

Contents lists available at ScienceDirect

Chemical Engineering Journal

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Color removal from water-based ink wastewater by bagasse fly ash, sawdust fly ash and activated carbon

Sirikan Noonpui^a, Paitip Thiravetyan^{a,*}, Woranan Nakbanpote^{b,1}, Suchapa Netpradit^c

^a Division of Biotechnology, School of Bioresources and Technology, King Mongkut's University of Technology Thonburi, Bangkok 10150, Thailand ^b Pilot Plant Development and Training Institute, King Mongkut's University of Technology Thonburi, Bangkok 10150, Thailand

^c Department of Printing and Packaging Technology, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand

ARTICLE INFO

Article history: Received 18 March 2010 Received in revised form 24 May 2010 Accepted 26 May 2010

Keywords: Bagasse fly ash Sawdust fly ash Water-based ink Activated carbon

ABSTRACT

Bagasse fly ash (BGFA), sawdust fly ash (SDFA) and activated carbon (AC) were investigated for color removal from wastewater from the printing ink industry after coagulation of water-based ink wastewater. Synthetic water-based ink was used to study the adsorption isotherm. The maximum adsorption capacity of BGFA increased with temperatures, having values of 7.30, 12.67, 21.60 and 29.07 mg g^{-1} at 30, 40, 50 and 60 °C, respectively. At 30 °C the maximum adsorption capacity of BGFA increased from 7.30 to 14.34 mg g⁻¹ when using water-washed BGFA. The Langmuir, Freundlich and Redlich–Peterson models were all able to explain the color removal of synthetic water-based ink by BGFA, water-washed SDFA (SDFA/W) and AC, whereas R^2 of these three models by SDFA was not high. It might be due to color removal by SDFA involved both precipitation and adsorption of the ink, whereas only adsorption was involved by SDFA/W, BGFA and AC. The synthetic water-based ink adsorption capacity at 30 °C was ranked as SDFA > AC > SDFA/W > BGFA with values of 85.47, 40.49, 30.21 and 7.30 mg g⁻¹, respectively. The efficiencies of BGFA, SDFA and AC for color removal from wastewater from printing ink industry after water-based ink coagulation showed that color removal by SDFA (90%) was higher than commercial AC (80%), SDFA/W (76%) and BGFA (68%), respectively at the same dosage of 0.3% (w/v). The system pH was increased from 1.7 to around neutral by SDFA, while the system pH of AC, SDFA/W and BGFA was still low (pH ~ 2-3). However, SDFA and BGFA had potential as alternative low-cost adsorbents for color removal of water-based ink wastewater from the printing ink industry.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Wastewater from printing industries represents an important environmental problem, and the printing industries in Thailand are under strong pressure to improve the quality of printing ink and its disposal. Wastewater associated with the use of water-based ink is contaminated with colorants (pigments and dyes), fluid carrier or vehicles (alkali-soluble, emulsions or colloidal dispersion chemistries), auxiliary solvents (alcohols, glycols and glycol ethers) and additives (driers, waxes, defoamers and dispersing aids) [1]. Colored wastewater is also of aesthetic concern, and the maximum discharge allowance for certain chemicals and pigments may be more problematic for particular regions and circumstances.

One of the most effective techniques for the removal of color from wastewater is adsorption by activated carbon (AC), but the high cost of AC limits its use, thus necessitating the development of suitable low-cost adsorbents. Bagasse and bagasse fly ash (BGFA) [2–5] have been used for removal of pesticides, heavy metals, colors and dyes. Also, various types of sawdust have been investigated for basic dye and heavy-metal removal. Some of these applications of BGFA and SDFA are summarized in Tables 1 and 2 [6–30].

Thailand generates a plentiful annual supply of bagasse from sugar production. Bagasse, a biomass fuel mostly used for steam and power supplies. A typical Thai sugar plant generates 4 MPa of steam at a bagasse boiler outlet with a temperature of 400 °C at 84% boiler efficiency. With bagasse and fuel oil LHV values of 7540 and 41,840 kJ kg⁻¹, respectively, with a 90% oil-burning boiler efficiency, 5.95 kg of bagasse could replace 1 kg of oil [31]. BGFA is a waste product left from sugar industry.

In addition, sawmill and plywood mills are major sources of biomass from wood industry. The rubber wood from the southern region of Thailand is also a major source of biomass. After latex is harvested, rubber trees are cut down for re-plantation. Wood from rubber tree is used as fuel and as timber which is an important source for the furniture industry. Furthermore, Eucalyptus is another source of wood-based biomass. It is the most common fast

^{*} Corresponding author. Tel.: +66 2 470 7535; fax: +66 2 452 3455.

