing in the char acidity of char. It might be too presumptuous to sum up the surface acidity/basicity by the FT-IR technique alone. Therefore, the back titration method was applied to quantify the total acidity/basicity of carbon surface.

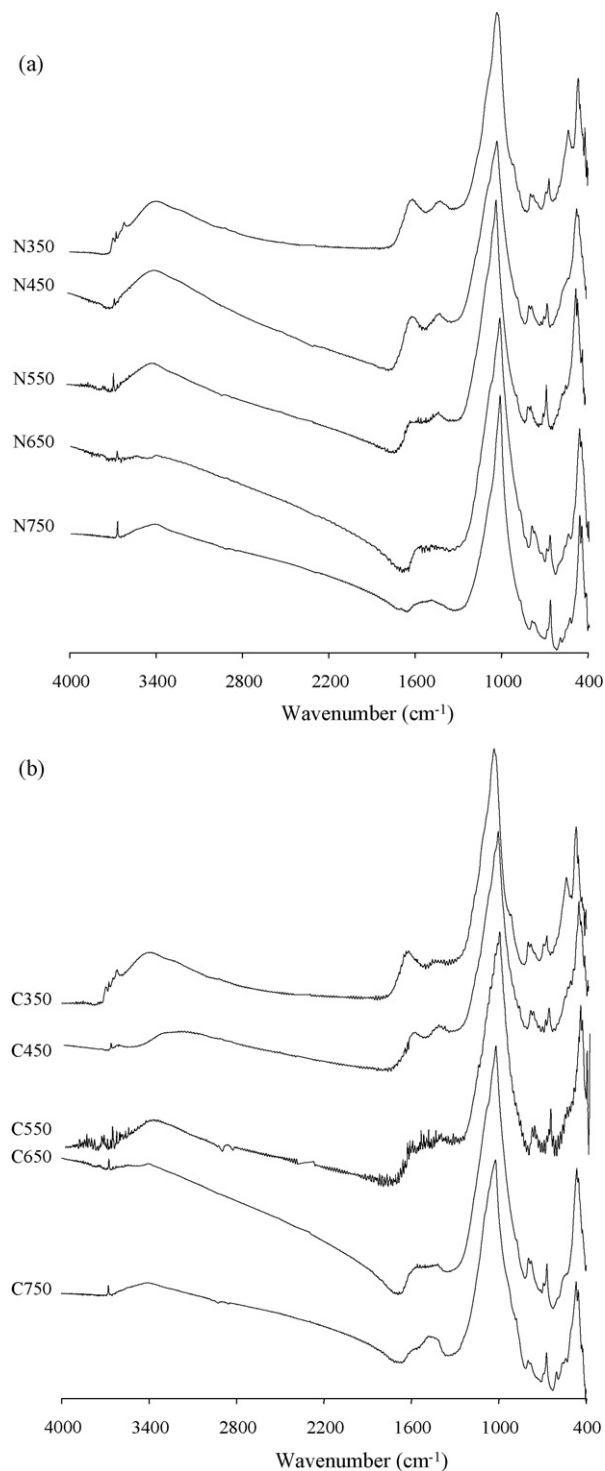


Fig. 4. FT-IR spectra of sewage sludge derived chars prepared at different temperatures (a) under N₂ atmosphere and (b) under CO₂ atmosphere.

The total acidity/basicity and pH_{PZC} of the sewage sludge derived char, amphoteric material, are shown in Table 2. The results showed that the acidity of the chars prepared either under the N₂ or CO₂ atmospheres decreases with an increase in the pyrolysis temperature resulted from the degradation of acidic oxygenated surface groups [21]. The acidity of both chars is insignificantly different. The basicity of both chars, on the other

