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6**Potential utilization of Jatropha curcas L. press-cake residue as new precursor for activated carbon preparation: Application in methylene blue removal from aqueous solution**

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37**ARTICLE INFO Article history: Received** 13 **October 2010 Received in revised form 23 February 2011 Accepted** 14 March **2011 Available online** 8 **May 2011 Keywords:**

Active carbon Adsorption Mechanism Methylene blue Residue ABSTRACT Low cost activated carbon was prepared from the press-cake residue of Jatropha curcas L. The effectiveness of this activated carbon and its modified forms (chemical and thermal activation) was evaluated for methylene blue (MB) dye removal from aqueous solution.

28**Adsorption experiments were conducted in batch system at various** pH and **temperatures.** The widely used **isotherm models, Langmuir** and **Freundlich, were** employed **to represent equilibrium data.**

Kinetic data were analyzed using pseudo- first order and pseudo-second order model. Thermodynamic properties (DG0, DH0 and DS0) of the adsorption of methylene blue onto Jatropha carbons were also obtained. The

26**thermal activated carbon** (JAC-3) **was more effective for** MB **dye removal compared to chemical** (JAC-2) **and parent** (JAC-1) activated **carbon.**

4**ß 2011 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved. 1. Introduction**

The textile and dye manufacturing industries play a significant role in the economy growth of Indonesia. Wastewater from these industries contain considerable amount of unused dyes, which are not readily biodegradable in natural environment. The direct discharge of colored wastewater from these kinds of industries into the aquatic streams harm the environment due to its toxicity and ability to impede the transmission of sunlight, retards photosyn- thesis activity by plant and phytoplankton, and inhibits the growth of biota and harm the stability of food web (Gad and El-Sayed, 2009). Additionally, most of synthetic dyes are very harmful to human life due to their acute and chronic effects. It is obvious that dyes are hazardous material hence their removal from industrial effluent is considered as an important step in the environmental protection. A number of treatment methods are available for dyes removal such as coagulation, oxidation, biodegradation, photolysis, filtra- tion and adsorption (Fernandez et al., 2010).

9**Among them, adsorption is generally considered** as **an effective method for** reducing **the concentration of dissolved dyes in**

industrial wastewater. Since adsorption process is widely known as promising technique, which produces treated dye effluents with * Corresponding author. Tel.: +62 313891164; fax: +62 313891167. E-mail addresses: suryadiismadji@yahoo.com, suryadi@mail.wima.ac.id (S. Ismadji). very low concentration, therefore in the past few years, the hundreds of studies have been conducted to develop different kind of cost effective/low cost adsorbents (Bhatnagar and Sillanpaa, 2010).

9**In this regard, activated** carbons have **been** developed **extensively for the removal of**

9**different classes of dyes** such as **acid, direct, basic, reactive, disperse,**

sulphur and metallic. Activated carbon is a versatile adsorbent from an industrial view of point due to its high adsorptive properties. It has complex nature and various surface properties with pore sizes ranging from micropores (<20 Å slit width) to macropores (>500 Å slit width). However, the large scale use of activated carbon in industrial wastewater treatment still limited due to its high cost. A method to overcome this limitation is by using agricultural or forestry wastes as precursor for activated carbon preparation, such as bagasse pith (Gad and El-Sayed, 2009), cashew nut shell (Kumar et al., 2011), rice straw (Fierro et al., 2010), cherry stones (Jaramillo et al., 2010), oak cups pulp (Timur et al., 2010), flower (Nethaji et al., 2010) and also various biodiesel solid residues

19**(Foo and Hameed, 2009;** Karagoz **et al., 2008;** Nunes et al., **2009).**

Jatropha curcas L. press-cake residue is one of promising biomass wastes that can be utilized as precursor for active carbon preparation. Their seeds contain high enough oil and have been widely used for biodiesel production in several Asia countries. However, the solid residues that produced after seed-pressing process just ended as mere waste. In Indonesia, approximately 2,105,400 tons of J. curcas L. seeds were produced in 2009 and 70% of it end up as solid residue. Accumulation of these wastes for long period of time often create environmental problem due to its

4**1876-1070/$ – see front matter ß 2011 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved. doi:10.1016/j.jtice.2011.**

03.001 unpleasant odor. Since the fixed carbon content in Jatropha press- cake residue is quite high, hence the utilization of this waste as activated carbon precursor can minimize the environmental problem.

42**To the best of our knowledge,** to the present, **there is no** information about **the** preparation and modification **of** activated **carbon from**

J. curcas L. press-cake residue available in the literature. The main objective of this present study is to develop low cost activated carbon from Jatropha waste and to investigate its adsorption performance for basic dye (methylene blue) removal from aqueous solution. 2. Materials and methods 2.1. Activated carbon preparation J. curcas L. press-cake residue was used as activated carbon precursor

12**in this study. Prior to** used, **the** biomass was **washed several times with** tap **water to remove**

physical impurities then dried in oven for overnight at 120 8C. Subsequently, the dry biomass was crushed into powder using microhammer mill and sieved to particle size fraction of 38–106 mm. The preparation of activated carbon was conducted by following procedure: 500 g of pretreated biomass were soaked in KOH solution for 24 h with impregnation ratio of 2:1. The choice of impregnation ratio 2:1 based on our preliminary experiments; at this impregnation ratio the pore structure of activated carbon was more developed than other impregnation ratio. The soaked biomass was then subjected to a two-step heating process at 120 8C for 2 h in an oven and then at 500 8C for 4 h in a horizontal tubular furnace at a constant heating rate of 10 8C/min under N2 stream at flow rate of 150 cm3/min (STP). After carbonization process, the char that produced was cooled to room temperature under the same gaseous flow then rinsed with 0.5 N HCl and hot

48**distilled water until no** significant **change in pH detected. The**

char (JAC-1) was then

7**dried in an oven at** 120 **8C for 24 h and** kept **in dessicator for** further **use.**

The ultimate and proximate analysis of J. curcas L. press-cake residue and JAC-1 was given in Table 1. 2.2. Chemical and thermal activation of JAC-1 Chemical activation of JAC-1 was conducted by following procedure (Huang et al., 2009): 50 g of JAC-1 was added into 500 mL round bottle flask containing 200 mL of concentrated nitric acid. The mixture was then heated at 80 8C for 7 h under continuous stirring at 100 rpm. Subsequently,