E-mail addresses: paitip@hotmail.com, paitip.thi@kmutt.ac.th (P. Thiravetyan). ¹ Present address: Department of Biology, Faculty of Science, Mahasarakarm University, Mahasarakam 44150, Thailand.

^{1385-8947/\$ –} see front matter $\ensuremath{\mathbb{C}}$ 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.cej.2010.05.051

Table 1

Summary of reports on bagasse fly ash used as an adsorbent for removal of various adsorbates from aqueous solution.

Pretreatment reagent	Adsorbate	$Q_{\rm max}({\rm mgg^{-1}})$	References
Hydrogen peroxide 60 °C, 24 h	DDD [2,2-bis(4- chlorophyenyl)-1,1- dichloroethane] DDE [2,2-bis(4- chlorophenyl)-1,1-	7.69 6.67	[6]
Hydrogen peroxide 60°C. 24 h	dichloroethene] Lindane	2.51	[7]
	Malathion	2.08	
Hydrogen peroxide 60°C, 24 h	Cu(II)	2.26	[8]
	Zn(II)	2.34	
0.1N NaOH followed by 0.1N CH₃COOH	Cr(VI)	-	[9]
	Ni(II)	-	[9]
Hydrogen peroxide 60°C, 24 h	Cd(II)	1.24	[10]
	Ni(II)	1.12	[10]
Hydrogen peroxide 60°C, 24 h	Lead	2.50	[11]
	Chromium	4.35	[11]
Hot water 70°C	Malachite green	170.33	[12]
Hot water 70°C -	Congo red Orange-G Methyl violet	11.89 18.80 26.25	[13] [14]
-	Auramine-O Brilliant green Phenol	31.18 116.28 23.83	[15] [16] [17]
Hot water 70°C -	2-Picoline Cd(II) Ni(II)	59.88 6.19 6.49	[18] [19] [19]

growing species for pulp and wood fuel production. Eucalyptus plantations are found mostly in the northeastern region of Thailand [32]. However, wood wastes and sawdust are biomass used as fuel for power generation. And sawdust fly ash (SDFA) is a waste product left from the process by various industries.

Thus, utilization of BGFA and SDFA for wastewater treatment has the advantages of abundant availability at no or low cost, and the elimination of wastes that could pose serious environmental problems.

From the literature reviews, no other reports were found on water-based ink from printing industry. Therefore, the objective of this research was to evaluate the relative efficiencies of BGFA, SDFA, SDFA washed with tap water (SDFA/W) and AC for removal of color from water-based ink wastewater after coagulation. The mechanisms of synthetic water-based ink adsorption by these adsorbents were also investigated.

2. Materials and methods

2.1. Preparation of the adsorbents

SDFA was studied in its original form (pH ~ 11) and after washing with tap water (SDFA/W) by stirring 50 g of SDFA in 11 of tap water for 1 h, and then changing the wash water until the pH was stable (pH ~ 9.5). BGFA was studied in its original form (pH ~ 9) and after washing with tap water (BGFA/W) until the pH was stable (pH ~ 8.8). The commercial AC of coconut shells used in this work was obtained from Mazuma (Thailand) Co., Ltd. The adsorbents were oven-dried at 105 °C for 2 h, sieved through Nos. 60, 80, 100 and 200 mesh sieves and then stored in a vacuum desiccator.

Table 2

Summary of reports on sawdust used as an adsorbent for removal of heavy metals and dyes from aqueous solution.