Table 2
Total acidity/basicity and pH_{PZC} values of sewage sludge derived char

Sample	Acidity (mequiv. g _{ACs} ⁻¹)	Basicity (mequiv. g _{ACs} ⁻¹)	Basicity–acidity (mequiv. g _{ACs} ⁻¹)	pH _{PZC}
N350	0.34	1.13	0.79	9.74
N450	0.25	1.13	0.88	9.43
N550	0.03	1.13	1.10	9.20
N650	0.08	1.17	1.09	9.67
N750	0.06	1.62	1.56	9.31
C350	0.26	1.10	0.84	9.72
C450	0.19	1.15	0.96	9.56
C550	−0.01	1.69	1.70	9.19
C650	0.08	1.86	1.78	9.87
C750	0.13	2.03	1.90	9.27

hand, increases with increasing pyrolysis temperature, and the temperature effect is more pronounced at the temperature above 550 °C. At the same temperature, it is obvious that the surface basicity of the char prepared under the CO₂ atmosphere is higher than that prepared under the N₂ atmosphere. For example, the basicity values of C750 and N750 are 2.03 and 1.62 mequiv. g⁻¹, respectively. Notably, the negative value of the char acidity in the case of C550 might be due to the acid leaching from the carbon surface.

The pH_{PZC} values of the char samples are quite similar. These values indicate the basic characteristic of the char since all chars are positively charge in the solution. However, there is no direct correlation between the total acidity/basicity and pH_{PZC} of the char. This might be due to the influence of the ash content in the char.

3.3. Equilibrium adsorption isotherms

The adsorption isotherms of three dyes (acid yellow 49, basic blue 41, and reactive red 198) on the sewage sludge char samples are shown in Fig. 5. The equilibrium data were fitted with Langmuir and Freundlich models as expressed in Eqs. (1) and (2), respectively:

$$q_e = q_m \frac{K_L C_e}{1 + K_L C_e} \quad (1)$$

$$q_e = K_F C_e^{1/n} \quad (2)$$

where C_e and q_e are the adsorbate equilibrium concentrations in the liquid and solid phases, q_m the maximum adsorption capacity according to the Langmuir model, K_L and K_F the constants for Langmuir and Freundlich models, and n is the reciprocal reaction order.

Tables 3 and 4 show the Langmuir and Freundlich parameters obtained by fitting both models to the dye adsorption capacities on the char. The applicability of the models was established from the regression correlation, R^2 . The results show that the regression correlations for the Langmuir model are between 0.97 and 1.00 while those of the Freundlich model are between 0.89 and 1.00. This suggests a greater fit by the Langmuir model in comparison to the Freundlich model. In other words, the homogeneity model is more favorable in the adsorption of these dyes.

Table 3
Parameters of the Langmuir model

Sample	Acid dye			Basic dye			Reactive dye		
	q_m^a	K_L^b	R^2	q_m^a	K_L^b	R^2	q_m^a	K_L^b	R^2
N350	12.71	0.04	0.99	212.77	0.04	0.99	12.69	0.006	0.99
N450	26.25	0.02	0.99	222.22	0.06	0.97	14.06	0.023	0.99
N550	45.35	0.01	0.99	357.14	0.03	0.98	15.17	0.011	1.00
N650	65.56	0.03	0.99	384.62	0.03	0.99	17.53	0.044	0.99
N750	71.43	0.03	0.99	416.67	0.03	0.99	18.93	0.054	0.99
C350	49.75	0.00	0.99	218.46	0.01	0.98	15.88	0.016	0.97
C450	53.76	0.01	0.98	342.56	0.06	0.98	16.10	0.017	0.97
C550	75.80	0.03	0.99	416.67	0.02	0.99	18.58	0.013	0.99
C650	83.33	0.03	0.99	454.55	0.03	0.97	22.37	0.017	0.99
C750	116.28	0.06	0.98	588.24	0.07	0.98	25.06	0.013	0.99

^a Maximum adsorption capability (mg g_{ACs}⁻¹).

^b Langmuir model constant (dm³ mg⁻¹).

3.4. Adsorption mechanism

The maximum dye adsorption capacities of the sewage sludge derived chars are shown in Fig. 6. In most cases, the dye adsorption capacities of the sewage sludge derived chars obtained from the CO₂ pyrolysis are higher than those obtained from the N₂ pyrolysis; even the surface areas are rather similar. The disparity in the dye uptakes for the different chars may be explained by the differences in the chemical nature of the prepared chars.