8**the oxidized carbon was** rinsed **with** deionized **water until no** significant **change in pH detected.** Finally, **the** activated carbon **sample was**

11**dried in an oven at** 120 8C **for 24 h and kept in**

dessicator. Thermal activation of JAC-1 was carried out in a horizontal tubular furnace (Thermolyne 21100) with the procedure as follows: 20 g of JAC-1 were placed in a stainless steel tubular Table 1 Proximate and ultimate analysis of Jatropha press-cake residue and JAC-1. Press-cake residue JAC-1 Ultimate analysis (wt%) Carbon Hydrogen Nitrogen Oxygen (*measured by difference) Proximate analysis (wt%) Volatile matter Fixed carbon Ash Moisture 47.8 92.3 6.7 1.2 4.3 0.1 41.2 6.4 50.9 2.3 39.2 86.6 2.6 11.1 7.3 – reactor and heated from room temperature to 750 8C

17**at a** constant **heating rate of 10** 8C **/min under N2** flow. **Once the** carbonization **temperature was reached, the** N2 **flow was switched to**

air (150 cm3/min) and maintained for 30 min.

17**The activated carbon** sample **was then cooled to room temperature under** N2 **flow**

and stored in dessicator. Here, chemical activation carbon and thermal activation carbon are referred as JAC-2 and JAC-3, respectively. 2.3. Characterizations of active carbons

45**The pore structure of** JAC **was analyzed by nitrogen** sorption at 77 K using an automatic Micromeritics ASAP-2010 volumetric sorption analyzer.

15**Prior to** the **gas adsorption measurements, the carbon** samples were **degassed at** 573 K **in a vacuum condition for a period of at least** 24 h. **Nitrogen** sorption isotherms were **measured over a relative pressure (P/P0) range from approximately 10**

to 5 0.995. The surface oxides of JAC were characterized by Boehm titration (Boehm, 2002). The Boehm titration is described as follow: 0.5 g of carbon sample

16**was added to** a **series of** conical **flasks containing 50** cm3 **of 0.**

05 M: NaOH, Na2CO3, NaHCO3 and HCl solutions. The conical flasks were then sealed and shaken for 24 h at room temperature. The solid suspension was decanted and 10 cm3 of the remaining solution was titrated with 0.05 M HCl or NaOH, depends on the original solution used. The

14**number of acidic** groups was **calculated** under **the assumptions that NaOH neutralizes** carbox- ylic, **phenolic and lactonic groups; Na2CO3 neutralizes carboxylic and lactonic groups; and NaHCO3 neutralizes only carboxylic groups. The number of basic sites** presented on **the**

carbon surface was determined from the amount of HCl reacted with sample. The pHpzc of JAC was analyzed using pH-drift technique (Faria et al., 2004). The pH-drift procedure is described as follows: 50 cm3 of

5**0.01** N **NaCl solution was placed in** several conical **flasks. The pH was adjusted to** value **between 2 and** 11 **by adding 0.1 M HCl or 0.1 M NaOH solutions.** After that, **0.15 g** of carbon was **added** to **the** solution and the **final pH was measured after 48 h**

(using digital pH meter Schott CG-825)

13**under agitation at room temperature. The**

surface functional groups of JAC were also characterized using infrared spectroscopy (FTIR SHIMADZU 8400S). This qualitative analysis was performed using KBr pelleting technique and all of the carbon spectra were recorded in mid-IR wave number range (500–4000 cm 1). 2.4. Adsorption experiments Methylene blue

34**(Basic Blue 9; C.I. 52015; chemical formula** C16H18N3SCl **.3H2O; MW: 373.90 g mol 1) was used as adsorbate in this study.** It was purchased **from**

Sigma–Aldrich as analytical reagent grade and directly used without any further treatment. The maximum wavelength of this dye is 664.1 nm. The dye stock

36**solution was prepared by dissolving a** fixed **amount of** methylene blue into **1 L** of deionized **water.**

46**To prevent** the **decolorization by direct sunlight, the** dye **stock** solution was **stored in dark bottle and kept in dark place before used.**

Adsorption equilibrium and kinetic studies were carried out in batch system. Adsorption equilibrium data were obtained by adding various mass of carbon (0.1–1.1 g) into a series of

27**250 mL conical flasks, containing 100 mL of** dye **solution with initial concentration of** 1000 **mg/L.**

The conical flasks were then covered with aluminum foil, placed in thermostat shaker (MEMMERT) and shaken with constant speed at desired operating temperature until equilibrium state was achieved. Product analysis showed that the equilibrium state was achieved within 6–10 h. After equilibrium time reached, the dye solution was centrifuged at 4000 rpm for 5 min (MLW T.51.1) to remove solid particles. The supernatant was then carefully taken and measured its residual dye concentration by

33**UV/vis spectrophotometer (SHIMADZU UV/VIS-1700**

PharmaS- pec). The pH of dye solution was also measured at the start and at the end of each experiment using digital pH-meter (Schott CG-825) to check for any drift. The results indicated that no significant change in pH was detected in all experiments. Isotherm experi- ments were conducted at various pH (3, 7 and 11) and temperatures (30 8C, 45 8C and 60 8C). To adjust the pH, an appropriate amount of

27**0.1 M NaOH or 0.1 M HCl solutions** were added to **the** system. **Adsorption**

kinetic experiments were performed in glass vessel of 11 cm in inner diameter, 15 cm in height and fitted with four glass baffles (1 cm in width). The

36**dye solution was prepared by** mixing **a known amount of** MB **dye**

with deionized water to yield various initial concentrations of 200, 500 and 800 mg/L. Prior to the addition of carbon (0.6 g), the glass vessel containing 500 mL of dye solution was placed in the thermostat water-bath at 30 8C. The mixture was then agitated at 500 rpm for 7 h. During the experiments, at predetermined interval of time, the dye solution was taken from the vessel (1 mL using micropipette), diluted with deionized water, centrifuged and analyzed its residual dye concentration spectrophotometrically. All of adsorption experi- ments in this study were conducted in triplicate and the experimental results were given as averages. The following equation was used to calculate the amount of MB dye adsorbed at equilibrium and at a certain time t: qe ¼ C0 Ce m qt ¼ C0 Ct m V (1) V (2) where qe and qt is the amount of dye adsorbed at equilibrium and at a certain time t (mg/g),