Adsorbent	Pretreatment reagent	Adsorbate	$Q_{\rm max} ({\rm mg}{\rm g}^{-1})$	References
Sawdust (cedrus deodar wood)	Sodium hydroxide	Cd(II)	73.62	[20]
Sawdust (S. robusta)	Formaldehyde	Cr(VI)	3.60	[21]
Sawdust (poplar tree)	Sulfuric acid	Cu(II)	13.95	[22]
Sawdust (Dalbergia	Sodium	Ni(II)	9.41	[23]
Sawdust (poplar tree)	Sodium	Cu(II)	6.92	[24]
ucc)	nyuroniuc	Zn(II)	15.80	[24]
Sawdust (fir tree)	-	Cu(II) Zn(II)	12.70 13.40	[24] [24]
Oak sawdust (Ouercus coccifera)	Hydrochloric acid	Cu(II)	3.38	[25]
(Quereus escenjeru)	uciu	Ni(II) Cr(VI)	3.34 1.72	[25] [25]
Maple sawdust	-	Ni(II)	_	[26]
Sawdust (Pinus svlvestris)	Formaldehyde in sulfuric acid	Pb(II)	9.78	[27]
		Cd(II)	9.29	[27]
Walnut sawdust	Formaldehyde in sulfuric acid	Cd(II)	4.51	[28]
		Ni(II) Pb(II)	6.43 4.48	[28] [28]
Sawdust (teak wood)	Reactive Orange 13	Cu(II)	8.07	[29]
noou)	orange is	Ni(II)	9.87	[29]
		Zn(II)	17.09	[29]
	-	Cu(II) Ni(II)	4.94	[29]
		Zn(II)	10.96	[29]
Sawdust	-	Basic dye (crystal violet)	341.00	[30]

The physical and chemical characteristics of the adsorbents were determined using standard procedures. The BET surface area, total pore volume and average pore volume of adsorbents were determined by a surface area analyzer (Quantachrom, Autosorb-1, USA). The adsorbent surfaces were characterized by scanning electron microscopy (SEM; JSM-6400, Japan) and the elemental composition was determined by energy dispersive X-ray spectroscopy (SEM/EDX). Particle size distributions were determined using standard sieve.

For determination of Ca, 0.5% (w/v) adsorbents (<75 μ m) were shaken with deionized water for 24 h at 150 rpm, 30 °C and then centrifuged. The supernatant was analyzed by inductive coupled plasma spectroscopy (ICP).

2.2. Adsorbates

Water-based ink wastewater from the printing industry after coagulation was used as the adsorbate to determine the color removal efficiency by BGFA, SDFA, SDFA/W and AC. The color remaining after adsorption was determined in ADMI units (American Dye Manufacturers Institute; ADMI) by UV–visible spectrophotometry (DR/4000, HACH, USA).

The synthetic water-based ink Barium Lithol Red, which is a monoazo organic pigment was used to study the adsorption isotherm. Its maximum wavelength (λ_{max}) is 560 nm. The physical and chemical properties of a synthetic water-based ink (Barium Lithol Red) are provided in Supplementary Information File A1. Calibration curves were produced by plotting absorbance as a function of various concentrations of synthetic water-based ink solutions.

Table 3
Multipoint BET, total pore volume and average pore diameter of adsorbents.

Adsorbents	Multipoint BET ^a $(m^2 g^{-1})$	$V_{\rm T} ({\rm cm^3g^{-1}})$	$V_{\rm Me}{}^{\rm b}~({\rm cm}^3{\rm g}^{-1})$	$V_{\rm Mi}{}^{\rm b}~({\rm cm}^3~{\rm g}^{-1})$	$V_{\rm Me}/V_{\rm T}{}^{\rm b}$ (%)	$V_{\rm Mi}/V_{\rm T}{}^{\rm b}~(\%)$	Average pore diameter (Å)
BGFA	31.89	0.0358	0.0245	0.0113	68	32	44.86
BGFA/W	100.63	0.0735	0.0377	0.0358	51	49	29.20
SDFA	15.77	0.0138	0.0082	0.0056	59	41	32.42
SDFA/W	80.41	0.0571	0.0285	0.0286	50	50	25.92
AC (coconut shell)	627.29	0.3876	0.1647	0.2229	42	58	22.41

^a Specific surface area.

^b V_T = total pore volume (cm³ g⁻¹); V_{Me} = mesopore volume (cm³ g⁻¹); V_{Mi} = micropore volume (cm³ g⁻¹).

2.3. Adsorption isotherms

Adsorption isotherms were prepared by mixing 10 ml $(20-360 \text{ mg L}^{-1})$ of a synthetic water-based ink solution with 10 mg of adsorbent (<75 μ m) in a 15 mL vial, control of various concentrations of synthetic water-based ink solution (without adsorbent) was also compared in all experiments. The mixtures were shaken overnight at 150 rpm, under various temperatures of 30, 40 and 60 °C, and then centrifuged at 4500 rpm for 15 min. The pH of the supernatant was determined using a pH meter (Mettler Delta 340, England), and the color intensity was measured with a UV-visible spectrophotometer (DR/4000, HACH, USA).

The equilibrium isotherms were analyzed by the Langmuir, Freundlich and Redlich–Peterson isotherm models.