Due to the steric hindrance associated with the size of the dyes, the maximum dye adsorption capacities are lower for large dye molecules, in this case the reactive dye. It was found that the maximum adsorption capacity of the basic dye is, in some cases, up to six-fold higher than the reactive dye maximum adsorption capacity as the ion size of the basic dye is smaller than that of the reactive dyes. Moreover, the presence of oxygen and nitrogen containing functional groups, which represent the electron rich surface sites, might have a negative effect on the adsorption of anionic dye (e.g., acid and reactive dye).

It was suggested that surface basicity is another important factor in the dye adsorption mechanism [16–18]. Typically, adsorption mechanisms of organic dyes include electrostatic interactions and dispersive interactions [18]. As indicated in our

Table 4
Parameters of the Freundlich model

Sample	Acid dye			Basic dye			Reactive dye		
	n^a	K_F^b	R^2	n^a	K_F^b	R^2	n^a	K_F^b	R^2
N350	2.38	1.07	0.91	1.71	7.81	0.96	2.70	1.23	0.92
N450	1.85	0.95	0.94	1.82	11.61	0.98	2.52	1.11	0.89
N550	1.73	1.56	0.93	1.53	10.34	1.00	2.68	1.34	0.91
N650	2.08	3.25	0.91	1.56	12.62	0.99	2.71	1.47	0.94
N750	1.99	3.67	0.91	1.46	10.84	0.96	2.76	1.63	0.95
C350	1.71	0.84	0.94	1.47	3.07	0.98	2.06	0.93	0.90
C450	1.53	0.90	0.96	1.93	11.77	1.00	1.80	0.65	0.93
C550	1.99	2.96	0.92	1.53	9.70	0.98	2.02	1.02	0.96
C650	2.09	4.50	0.98	1.50	10.76	0.99	2.17	1.24	0.96
C750	3.06	14.71	0.98	1.52	21.22	0.95	2.91	2.54	0.97

^a Reciprocal order.

^b Freundlich model constant ((mg g_{ACs}⁻¹) (dm³ mg⁻¹)^{1/n}).