29**C0 and Ce are the initial and equilibrium** dye **concentration** in **liquid phase (mg/L),** respectively, m **is the** amount **of** adsorbent **used** (g) **and** V **is the** volume **of** dye solution (L). **3. Results and discussion 3.1.**

Textural characterizations of active carbons The physical characteristics of the adsorbent are related to the pore structure of adsorbent such as micropore surface area (Smicro), mesopore surface area (Smeso), micropore volume (Vmicro), and specific surface area (SBET). The pore structure of JAC was analyzed by nitrogen sorption technique. The specific BET surface area (SBET), micropore volume (Vmicro) and micropore surface area (Smicro) was

12**determined by application of the Brunauer–Emmett–Teller (BET) and Dubinin–Asthakov (DA) analysis software available** within **the instrument, respectively. The**

specific

13**BET surface area** of JAC **was determined by means of the standard BET equation applied in the relative pressure range from 0.06 to 0.3** while for **the** micropore **volume**

42**(Vmicro) and micropore surface area (Smicro) were**

deter- mined by application of the t-plot method on the adsorption isotherm. The values of physical characteristic of JAC carbons are given in Table 2.

8The pore size distribution of JAC was determined from adsorption isotherm data using

the Density Functional Table 2 Physical properties of JAC. Active carbon Surface characteristic

45SBET (m2/g) Smicro (m2/g) Smeso (m2 /g) Vmicro (cm3/g) JAC -1

845.55 JAC-2 792.23 JAC-3 904.72 761.81 83.74 714.32 77.91 817.19 87.53 Fig. 1. Nitrogen sorption isotherms of JAC. Theory (DFT) software with medium regularization. Nitrogen sorption results (Fig. 1) show the largely microporous nature of the carbons, with some mesopores leading to gradual increase in the adsorption after the initial filling of the micropores, followed by rapid increase near saturation. This statement was also supported by DFT results (Fig. 2), which showed that all JAC exhibited several peaks at pore width ranging from 5 to 30 Å. Chemical treatment on activated carbon using various oxidizing agents such as HNO3, H2O2, Fe(NO3)3, (NH4)2S2O8, etc. can increase the

7amount of acidic surface groups, mainly carboxylic acid and also anhydrides, lactone and phenol groups

in less extent. Among them, chemical treatment by HNO3 is generally considered as the most effective method to increase the acidic groups on carbon surface (Faria et al., 2004). The acidic groups, specifically carboxylic acids are known to be the binding sites for basic dyes such as methylene blue hence the presence of this group can improve the adsorption capacity of activated carbon. It was also known that chemical (wet) oxidation can reduce the surface area of carbon (JAC-2) due to the presence of numerous oxygenated groups that partially blocked the access of N2 molecules to the small pores. Moreover, oxidation of carbon by HNO3 also caused nitration attack by nitronium ions (NO2+) on the polyaromatic sheets. The nitronium ion is a strong electrophile (Lewis acid), which can substitute hydrogen atom in aromatic ring based on electrophilic aromatic substitution mechanism (Draper and Ridd, 1978). 1.0 JAC-2 Pore size distribution, cm3/g.nm JAC-1 0.8 JAC-3 0.6 0.4 0.2 0.0 0.396 0.3 0.5 0.7 1 3 5 7 10 30 0.374

8Pore width, nm 0.427 Fig. 2. Pore size distribution of

JAC. In thermal treatment, most of the oxygenated groups on carbon surface (carboxylic acid, lactone and phenol) were decomposed to CO2 and CO at high temperature carbonization,

25resulting in the extension of carbon surface area and the generation of large amounts of reactive sites on the carbon basal planes which have electron rich oxygen free-radical character

(Leon et al., 1992). These reactive sites reacted with oxygen contained in the air thus producing new surface oxides,

31which can be assigned to carbonyl, pyrone or chromene type structures. These surface groups have basic surface properties, corresponding to the basic nature of

JAC- 3. By comparing nitrogen sorption and pore size distribution results of all JAC that have similar characteristic, it is obvious that both chemical and thermal treatment gave insignificant effect on the textural properties hence the adsorption capacity of JAC for MB dye removal will also depend on their surface chemistry properties. 3.2. Surface chemistry characterization of active carbons The surface functional groups of JAC were analyzed by FTIR spectroscopy. The analysis results showed that several major peaks on JAC-1 was appeared at the following wave numbers: 805 cm 1 attributed to O–H stretch in out-of-plane bending; 1176 cm 1 related to the C 5O stretch in lactone; 1589 cm 1 associated to C 5C stretch in aromatic skeletal; 1729 cm 1 attributed to C 5O stretch in carboxylic acid; 2945 cm 1 ascribed to the presence of symmetric C–H stretch in methylene (–CH2) groups; 3021 cm 1 revealed to C–H stretch

26in aromatic ring and the last peak at 3440 cm 1 contributed to the presence of O–H stretch in phenolic groups. The intensity of some peaks in JAC-2 spectra that are characteristic of C 5O functional groups at wave number of 1730 cm 1 (carboxylic acid), 1177 cm 1 (lactone) and 3400 cm 1 (phenol) increased during chemical oxidation by HNO3. New peak was also observed at wave number of 1600 cm 1, which assigned to the nitro groups as the result of nitration attack by NO2+ ions on the aromatic ring groups in carbon skeletal. The FTIR spectra of JAC-3 reflected similar characteristic with JAC-1, denoting that JAC-3 carbon had essentially the same species of surface groups except for the new peak assignment that appeared at wave number of 1582 cm 1. This peak may assign to carbonyl or quinone groups, which have basic surface nature (Lewis basicity). Furthermore, the decrease in intensity of several peaks that attributed to carboxylic acid, phenol and lactone was also noticed due to the decomposition of these oxygenated groups during carbonization process at 750 8C. The surface oxides of JAC carbons obtained by Boehm titration are summarized in Table 3. 3.3. Chemisorption mechanisms of MB dye onto JAC In order to investigate the dominant mechanism that may occur in the adsorption of methylene blue, some information relating to adsorbent nature and pH must be imparted. It is known that pH is one of key parameter in the adsorption study as it affects the chemistry of the solution, the ionic species of adsorbate as well as the surface charge density of adsorbent. In this study, the chemisorption mechanisms of MB dye onto JAC were proposed using molecular modeling by ChemDraw software package (Fig. 3). At pH 3 (pH < pHpzc), the surface all of JAC were influenced mainly by positive charge due to the excessive protonation on the carbon basal planes through electrostatic interaction with the p- electrons of the graphene layers (Montes-Moran et al., 2004). As the carbon surface exhibited positive charge, the MB dye existed in triple protonated form (Khalid, 2001). Under this condition, the dye uptake was limited by repulsion forces which occurred between MB dye cations and positively charged of carbon surface. Electrostatic interaction also existed between MB dye cations and carboxylate anions (COO) on the JAC surface, however, this interaction much weaker compared to the repulsion forces resulting low dye uptake in this pH value. The carboxylic groups on JAC surface were in the order of JAC- 2 > JAC-1 > JAC-3, in which the MB dye uptake must follows this order. It is also known that carboxylic groups can dissociate in water when the pH of the system lies between 2 and 6, resulting in the formation of carboxylate anions. The carboxylate anions are known to be the active binding sites for basic dyes such as methylene blue hence the presence of this group enhanced the dye uptake. However, the inconsistency in the experimental results was observed (JAC-3 > JAC-2 > JAC-1), an indication that another interaction may also took place during dye adsorption process. The high dye uptake by JAC-3 (basic nature carbon) due to the