2.4. The efficiency of color removal of BGFA, SDFA, SDFA/W and AC

The experiment of the color removal from synthetic waterbased ink by various adsorbents were prepared by mixing 10 ml of a synthetic water-based ink solution (60 mg L^{-1}) with various dosages (0.0050-5% (w/v)) of adsorbent (<75 µm) in a 15 mL vial. The mixtures were shaken overnight at 150 rpm, 30 °C and then centrifuged at 4500 rpm for 15 min. The pH of the supernatant was determined using a pH meter (Mettler Delta 340, England), and the color intensity was measured with a UV–visible spectrophotometer (DR/4000, HACH, USA) at 560 nm.

The experiment of the color removal from wastewater from printing ink industry after water-based ink coagulation by various adsorbents were prepared by mixing 10 ml of wastewater solution with various dosages (0.01-0.06% (w/v)) of adsorbent (<75 μ m) in a 15 mL vial. The mixtures were shaken overnight at 150 rpm, 30 °C and then centrifuged at 4500 rpm for 15 min. The pH of the supernatant was determined using a pH meter (Mettler Delta 340, England), and the color remaining after adsorption was measured in ADMI units with a UV-visible spectrophotometer (DR/4000, HACH, USA).

3. Results and discussion

3.1. Characterization of adsorbents

The particle sizes distribution of BGFA and SDFA were determined and are shown in Supplementary Information File A2. The major of particle sizes distribution of BGFA is <75 μ m (72%) and 75–150 μ m (17%), respectively. While, the major of particle sizes distribution of SDFA is >250 μ m (41%) and <75 μ m (34%), respectively.

The elemental composition of surface and crystal area of BGFA and SDFA were determined by SEM/EDX, and the result is provided separately in Supplementary Information File A3. The BET surface area, total pore volume and average pore volume of the adsorbents (<75 μ m) are listed in Table 3.

BGFA contains fibrous and non-fibrous components with various shapes and pore sizes. Some particles have slits and others exhibit surface crystals. The major surface elements determined by SEM/EDX analysis of BGFA (<75 μ m) are C, O, Si and Ca, while those in the crystals are O, Si and C.

SDFA contained several different pore sizes distributed over its surface with many crystals both on the surface and within the pores. These crystals might be tar or other components produced in the burning process. Analysis of these crystals by SEM/EDX identified the major elements as K, O, Ca, Fe, S, Cl and P. In SDFA/W, the BET surface area increased after washing with tap water (Table 3).

AC also had several shapes, variable surface porosity, and contained many surface crystals. Its BET surface area was higher than those of SDFA, SDFA/W and BGFA (Table 3).

3.2. Effect of pH on wastewater and synthetic water-based ink solution

The stability of many types of dye, including Lithol Red 49, is affected by pH. The pH of the synthetic water-based ink solution (initial pH \sim 7.0) was adjusted over a pH range of 1–13. Precipitation occurred at pH 1–4, and a yellow shade was observed at higher pH ranges (9–13). But for the water-based ink wastewater after coagulation process, the pH of was 1.7, which subsequently was adjusted over a range of 1–10. The color of the solution changed to yellow in the pH range of 4–10.

3.3. Adsorption equilibrium study

The data for the adsorption of synthetic water-based ink by BGFA, SDFA, SDFA/W and AC ($<75 \,\mu$ m) were analyzed by the Langmuir, Freundlich and Redlich–Peterson isotherm models. The Langmuir model is most often used and has an ideal assumption of an entirely homogeneous adsorption surface. By contrast, the Freundlich model is appropriate for a heterogeneous surface, and the Redlich–Peterson isotherm model is a combination of the Langmuir and Freundlich models.

3.3.1. Langmuir isotherm

The Langmuir relationship [33] can be linearized by plotting $1/q_e$ versus $1/C_e$. The linear form of the Langmuir isotherm is given by Eq. (1):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{bq_m C_e} \tag{1}$$

where q_e is the amount of dye adsorbed at equilibrium (mgg⁻¹), C_e is the concentration of dye at equilibrium (mgL⁻¹), q_m is the maximum adsorption capacity (mgg⁻¹) and b is the Langmuir adsorption constant related to the energy of adsorption (Lmg⁻¹).