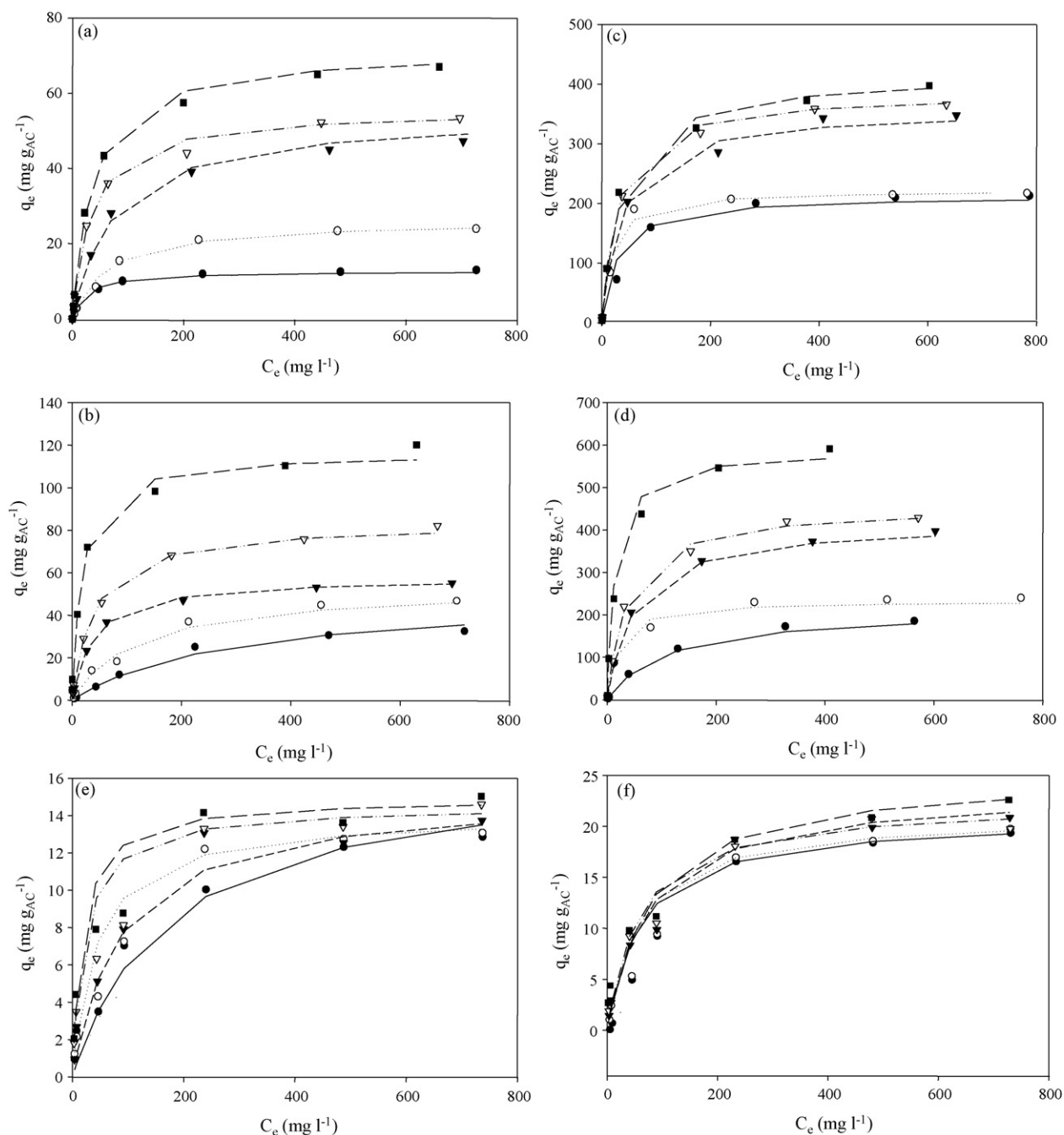


Fig. 5. Dye adsorption isotherms of sewage sludge derived chars prepared at different temperatures (a) acid dye adsorption on N_2 -char, (b) acid dye adsorption on CO_2 -char, (c) basic dye adsorption on N_2 -char, (d) basic dye adsorption on CO_2 -char, (e) reactive dye adsorption on N_2 -char and (f) reactive dye adsorption on CO_2 -char. (●) 350 °C, (○) 450 °C, (▼) 550 °C, (▽) 650 °C and (■) 750 °C.

results, the acid dye (anionic dye) maximum adsorption capacity increases with an increase in the surface basicity while the reactive dye (anionic dye) maximum adsorption capacity is rather still. The adsorption of the acid dye is mainly due to the electrostatic interaction between the anions and the positively charged of the char surface [17,18]. It should be noted that the ion size of the reactive dye is rather large (mostly excluded from adsorption in the pore); hence, the effect of surface basicity on the adsorption is insignificant. The results also indicate that the acid dye maximum adsorption capacity of CO_2 -char is higher than that

of N_2 -char when high pyrolysis temperature was applied. This supports the claim that the adsorption of acid dye is due to the effect of electrostatic interaction, which is strongly influenced by the surface basicity, since the basicity of the CO_2 -char is higher than that of the N_2 -char. As stated above, the adsorption of the basic dye is achieved mainly through electrostatic interaction; as a result, an increase in surface basicity does not have an adverse effect on the basic dye uptake of char. This can be seen from Fig. 6b that the basic dye uptakes of the CO_2 -char and the N_2 -char are rather similar.