7**existence of two parallel mechanisms: electrostatic and dispersive interactions. The**

latter interaction was occurred

47**between the delocalized** p **-electrons on the carbon basal planes and the free electrons** of **dye molecules** present **in the aromatic rings**

or multiple bonds (–N 5C–C 5C–). This interaction played a dominant role in the adsorption process of methylene blue on JAC-3. The pore characteristic of JAC-3 also contributes a significant role in the dye removal due to the enlargement in the micropores and mesopores structures

48**as a result of the** decomposition **of** surface oxygenated **groups** during **heat treatment.**

Low dye uptake by JAC-2 (acid nature carbon) suggests that other interaction such as water bonding and electrostatic repulsion may also play an important role in the adsorption process. It was reported that water molecules can bind into acidic surface oxides, especially carboxylic groups through H-bonding (Coughlin and Ezra, 1968) hence the presence of this group could reduce the amount of dye uptake due to the blockade on the micropores region by water. Chemical oxidation on carbon using HNO3 also gave a negative effect on the dye uptake due to the insertion of nitrogen functionalities (NO2) which provides more positive surface sites. The presence of abundant positive surface sites increased the repulsion forces therefore less molecules dye adsorbed in the surface of carbon. Higher dye by JAC-2 compared to JAC-1 (parent carbon) may correspond to the stronger effect of electrostatic interaction of carboxylate anions and MB molecules. As mentioned before, the JAC-2 possesses more carboxylics groups than JAC-1, therefore more carboxylate anions are available on the JAC-2 surface. In addition, low dye uptake at pH 3 was also caused by the competition between protons (H+) and MB dye cations in bulk solution onto the active binding sites on carbon surface. In neutral pH, the JAC-2 surface is predominated by negative charge (pH > pHpzc) while for JAC-1 and JAC-3, the overall charge Table 3 Surface chemistry of JAC. Active carbon pHpzc Carboxylic Lactone Phenol Acidity Basicity All groups (mequiv./g) (mequiv./g) (mequiv./g) (mequiv./g) (mequiv./g) (mequiv./g) JAC-1 8.2 JAC-2 3.7 JAC-3 10.1 0.143 0.095 0.372 0.157 0.061 0.012 0.109 0.347 0.264 0.793 0.043 0.116 0.521 0.214 0.817 0.868 1.007 0.933 Fig. 3. Chemisorption mechanism of MB dye onto JAC at pH 3 (I) and pH 11 (II). on their surface is positive (pHpzc > pH). As given in Fig. 4, the dye uptake at pH 7 are in the order of JAC-3 > JAC-2 > JAC-1, indicates the mechanisms involved in the adsorption of dye in pH 7 are similar with pH 3. The dye uptake at pH 7 was higher than pH 3. At pH 7, the presence of protons (H+) in the solution was much less than at pH 3, therefore less competition between protons (H+) and MB dye cations in bulk solution onto the active binding sites on carbon surface occurred. In basic solution (pH 11), the surface of all JAC were predominated by negative surface sites due to pH > pHpzc and the dissociation of phenol

30**groups on carbon surface** occurred, **leading to the** formation **of**

phenolate anions, while MB dye existed in single protonated form. In this case, the MB dye uptake onto JAC caused

41**by the electrostatic** interaction **between negatively charged** on the carbon **surface and**

dye cations. Another interaction, the p– p dispersion, may also take place during adsorption of dye. This interaction was generated between the p-electrons on

31**carbon basal planes and the** p-electrons on **aromatic rings** of dye **molecules.** Furthermore, **the**

excessive presence of hydroxyl groups (OH) in bulk solution also gives a positive effect on the p–p dispersion interaction, which increased the p

30**-electron density on carbon basal planes,** hence enhanced **the** adsorption **of**

MB dye. Highest dye uptake at pH 11 compared with other systems (pH 3 and pH 7) due to the existence of two parallel mechanisms, the p–p dispersion and electrostatic interaction. 3.4. Adsorption isotherms Equilibrium relationship between adsorbate and adsorbent can be determined by adsorption isotherm study, which describes

44**how the** adsorbate **molecules distribute between the liquid phase and the solid phase when the adsorption reaches equilibrium.** Various **adsorption isotherm**

models for the gas phase adsorption such as Langmuir, Freundlich, Toth, Sips, etc., can in principle be extended to liquid phase adsorption. Among these isotherms, the Langmuir and the Freundlich isotherm are the most widely used models to represent the liquid phase adsorption experimental data (Ai et al., 2010; Demirbas et al., 2009; Liu et al., 2011). The Langmuir isotherm is expressed as follows: qe ¼ qmax 1 þKLKCLeCe (3) where qmax and KL are the Langmuir parameters corresponded to the maximum adsorption capacity for specific adsorbent (mg/g) and the equilibrium constant (L/mg), respectively. The essential characteristic of the Langmuir isotherm can be expressed by qe (mg/g) (I) 500 400 300 200 100 0 0 pH 3 100 200 300 400 Ce (mg/L) JAC-1 JAC-2 JAC-3 Langmuir fit Freundlich fit 500 600 qe (mg/g) 700 600 500 300 400 200 100 0 0 pH 7 100 200 300 400 500 600 Ce (mg/L) JAC-1 JAC-2 JAC-3 Langmuir fit Freundlich fit qe (mg/g) 800 700 600 500 400 300 200 100 0 0 pH 11 100 JAC-1 JAC-2 JAC-3 Langmuir fit Freundlich fit 200 300 400 500 600 Ce (mg/L) (II) 500 750 900 400 600 750 600