3.3.2. Freundlich isotherm

The Freundlich isotherm [34] is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. The linearized Freundlich isotherm is represented by the following equations:

$$\log(q_e) = \log(K_F) + \frac{1}{n_F \log(Ce)}$$
(2)



Fig. 1. Comparison of color removal of a synthetic water-based ink solution by bagasse fly ash (BGFA), sawdust fly ash (SDFA), sawdust fly ash washed with tap water (SDFA/W) and activated carbon (AC).

where K_F is the Freundlich constant related to the capacity (L mg⁻¹), and $1/n_F$ is the heterogeneity factor. The $1/n_F$ value ranges between 0 and 1; the more heterogeneous the surface, the closer the $1/n_F$ value is to 1.

3.3.3. Redlich-Peterson (R-P) isotherm

Redlich and Peterson [35] incorporated three parameters into an empirical isotherm, which has a linear dependence on concentration in the numerator and an exponential function in the denominator. It approaches the Freundlich model at high concentrations and is in accordance with the low concentration limit of the Langmuir equation. Because the R–P equation incorporates three parameters into an empirical isotherm, it can be applied either in homogenous or heterogeneous systems, and can be described as follows:

$$q_e = \frac{ACe}{1 + BC_e^g} \tag{3}$$

where *A* is the R–P isotherm constant (Lg^{-1}) , *B* is the R–P isotherm constant $(L/mg^{1-1/A})$, and *g* is the exponent and lies between 1 and 0. When *g* = 1, it becomes a Langmuir equation (Eq. (4)). When *g* = 0, it becomes Henry's law equation, and as shown in Eq. (5), Eq. (3) can be converted to a linear form by taking logarithms (Eq. (6)).

$$q_e = \frac{ACe}{1 + BC_e} \tag{4}$$

$$q_e = \frac{ACe}{1+B} \tag{5}$$

$$\ln\left[A\frac{C_e}{q_e} - 1\right] = g\ln(C_e) + \ln(B) \tag{6}$$

The linearized form of the R–P isotherm equation contains three unknown parameters A, B and g, and a minimization procedure is adopted to maximize the coefficient of determination r^2 between

Table 4

Linear isotherm parameters for color removal of synthetic water-based ink solution by bagasse fly ash at various temperatures.

Langmuir ^a					
Temp. (°C)	$q_m (mgg)$	-1)	$b (Lmg^{-1})$	R ²	
30	7.30		0.1603	0.9958	
40	12.67		0.3053	0.9986	
50	21.60		0.0783	0.9909	
60	29.07		0.1268	0.9920	
Freundlich ^b					
Temp. (°C)	$K_f (\mathrm{mg}\mathrm{g}^{-1})$	$(Lg^{-1})^n$	1/n	R ²	
30	2.2532		0.2679	0.9238	
40	5.6092		0.1906	0.8857	
50	4.4025		0.3421	0.9762	
60	6.5163		0.3507	0.9168	
Redlich–Peterson ^c					
Temp. (°C)	g	$B\left(L/\mathrm{mg}^{1-1/A}\right)$	$A(Lg^{-1})$	R^2	
30	0.7531	4.0320	10	0.9906	
40	0.8610	1.4189	10	0.9953	
50	0.7123	1.7752	10	0.9927	
60	0.7630	0.9480	10	0.9757	

^a $q_e = q_m bC_e/(1 + bC_e)$.

^b $q_e = q_f C_e^{1/n}$.

^c $q_e = AC_e/(1 + BC_e^g)$.

the theoretical data for q_e predicted from the linearized form of the Redlich–Peterson isotherm equation.

The Langmuir isotherm and its parameters for the removal of synthetic water-based ink by BGFA are shown in Table 4. The adsorption capacity increased with temperature, having maximum values of 7.30, 12.67, 21.60 and 29.07 mg g⁻¹ BGFA at 30, 40, 50 and 60 °C, respectively. These results implied that the mechanism might be involved chemical adsorption. The maximum adsorption capacity of BGFA/W (at 30 °C) was 14.34 mg g⁻¹, which is higher than BGFA (7.30 mg g⁻¹). It is possible that some tar and crystals from BGFA were washed away by the tap water, resulting in an increased surface area of the adsorbents (Table 3).

The adsorption data for synthetic water-based ink on various adsorbents (<75 μ m) were analyzed by the Langmuir, Freundlich and Redlich–Peterson isotherms, and the values of the parameters for these isotherms are shown in Table 5. The maximum adsorption capacities of BGFA, SDFA, SDFA/W and AC at 30 °C were 7.30, 85.47, 30.21 and 40.49 mg g⁻¹ of adsorbent, respectively. The R^2 values for the linear adsorption isotherm indicate that all three models could account for the removal of synthetic water-based ink by BGFA, SDFA/W and AC, but R^2 of SDFA was quite low. This might be due to the mechanism for color removal by SDFA involved both precipitation and adsorption of the ink,

Table 5

Isotherm parameters for the removal of synthetic water-based ink solution by various adsorbents.