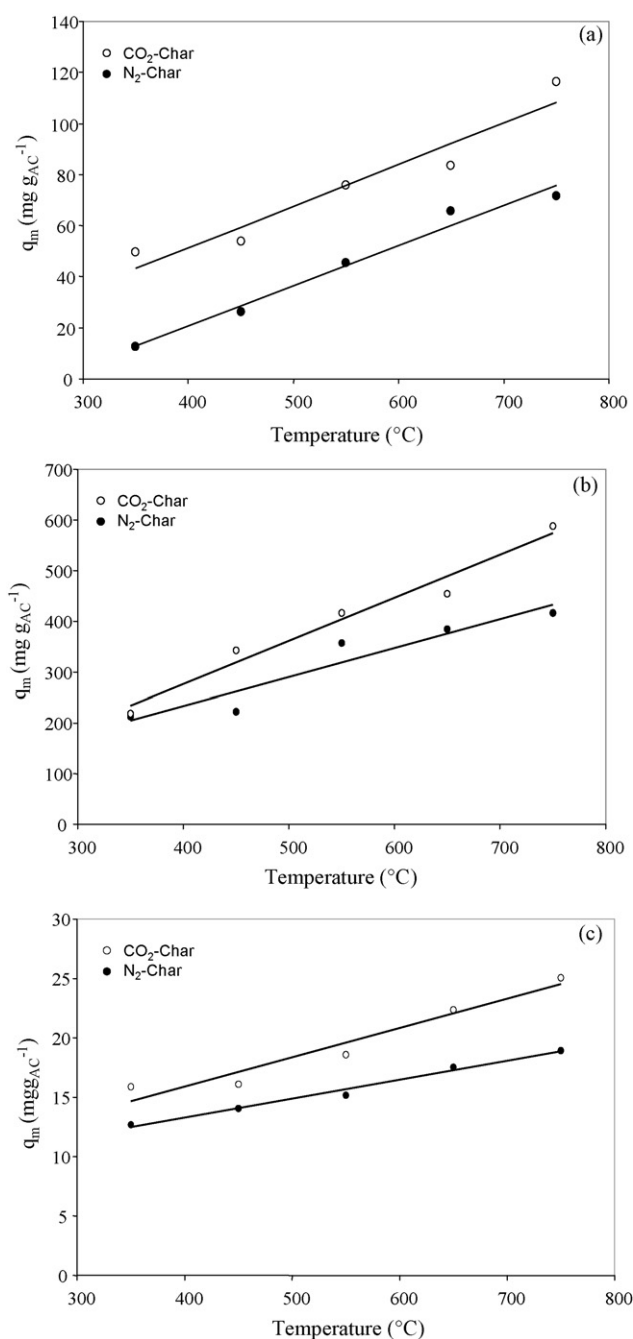


Fig. 6. Maximum adsorption capacities of (a) acid dyes, (b) basic dyes and (c) reactive dyes over sewage sludge derived char vs. pyrolysis temperature.

For the basic dye (cationic dye), the surface adsorption mechanism is, on the other hand, dominated by the ion exchange mechanism between the protonated surface functional groups and cationic ion resulting from the dissolution of the basic dye in water. As expected, the basic dye adsorption capacity increases with the char basicity due to the increase in the positively charged ion on the surface. It is of interest to note that the very high basic dye adsorption capacity is obtained. This might be due to another important factor, which is the adsorption on the silicon matrix of the char and on the nitrogen containing surface groups. The similar result was reported in the adsorption of metal cation

on the sewage sludge ash [20]. From different experiment, it was found that the ash content in these char samples are up to 60 wt%; therefore, the adsorption by the silicon matrix seems to be another possible important mechanism.

4. Conclusion

In conclusion, sewage sludge derived char prepared from the pyrolysis/gasification (CO_2 -pyrolysis) possesses higher surface area and basicity than that of prepared by pyrolysis under the N_2 atmosphere. Adsorption studies showed that these chars are considerably efficient for the removal of dyes. The adsorption mechanism was found to rely on the electrostatic interactions and dispersive interactions. The equilibrium data fit well with the Langmuir model suggesting the monolayer coverage of dye molecules at the outer surface of sewage sludge derived chars.

Acknowledgements

This work was supported by the Research Unit for Petrochemical and Environmental Catalysts, Ratchadapisek Somphot Endowment, Chulalongkorn University, the Postgraduate Education and Research Programs in Petroleum and Petrochemical Technology (PTT consortium), Chulalongkorn University, and the Thailand Research Fund (under Waste-to-Energy project and Royal Golden Jubilee Ph.D. Program: Grant 0061/45).