35**qe (mg/g)** 300 **qe (mg/g)** 450 **qe (mg/g)** 200 100 JAC **-1**

JAC-2 JAC-3 Langmuir fit 300 150

18**JAC-1 JAC-2 JAC-3**

Langmuir fit 450 300 150

18**JAC-1 JAC-2 JAC-3**

pH 3 Freundlich fit pH 7 Freundlich fit pH 11 Langmuir fit Freundlich fit 0 0 0 0 50 100 150 200 250 300 350 400 450 Ce

40**(mg/L) 0 50 100 150 200 250 300 350** 400 450 Ce **(mg/L) 0 50 100 150 200 250 300 350**

400 450 Ce (mg/L) (III) 600 qe (mg/g) 200 300 100 150 0 500 400 300 0 0 50 100 150 200 250 300 350 0 50 100 150 200 250 300 Ce (mg/L) Ce (mg/L) JAC-1 JAC-2 JAC-3 Langmuir fit pH 3 Freundlich fit qe (mg/g) 800 200 100 0 700 600 500 400 300 JAC-1 JAC-2 JAC-3 Langmuir fit pH 7 Freundlich fit qe (mg/g) 900 750 600 450 0 JAC-1 JAC-2 JAC-3 Langmuir fit pH 11 Freundlich fit 50 100 150 200 250 300 Ce (mg/L) Fig. 4. Isotherm plots of MB dye uptake onto JAC at 30 8C (I), 45 8C (II) and 60 8C (III). dimensionless constant called equilibrium parameter, RL, which defined by following equation: RL ¼ 1 þ KLC0 1 (4)

32**The value of RL** indicates **the** various nature **of isotherm to be irreversible (RL = 0), favorable (0 < RL < 1), linear (RL = 1) or unfavorable (RL > 1).** Another empirical **isotherm** model **that**

widely used to represent equilibrium data is Freundlich model, which has the form: qe ¼ KF Ce1=n (5) where

23**KF and n are the Freundlich** parameters represented the **adsorption** affinity **[(mg/g) (L/mg)1/n] and**

the heterogeneity of the system, respectively. The isotherm plots of Langmuir and Freundlich models at various pH and temperatures are given in Fig. 4. As shown in this figure, Langmuir model could represent

23**the experimental data** better **(R2 > 0.99) than** Freundlich equation. **The** parameters of **Table** 4 **Isotherm** model **parameters for** MB dye **adsorption onto**

JAC. Active Isotherm Parameter pH T (K) pH T (K) pH T (K) carbon model 303.15 318.15 333.15 303.15 318.15 333.15 303.15 318.15 333.15 JAC-1 JAC-2 JAC-3 Langmuir Freundlich Langmuir Freundlich Langmuir Freundlich

22**KL (L/mg)** qmax **(mg/g)** RL R2 **KF [(mg/g) (mg/L) 1/n] n**

22**R2 KL (L/mg)** qmax **(mg/g)** RL R2 **KF [(mg/g) (mg/L) 1/n] n** R2 KL **(L/mg)**

qmax (mg/g) RL R2 KF [(mg/g) (mg/L) 1/n] n R2 3 1.8854 177.92 0.0078 0.9987 111.42 0.0798 0.9731 2.2149 317.63 0.0047 0.9995 217.09 0.0643 0.9884 2.8564 419.75 0.0023 0.9987 321.75 0.0640 0.9895 2.8219 3.7501 206.73 230.51 0.0059 0.0044 0.9984 0.9982 128.89 144.37 0.1567 0.3312 0.9735 0.9850 3.2861 4.6307 379.52 424.42 0.0033 0.0027 0.9996 0.9994 260.24 293.24 0.1458 0.3126 0.9880 0.9895 4.5264 6.2962 453.26 510.32 0.0016 0.0015 0.9985 0.9977 355.83 388.49 0.1371 0.3014 0.9905 0.9914 7 2.6365 292.05 0.0070 0.9980 182.70 0.0688 0.9717 2.8537 366.76 0.0048 0.9965 234.71 0.0570 0.9824 3.6321 624.55 0.0028 0.9998 475.24 0.0561 0.9926 4.1524 5.1971 306.63 357.59 0.0052 0.0039 0.9982 0.9978 195.11 219.72 0.1241 0.3154 0.9722 0.9761 4.0663 5.9347 467.19 546.93 0.0032 0.0029 0.9968 0.9991 307.60 364.44 0.1135 0.3083 0.9828 0.9822 5.7313 7.7755 685.49 706.88 0.0016 0.0012 0.9995 0.9998 535.16 566.66 0.1062 0.3004 0.9926 0.9936 11 3.5549 327.56 0.0063 0.9982 201.11 0.0835 0.9799 3.6859 469.36 0.0054 0.9994 302.36 0.0646 0.9793 5.1553 730.34 0.0030 0.9997 531.55 0.0563 0.9895 5.1832 359.11 0.0046 0.9989 221.94 0.1552 0.9749 5.5241 515.45 0.0039 0.9996 340.03 0.1462 0.9794 7.1871 785.33 0.0021 0.9990 589.73 0.1396 0.9902 7.2228 393.06 0.0028 0.9963 257.55 0.3461 0.9918 7.5831 590.65 0.0025 0.9994 406.39 0.3282 0.9814 9.6732 827.34 0.0012 0.9999 657.94 0.3218 0.9924 each model were obtained by non-linear regression method (Table 4). Based on the value of RL (0 < RL < 1), all systems show favorable adsorption process. The value of parameters KL and qmax in Langmuir model increased as the temperature increased. Similar trend was also observed

28**in Freundlich model. The** increase **of** these parameters **with** the **increase of**

temperature indicated that the adsorption process of MB in JAC carbons was an endothermic process. Table 5 shows the comparison of the maximum adsorption capacity of various low cost and commercial active carbons for MB dye removal. The adsorption capacity of JAC-3 is higher than other adsorbents, indicates that JAC-3 is suitable as the adsorbent for dye removal from wastewater. 3.5. Adsorption kinetics In the design of the adsorption system, the data obtained from the adsorption kinetic study are very important since it contain the information about the adsorption mechanism, the potential rate controlling steps, etc. This information