Linear method	Isotherm parameters (30 °C)	Adsorbents				
		BGFA	SDFA	SDFA/W	AC	
Langmuir	$Q_{\max} (mgg^{-1})$ $b (Lmg^{-1})$ R^2	7.30 0.1603 0.9958	85.47 0.8125 0.9820	30.21 0.0370 0.9575	40.49 0.3115 0.9932	
Freundlich	$\frac{1/n}{K_f (\operatorname{mg} g^{-1})(L g^{-1})^n} R^2$	0.2679 2.2532 0.9238	0.4837 33.2506 0.8231	0.4891 2.8074 0.9894	0.2986 13.4524 0.9777	
Redlich-Peterson	g B (L/mg ^{1-1/A}) A (Lg ⁻¹) R ²	0.7531 4.0320 10 0.9906	0.7767 1.6658 100 0.7864	0.5143 1.4275 100 0.9903	0.7876 5.5940 100 0.9984	



Fig. 2. Removal of color and system pH from a synthetic water-based ink solution by (a) SDFA, (b) SDFA/W, (c) BGFA and (d) AC.

whereas adsorption is the only mechanism by SDFA/W, BGFA and AC.

3.4. Comparison of adsorption efficiency of bagasse fly ash, sawdust fly ash and activated carbon

A comparison of color removal by various adsorbents (<75 μ m) is shown in Figs. 1 and 2. Adsorption efficiencies increased when increasing dosage of adsorbents. Analysis of variance and means separation using the Duncan multiple range test (DMRT) revealed that removal efficiencies of the synthetic water-based ink by various adsorbents were significantly different at the 95% confidence level (SPSS-MANOVA (multivariate analysis of variance) at $P \le 0.05$). SDFA was the best adsorbent when compared to AC, SDFA/W and BGFA.

The color removal efficiency of BGFA was less than those of SDFA, AC and SDFA/W, presumably as a result of having a smaller BET surface area than the other adsorbents. Therefore, further studies might consider increasing the BET surface area of BGFA to improve its color removal efficiency.

SDFA (<75 μ m) at all concentrations caused color removal from the solution by precipitating the ink, possibly because of the large amounts of Ca cations interacting with the anionic azo group of the pigment. Therefore, color removal from synthetic water-based ink by SDFA involved both precipitation and adsorption. The synthetic water-based ink was not precipitated with SDFA/W, for which adsorption was the sole color removal mechanism. The absence of precipitation with this adsorbent was probably because Ca were removed during the water washing. ICP analysis showed Ca concentrations in solution containing SDFA, BGFA, AC and SDFA/W was 132.67, 11.67, 10.79 and 10.12 mgL⁻¹, respectively. In addition, precipitation of synthetic water-based ink was occurred when adding Ca(OH)₂ (data not shown). This evidence and the ICP result confirmed that Ca²⁺ in SDFA caused the precipitation of synthetic water-based ink.

3.5. Application in wastewater from printing ink industry after water-based ink coagulation

The efficiencies of BGFA, SDFA and AC for color removal from wastewater from printing ink industry after water-based ink coagulation are shown in Fig. 3. SDFA, SDFA/W and BGFA were highly effective adsorbents. Color removal by SDFA (90%) was higher than commercial AC (80%) at the same dosage of 0.3% (w/v). In addition, the pH was increased from 1.7 to around neutral by SDFA.



Fig. 3. Removal of color and system pH from water-based ink wastewater after coagulation by (a) SDFA, (b) SDFA/W, (c) BGFA and (d) AC.

Color removal by SDFA/W at 0.3% (w/v) was 76% and the system pH was 2.86. However, color removal was increased to 91% with 0.5% (w/v) dosage of SDFA/W, and the pH was around neutral. Therefore, SDFA is an effective adsorbent for color and pH treatment of wastewater from the printing ink industry after water-based-ink coagulation.

The efficiency of BGFA for color removal was comparable to other adsorbents and increased with dosage to reach 85% at 0.5% (w/v) BGFA. However, the system pH was still low $(pH \sim 2)$.

The water-based ink wastewater after the coagulation process (initial pH = 1.7) changed to a yellow shade with increasing pH values (pH = 4-10). After adding SDFA and SDFA/W in wastewater, the pH system was around neutral ($pH \sim 7$). But this wastewater turned from red to colorless and did not ever display a yellow color. This result confirmed SDFA is suitable for color removal from water-based ink wastewater.