References

- [1] M. Dogru, A. Midili, C. Howarth, Gasification of sewage sludge using a throated downdraft gasifier and uncertainty analysis, *Fuel Process. Technol.* 75 (2002) 55–82.
- [2] A. Fullana, J.A. Conesa, R. Font, I. Martín-Gullón, Pyrolysis of sewage sludge: nitrogenated compounds and pretreatment effects, *J. Anal. Appl. Pyrol.* 68/69 (2003) 561–575.
- [3] D.A. Bright, N. Healey, Contaminant risks from biosolids land application: contemporary organic contaminant levels in digested sewage sludge from five treatment plants in Greater Vancouver, British Columbia, *Environ. Pollut.* 126 (2003) 39–49.
- [4] Y.S.G. Chan, L.M. Chu, M.H. Wong, Codisposal of municipal refuse, sewage sludge and marine dredgings for methane production, *Environ. Pollut.* 106 (1999) 123–128.
- [5] S. Yaman, Pyrolysis of biomass to produce fuels and chemical feedstocks, *Energy Convers. Manage.* 45 (2004) 651–671.
- [6] A.V. Bridgwater, D. Meier, D. Radlein, An overview of fast pyrolysis of biomass, *Org. Geochem.* 30 (1999) 1479–1493.
- [7] D. Meier, O. Faix, State of the art of applied fast pyrolysis of lignocellulosic materials a review, *Bioresour. Technol.* 68 (1) (1999) 71–77.
- [8] M. Inguanzo, A. Dominguez, J.A. Menendez, C.G. Blanco, J.J. Pis, On the pyrolysis of sewage sludge: the influence of pyrolysis conditions on solid, liquid and gas fractions, *J. Anal. Appl. Pyrol.* 63 (2002) 209–222.
- [9] J.A. Caballero, R. Front, A. Marcilla, J.A. Conesa, Characterization of sewage sludges by primary and secondary pyrolysis, *J. Anal. Appl. Pyrol.* 40/41 (1997) 433–450.
- [10] V. Minkova, S.P. Marinov, R. Zanzi, E. Björnbom, T. Budinova, M. Stefanova, L. Lakov, Thermochemical treatment of biomass in a flow of steam or in a mixture of steam and carbon dioxide, *Fuel Process. Technol.* 62 (2000) 45–52.
- [11] J. Pastor-Villegas, C.J. Durán-Valle, Pore structure of chars and activated carbons prepared using carbon dioxide at different temperatures from extracted rockrose, *J. Anal. Appl. Pyrol.* 57 (2001) 1–13.

- [12] H. Teng, J.-A. Ho, Y.-F. Hsu, Preparation of activated carbons from bituminous coals with CO₂ activation-influence of coal oxidation, *Carbon* 35 (1997) 275–283.
- [13] P. Thipkhanthod, V. Meeyoo, P. Rangsunvigit, B. Kitiyanan, K. Siemanond, T. Rirksomboon, Pyrolytic characteristics of sewage sludge, *Chemosphere* 64 (6) (2006) 955–962.
- [14] M.F.R. Pereira, S.F. Soares, J.J.M. Órfão, J.L. Figueiredo, Adsorption of dyes on activated carbon: influence of surface chemical groups, *Carbon* 41 (2003) 811–821.
- [15] E. Papirer, S. Li, J.B. Donnet, Contribution to the study of basic surface groups on carbon, *Carbon* 25 (1987) 243–247.
- [16] X. Chen, S. Jeyaseelan, N. Graham, Physical and chemical properties study of the activated carbon made from sewage sludge, *Waste Manage.* 22 (2002) 755–760.
- [17] K. László, A. Bóta, L.G. Nagy, Characterization of activated carbon from waste materials by adsorption from aqueous solutions, *Carbon* 35 (5) (1997) 593–598.
- [18] M.J. Martín, A. Artola, M.D. Balaguer, M. Rigola, Activated carbons developed from surplus sewage sludge for the removal of dyes from dilute aqueous solutions, *Chem. Eng. J.* 94 (2003) 231–239.
- [19] E. Fuente, D. Menéndez, D. Suárez, M.A. Montes-Morán, Basic surface oxides on carbon materials: a global view, *Langmuir* 19 (2003) 3505–3511.
- [20] S.C. Pan, C.C. Lin, D.H. Tseng, Reusing sewage sludge ash as adsorbent for copper removal from waste water, *Resour. Conserv. Recy.* 39 (2003) 79–90.
- [21] H.P. Boehm, Surface oxides on carbon and their analysis: a critical assessment, *Carbon* 40 (2002) 145–149.