10**is required to select the optimum condition for full scale batch metal removal processes. Several adsorption kinetic models have been** developed **to understand the adsorption kinetics and rate limiting step.** The **pseudo-first and second order**

51**kinetic models are well known models to correlate the adsorption dynamic or kinetic data for various systems. The**

pseudo-first order, which also known as Lagergren kinetic model (Lagergren, 1898) has the form: ddqtt ¼ k1ðqe q t Þ (6) Integrating Eq. (6) with the boundary conditions t = 0 ! t = t and qt = 0 ! qt = qt gives: qt ¼ qeð1 expð k1tÞÞ (7) While the pseudo-second order model (Ho and McKay, 1999) can be expressed as: ddqtt ¼ k2ðqe qt Þ2 (8) Integrating Eq. (8) with the boundary condition: t = 0 ! t = t and qt = 0 ! qt = qt gives qt ¼ qe 1 þqeqke2kt2t (9) where k1 and k2 are the pseudo-first order (min 1) and pseudo- second order (g mg 1 min 1) rate constants, respectively. Table 5 Maximum adsorption capacity (qmax) of several adsorbents for MB dye removal. qmax (mg/g) Reference Commercial active carbon Filtrasorb 300 Filtrasorb 400 Norit Picacarb Biomass based – active carbon Vetiver roots Oak cups pulp Corncob hull Bamboo Olive seed waste residue Defective coffee press-cake residue Sunflower oil cake JAC-1 JAC-2 JAC-3 240 476 276 246 375–423 384.6–454.5 684.24 195.8–618.5 190–263 14.9 16.4 177.9–393.0 317.6–590.6 419.7–827.3 Stavropoulos and Zabaniotou (2005) El Qada et al. (2008) Raposo et al. (2009) Raposo

19**et al. (2009)** Altenor **et al. (2009)** Timur **et al. (2010)** Wu **et al. (2011)** Liu **et al.** (2011) Stavropoulos **and** Zabaniotou **(2005)** Nunes **et al.** (2009) Karagoz **et al. (2008)**

This study This study This study qt (mg/g) 140 120 100 80 60 40 20 C = 200 mg/L 0 C = 500 mg/L 0 C = 800 mg/L 0

50**Pseudo-first order** fit **Pseudo-second order** fit 300 250 **qt (mg/g)**

200

3**150 100 50 C0** = 200 **mg/L C0** = 500 **mg/L C0** = 800 **mg/L**

20**Pseudo-first order** fit **Pseudo-second order**

fit 350 300

3**qt (mg/g) 250 200 150 100 50 C0** = 200 **mg/L C0** = 500 **mg/L C0** = 800 **mg/L**

20**Pseudo-first order** fit **Pseudo-second order**

fit (I) 180 160 JAC-1 350 JAC-2 450 400 JAC-3 0 0 0 50 100 150 200 250 300 350 400 450 t (min) 0 0 50 100 150 200 250 300 350 400 450 0 t (min) 50 100 150 200 250 300 350 400 450 t (min) (II) 350 300 400 JAC-1 350 700 JAC-2 600 JAC-3 qt (mg/g) 250 200 150 100 50 0 0 300

3**qt (mg/g) 250 200 150 C0** = 200 **mg/L C0** = 500 **mg/L** 100 **C0** = 800 **mg/L**

Pseudo-first order fit Pseudo-second order fit 50 0 50 100 150 200 250 300 350 400 450 t (min) 0 50 100 150 200 250 300 350 400 450 t (min)

20**C0 = 200 mg/L C0 = 500 mg/L** 500 **C0** = 800 **mg/L**

2**Pseudo-first order** fit 400 **Pseudo-second order** fit qt **(mg/g)**

300 200 100 0 0 50 100 150 200 250 300 350 400 450 t (min) qt

24**(mg/g) 300 250 200 150 100 50** 0 C0 = 200 **mg/L** C0 = 500 **mg/L** C0 = 800 **mg/L**

20**Pseudo-first order** fit **Pseudo-second order**

fit 400 350 qt

24**(mg/g) 300 250 200 150 100 50** 0 C0 = 200 **mg/L** C0 = 500 **mg/L** C0 = 800 **mg/L**

50**Pseudo-first order** fit **Pseudo-second order** fit 600 500 **qt (mg/g)**

400 300 200 100 0 (III) 350 JAC-1 450 JAC-2 JAC-3 500 700 0 50 100 150 200 250 300 350 400 450 0 50 100 150 200 250 300 350 400 450 0 50 100 150 200 250 300 350 400 450 t (min) t (min) t (min) Fig. 5. Kinetic

39**plots of pseudo-first order** (Lagergren) **and pseudo-second order** model **for MB** dye uptake **onto**

JAC at pH 3 (I), pH 7 (II) and pH 11 (III). The adsorption kinetics data of MB in JAC carbons and the fitted models are depicted in Fig. 5, and the fitted kinetic parameters of pseudo-first order and pseudo-second order are summarized in Tables 6 and 7, respectively. In this figure, the kinetic plots are characterized by fast dye uptake and the sharp rise in solid phase concentration. By comparing the fitting result by pseudo first order and pseudo second order, the latter seems to give better representation. Additionally, the fitted parameter qe in pseudo- second order agree quite well with the experimental data. The applicability of the pseudo-second order model to correlate the adsorption kinetic data of MB on JAC carbons

21**suggested that the rate-controlling step**

in MB dye uptake onto JAC

21**is chemisorption involving valence forces through the exchange or sharing of electrons between the adsorbate molecules and the surface functional groups of adsorbent.**

3.6. Thermodynamic aspects In order to gain complete understanding about the MB adsorption onto JAC surface,

41**the thermodynamic** properties **such as** the **change in standard** Gibb's **free energy** (DG0), **enthalpy** (DH0) **and entropy**

(DS0) also have been investigated. The standard Gibb's free energy change was calculated by following equation: DG0 ¼ RT ln KD (10) Table 6