In addition, waste from adsorbents after the wastewater treatment was still occurred. Nowadays landfill system could be used for this waste management. However, from our study on elution test (data not shown) we found that dyes-adsorbed SDFA and BGFA could not be eluted with water ($30 \circ C$), hot water ($100 \circ C$) and acidic solution. This result confirmed that these adsorbents after disposal in the landfill system might be safe to dispose. Therefore, SDFA and BGFA are alternative adsorbents for color removal from the printing ink industry.

4. Conclusions

SDFA, SDFA/W and BGFA were all effective adsorbents in removing the color from wastewater from the printing ink industry after water-based ink coagulation. The maximum adsorption capacities of BGFA at 30, 40, 50 and 60 °C were 7.30, 12.67, 21.60 and 29.07 mg g⁻¹, respectively. In addition, the maximum adsorption capacity of BGFA increased from 7.30 to 14.34 mg g⁻¹ by waterwashed BGFA. The Langmuir, Freundlich and Redlich–Peterson models were all able to explain color removal of synthetic waterbased ink by BGFA, SDFA/W and AC, whereas R^2 of color adsorption by SDFA of these three models were not high. This might be due to the fact that the mechanism for color removal by SDFA involved both precipitation and adsorption of the ink, whereas adsorption was the only mechanism with SDFA/W, BGFA and AC.

Acknowledgment

The authors thank Dr. Bernard A. Goodman for valuable discussion.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2010.05.051.

References

- P.J. Laden, S. Fingerman, Design and formulation of water based ink systems, in: P. Laden (Ed.), Chemistry and Technology of Water Based Inks, Blackie Academic and Professional, London, 1997, pp. 220–254.
- [2] I.D. Mall, J. Prasad, Pyrolysed bagasse char a low cost effective effluent system for pulp and paper mill, J. Indian Pulp Paper Technol. Assoc. 10(2)(1998) 11–19.
- [3] A.G. Liew Abdullah, M.A. Mohd Salleh, M.K. Siti Mazlina, M.J. Megat Mohd Noor, M.R. Osman, R. Wagiran, S. Sobri, Azo dye removal by adsorption using waste biomass: sugarcane bagasse, Int. J. Eng. Technol. 2 (1) (2005) 8–13.

- [4] S. Kavitha, M. Manimaran, K. Subanadan, Venkatanarasaiah, Removal of colorcongo red from dye waste waters using low cost adsorbents, J. Chem. Environ. 3 (3) (1999) 21–24.
- [5] C.K. Jain, A. Kumar, M.H. Izazy, Color removal from paper mill effluent through adsorption technology, Environ. Monit. Assess. 149 (2009) 343–348.
- [6] V.K. Gupta, I. Ali, Removal of DDD and DDE from wastewater using bagasse fly ash, a sugar industry waste, Water Res. 35 (2001) 33–40.
- [7] V.K Gupta, C.K. Jain, I. Ali, S. Chandra, S. Agarwal, Removal of lindane and malathion from wastewater using bagasse fly ash-a sugar industry waste, Water Res. 36 (2002) 2483–2490.
- [8] V.K. Gupta, I. Ali, Utilization of bagasse fly ash (a sugar industry waste) from the removal of copper and zinc from wastewater, Sep. Purif. Technol. 18 (2000) 131–140.
- [9] M. Rao, A.V. Parwate, A.G. Bhole, Removal of Cr⁶⁺ and Ni²⁺ from aqueous solution using bagasse and fly ash, Waste Manage. 22 (2002) 821–830.
- [10] V.K. Gupta, C.K. Jain, I. Ali, M. Sharma, V.K. Saini, Removal of cadmium and nickel from wastewater using bagasse fly ash – a sugar industry waste, Water Res. 37 (2003) 4038–4044.
- [11] V.K. Gupta, I. Ali, Removal of lead and chromium from wastewater using bagasse fly ash – a sugar industry waste, J. Colloid Interface Sci. 271 (2004) 321–328.
- [12] I.D. Mall, V.C. Srivastava, N.K. Agarwal, I.M. Mishra, Adsorptive removal of malachite green dye from aqueous solution by bagasse fly ash and activated carbon – kinetic study and equilibrium isotherm analyses, Colloids Surf. A 264 (2005) 17–28.
- [13] I.D. Mall, V.C. Srivastava, N.K. Agarwal, I.M. Mishra, Removal of congo red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analyses, Chemosphere 61 (2005) 492–501.
- [14] I.D. Mall, V.C. Srivastava, N.K. Agarwal, Removal of Orange-G and Methyl Violet dyes by adsorption onto bagasse fly ash – kinetics study and equilibrium isotherm analyses, Dyes Pigment 69 (2006) 210–223.
- [15] I.D. Mall, V.C. Srivastava, N.K. Agarwal, Adsorptive removal of Auramine-O: kinetic and equilibrium study, J. Hazard. Mater. 143 (2007) 386–395.
- [16] V.S. Mane, I.D. Mall, V.C. Srivastava, Use of bagasse fly ash as an adsorbent for the removal of brilliant green dye from aqueous solution, Dyes Pigment 73 (2007) 269–278.
- [17] V.C. Srivastava, M.M. Swamyl, I.D. Mall, B. Prasad, I.M. Mishra, Adsorptive removal of phenol by bagasse fly ash and activated carbon: equilibrium, kinetics and thermodynamics, Colloids Surf. A 272 (2006) 89–104.
- [18] D.H. Lataye, I.M. Mishra, I.D. Mall, Adsorption of 2-picoline onto bagasse fly ash from aqueous solution, Chem. Eng. J. 138 (2008) 35–46.
- [19] V.C. Srivastava, I.D. Mall, I.M. Mishra, Equilibrium modeling of single and binary adsorption of cadmium and nickel onto bagasse fly ash, Chem. Eng. J. 117 (2006) 79–91.
- [20] S.Q. Memon, N. Memon, S.W. Shah, M.Y. Khuhawar, M.I. Bhanger, Sawdust a green and economical sorbent for the removal of cadmium(II) ions, J. Hazard. Mater. 139 (2007) 116–121.
- [21] S.S. Baral, S.N. Das, P. Rath, Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust, Biochem. Eng. J. 31 (2006) 216–222.
- [22] F.N. Acar, Z. Eren, Removal of Cu(II) ions by activated poplar sawdust (Samsun Clone) from aqueous solutions, J. Hazard. Mater. 137 (2006) 909–914.
- [23] H. Rehman, M. Shakirullah, I. Ahmad, S. Shah, Hamedullah, Sorption studies of nickel ions onto sawdust of *Dalbergia sissoo*, J. Chin. Chem. Soc. 53 (2006) 1045–1052.
- [24] M. Šćiban, M. Klašnja, B. Škrbić, Modified softwood sawdust as adsorbent of heavy metal ions from water, J. Hazard. Mater. 136 (2006) 266–271.
- [25] M.E. Argun, S. Dursun, C. Ozdemir, M. Karatas, Heavy metal adsorption by modified oak sawdust: thermodynamics and kinetics, J. Hazard. Mater. 141 (2007) 77–85.
- [26] S.S. Shukla, L.J. Yu, K.L. Dorris, A. Shukla, Removal of nickel from aqueous solutions by sawdust, J. Hazard. Mater. 121 (2005) 243–246.
- [27] V.C. Taty-Costodes, H. Fauduet, C. Porte, A. Delacroix, Removal of Cd(II) and Pb(II) ions from aqueous solutions by adsorption onto sawdust of *Pinus* sylvestris, J. Hazard. Mater. 105 (2003) 121–142.
- [28] Y. Bulut, Z. Tez, Removal of heavy metal ions by modified sawdust of walnut, Fresenius Environ. Bullet. (2003) 1499–1504.
- [29] S.R. Shukla, R.S. Pai, Adsorption of Cu(II), Ni(II) and Zn(II) on dye loaded groundnut shells and sawdust, Sep. Purif. Technol. 43 (2005) 1–8.
- [30] S. Chakraborty, S. De, S. DasGupta, J.K. Basu, Adsorption study for the removal of a basic dye: experimental and modeling, Chemosphere 58 (2005) 1079–1086.
- [31] Y. Wakamura, Utilization of bagasse energy in Thailand, Mitiga. Adapt. Strategy Global Change 8 (2003) 253–260.
- [32] The EC-ASEAN COGEN Programme, Evaluation of conditions for electricity production based on biomass: final report for RAMBOLL, Bangkok, Thailand, 1998.
- [33] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.
- [34] H.M.F. Freundlich, Over the Adsorption in solution, J. Phys. Chem. 57 (1906) 385–470.
- [35] O. Redlich, D.L. Peterson, A useful adsorption isotherm, J. Phys. Chem. 63 (1959) 1024–1026.