33**Kinetic parameters of pseudo-first order for** MB dye **adsorption**

onto JAC. C0, mg/L JAC-1 k1 (1/min) qe (mg/g) qe exp (mg/g) JAC-2 k1 (1/min) qe (mg/g) qe exp (mg/g) JAC-3 k1 (1/min) qe (mg/g) qe exp (mg/g) pH 3 200 500 800 pH 7 200 500 800 pH 11 200 500 800 0.0298 132.06 0.0410 158.57 0.0425 162.65 0.0680 151.32 0.1306 269.25 0.1385 277.33 0.0581 150.58 0.1118 300.61 0.1388 309.77 146.33 0.0624 173.92 0.1097 175.50 0.1116 160.85 0.0733 281.28 0.1115 288.93 0.1103 162.23 0.0618 313.78 0.1133 322.61 0.1116 154.52 163.21 296.60 307.29 303.08 313.68 155.92 163.31 335.02 346.28 350.02 360.93 153.27 164.26 378.16 393.77 443.49 459.39 0.0724 155.07 0.1147 369.23 0.1332 397.37 0.0817 156.61 0.1567 398.82 0.1964 586.17 0.0760 156.35 0.1499 399.78 0.1954 630.45 164.65 383.33 413.13 165.61 411.06 598.80 165.78 411.77 644.18 Table 7

33**Kinetic parameters of pseudo-second order for** MB dye **adsorption**

onto JAC. C0, mg/L JAC-1 k2 (g/mg min) qe (mg/g)

38**qe exp (mg/g)** JAC-2 **k2 (g/mg min) qe (mg/g) qe exp (mg/g)** JAC-3 **k2** (g **/mg min) qe (mg/g)**

qe exp (mg/g) pH 3 200 0.0003 500 0.0004 800 0.0004 pH 7 200 0.0007 500 0.0008 800 0.0009 pH 11 200 0.0006 500 0.0006 800 0.0007 147.38 146.33 173.42 173.92 177.11 175.50 160.85 160.85 282.31 281.28 288.03 288.93 161.97 162.23 314.17 313.78 323.31 322.61 0.0006 163.79 0.0006 308.50 0.0005 314.38 0.0008 164.05 0.0008 347.60 0.0009 361.26 0.0006 163.94 0.0007 392.98 0.0008 459.39 163.21 0.0008 307.29 0.0009 313.68 0.0009 163.31 0.0009 346.28 0.0009 360.93 0.0010 164.26 0.0008 393.77 0.0009 459.39 0.0009 165.73 164.65 385.99 383.33 414.11 413.13 165.98 165.61 410.38 411.06 597.93 598.80 166.07 165.78 411.39 411.77 645.08 644.18

11**where R is the universal gas constant (8.314 J/mol K), T is temperature (K) and** KD **is the** thermodynamic **distribution coefficient** (KD = qe/Ce). **The** enthalpy and entropy **change**

were correlated to the KD by Van’t Hoff equation which expressed as follow: lnKD ¼ DRHT0 þ DS0 R (11) The value of DH0 and DS0 was

43**obtained from the slope and** the **intercept from the linear plot of ln KD versus 1/T** (Fig. 6), respectively. **The** calculated **thermodynamic parameters** were summarized **in**

Table 8. From this table it can be seen that all systems showed the favorability of the process and spontaneous nature of dye adsorption onto JAC carbons. By increasing the temperature, more negative value of DG0 was observed; this phenomenon indicates that higher tempera- tures are more preferred for higher sorption results. The binding affinity of adsorbate molecules toward adsorbent surface increased with the increased of temperature. The positive value of DH0 reveals that the adsorption process is endothermic in nature and could be classified into chemisorption since all of DH0 values fall into the range of 20.9–418.4 kJ/mol (Tan et al., 2011). On the other hand, the positive value of DS0 denotes the increased in randomness at solid–solution interface during 2.2 2.0 1.8 1.6 ln KD 1.4 1.2 1.0 0.8 0.6 JAC-1 ln KD pH 3 pH 7 pH 11 0.4 0.0029 0.0030 0.0031 0.0032 0.0033 0.0034 1/T (K-1) 2.2 2.0 JAC-2 1.8 1.6 1.4 ln KD 1

35**.2 1.0 pH** 3 **pH 7** 0.8 **pH** 11 **0.** 6 **0.** 0029 **0.** 0030 **0.** 0031 **0.**

0032 0.0033 0.0034 1/T (K-1) 2.4 2.2 JAC-3 2.0 1.8 1.6 1.4 1.2 pH 3 1.0 pH 7 pH 11 0.8 0.0029 0.0030 0.0031 0.0032 0.0033 0.0034 1/T (K-1) Fig. 6. Thermodynamic plots of ln KD versus 1/T for MB dye adsorption onto JAC. (I) 100 (II) 100 (III) 100

18**JAC-1 JAC-2** 80 **JAC-3**

% MB Dye Sorption 60 40 % MB Dye Sorption 20

18**JAC-1 JAC-2** 80 **JAC-3**

60 40 % MB Dye Sorption 20

18**JAC-1 JAC-2** 80 **JAC-3**

60 40 20 0 0 0 1 2 3 4 5 6 7 1 2 3 4 5 6 7 1 2 3 4 5 6 7 Cycle Cycle Cycle

39**Fig. 7. Effect of** recycling **time on MB** dye **adsorption** by JAC at pH 3 (I), pH 7 (II) and pH 11 (III). Table 8 Thermodynamic parameters for MB dye adsorption onto JAC. pH T (K) DG0 (kJ/mol) DH0 (kJ/mol) DS0 (kJ/mol K) R2 JAC-1 3 303.15 318.15 333.15 7 303.15 318.15 333.15 11 303.15 318.15 333.15 JAC-2 3 303.15 318.15 333.15 7 303.15 318.15 333.15 11 303.15 318.15 333.15 JAC-3 3 303.15 318.15 333.15 7 303.15 318.15 333.15 11 303.15 318.15 333.15 1.5983 2.7441 3.6611 2.4434 3.5078 4.5649 3.1967 4.5323 5.4766 21.2082 21.1790 21.1567 2.0043 3.1469 4.2453 2.6429 3.7104 4.9325 3.2879 4.5208 5.6114 21.6492 21.4678 21.2148 2.6453 3.9939 5.0963 3.2508 4.6182 5.6808 4.1335 5.2169 6.2857 22.1634 21.8355 21.5060 0.0690 0.9948 0.0713 0.9727 0.0760 0.9999 0.0747 0.9998 0.0762 0.9979 0.0776 0.9982 0.0820 0.9954 0.0830 0.9925 0.0857 0.9998 adsorption of dyes while the negative value of DS0 describes the opposite phenomena. 3.7. Reusability of the adsorbent The reusability of the adsorbent is important in industrial practice. To assess the stability of the repeated used of JAC for MB dye removal, the adsorption–desorption cycles was also conducted. In this study, dilute hydrochloric acid was used as elution solution and the procedure was repeated seven times under following operating condition (initial dye concentration = 1000 mg/L; contact time = 4 h; T = 30 8C; mass of adsorbent = 1 g). The effect of recycling time on the adsorption capacity of JAC is given in Fig. 7. In this figure, it can be seen that all of JAC can be repeatedly used at least five times without significantly losing its adsorption capacity toward MB dye. 4. Conclusions J.

6**curcas L. press-cake residue** can be utilized **as new precursor for** low cost **activated carbon preparation. In**

order to improve the adsorption capacity for dyes removal, the surface properties of carbon could be tailored appropriately by chemical and thermal treatment.

30**Based on the experimental results, it was** found **that** thermal **activated carbon**

(JAC-3) showed higher adsorption capacity for MB dye removal than the parent carbon (JAC-1) and oxidized carbon (JAC-2). The Langmuir model represented the experimental data better than Freundlich equation. The pseudo- second order model gave better representation in correlating kinetic data than pseudo-first order model. The adsorption of MB dye onto JAC was controlled by chemisorption mechanism. The thermodynamic behavior of the adsorption MB onto JAC carbons was endothermic (DH0 > 0), irreversible (DS0 > 0) and spontane- ous (DG0 < 0). Desorption studies indicated that all of JAC could be regenerated and reused at least five times without significantly losing its adsorption capacity. References Ai, L., H. Huang, Z. Chen, X. Wei, and J. Jiang, ‘‘Activated Carbon/CoFe2O4 Composites: Facile Synthesis, Magnetic Performance and Their Potential Application for the Removal of Malachite Green from Water,’’ Chem. Eng. J., 156, 243 (2010). Altenor, S., B. Carene, E. Emmanuel, J. Lambert, J. J. Ehrhardt, and S. Gaspard, ‘‘Adsorp- tion Studies of Methylene Blue and Phenol onto Vetiver Roots Activated Carbon Prepared by Chemical Activation,’’ J. Hazard. Mater., 165, 1029 (2009). Bhatnagar, A. and M. Sillanpaa, ‘‘Utilization of Agro-Industrial and Municipal Waste Materials as Potential Adsorbents for Water Treatment – A Review,’’ Chem. Eng. J., 157, 277 (2010). Boehm, H. P., ‘‘Surface Oxides on Carbon and Their Analysis: A Critical Assessment,’’ Carbon, 40, 145 (2002). Coughlin, R. W. and F. S. Ezra, ‘‘Role of Surface Acidity in the Adsorption of Organic Pollutants on the Surface of Carbon,’’ Environ. Sci. Technol., 2, 291 (1968). Demirbas, E., N. Dizge, M. T. Sulak, and M. Kobya, ‘‘Adsorption Kinetics and Equilibrium of Copper from Aqueous Solutions Using Hazelnut Shell Activated Carbon,’’ Chem. Eng. J., 148, 480 (2009). Draper, M. R. and J. H. Ridd, ‘‘Nitration of Mesitylene: Comparison with Reactions of the Cation-radical C6H3Me3+,’’ J. Chem. Soc., Chem. Commun., 10, 445 (1978). El Qada, E. N., S. J. Allen, and G. M. Walker, ‘‘Adsorption of Basic Dyes from Aqueous Solution onto Activated Carbons,’’ Chem. Eng. J., 135, 174 (2008). Faria, P. C. C., J. J. M. Orfao, and M. F. R. Pereira, ‘‘Adsorption of Anionic and Cationic Dyes on Activated Carbons with Different Surface Chemistries,’’ Water Res., 38, 2043 (2004). Fernandez, C., M. S. Larrechi, and M. P. Callao, ‘‘An Analytical Overview of Processes for Removing Organic Dyes from Wastewater Effluents,’’ Trends Anal. Chem., 29, 1202 (2010). Fierro, V., G. Muniz, A. H. Basta, H. El-Saied, and A. Celzard, ‘‘Rice Straw as Precursor of Activated Carbons: Activation with Ortho-phosphoric Acid,’’ J. Hazard. Mater., 181, 27 (2010). Foo, K. Y. and B. H. Hameed, ‘‘Utilization of Biodiesel Waste as a Renewable Resource for Activated Carbon: Application to Environmental Problems,’’ Renew. Sustain. Energy Rev., 13, 2495 (2009). Gad, H. M. H. and A. A. El-Sayed, ‘‘Activated Carbon from Agricultural By-products for the Removal of Rhodamine-B from Aqueous Solution,’’ J. Hazard. Mater., 168, 1070 (2009). Ho, Y. S. and G. McKay, ‘‘Pseudo-second-order Model for Sorption Processes,’’ Process Biochem., 34, 451 (1999). Huang, G., J. X. Shi, and T. A. G. Langrish, ‘‘Removal of Cr(VI) from Aqueous Solution Using Activated Carbon Modified with Nitric Acid,’’ Chem. Eng. J., 152, 434 (2009). Jaramillo, J., P. M. Alvarez, and V. G. Serrano, ‘‘Oxidation of Activated Carbon by Dry and Wet Methods: Surface Chemistry and Textural Modifications,’’ Fuel Process. Technol., 91, 1768 (2010). Karagoz, S., T. Tay, S. Ucar, and M. Erdem, ‘‘Activated Carbons from Waste Biomass by Sulfuric Acid Activation and Their Use on Methylene Blue Adsorption,’’ Bioresour. Technol., 99, 6214 (2008). Khalid, Z., ‘‘Studies of the Photochemical Kinetics of Methylene Blue with Reductants,’’ Ph.D. Thesis, Department of Chemistry, University of Karachi, Karachi, Pakistan (2001). Kumar, P. S., S. Ramalingam, and K. Sathishkumar, ‘‘Removal of Methylene Blue Dye from Aqueous Solution by Activated Carbon Prepared from Cashew Nut Shell as a New Low-cost Adsorbent,’’ Korean J. Chem. Eng., 28, 149 (2011). Lagergren, S., ‘‘About the Theory of So-called Adsorption of Soluble Substances,’’ Kungliga Svenska

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