

Activated carbons by zinc chloride activation for dye removal – a commentary

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Abstract: Zinc chloride is a commonly used activator in chemical activation of activated carbon. Various carbonaceous materials have been studied as potential source of activated carbon. The operating conditions are manipulated with attention to improve the properties and performance of activated carbon in the adsorption of water pollutants. However, the generalized attributes of zinc chloride activation in relation to the adsorptive performance of activated carbon are not well documented in much of published literature. Therefore, the present work is aimed to highlight the activation strategies and mechanisms of zinc chloride activation of activated carbon. The roles of impregnation ratio, period of activation and temperature are discussed to offer some insight into textural characteristics of activated carbon. The case studies on methylene blue adsorption are integrated to shed light on the external factors affecting the adsorption.

Keywords: Activated carbon, adsorption, methylene blue, zinc chloride activation

Introduction

Activated carbon has been widely used to remove dyes, toxic gases and water pollutants because of their excellent surface area for high adsorption capacity. It is a highly porous adsorptive medium that has a complex structure composed primarily of graphitic structure of carbon atoms (Plaza et al., 2009). It consists of networks of pores with channels generated inside of a rigid skeleton of disordered layers of carbon atoms, linked together by chemical bonds, stacked unevenly, hence generating a highly porous structure of nooks, crannies, cracks and crevices between the carbon layers. Activated carbon can be manufactured from a number of carbonaceous materials such as palm kernel shells (Abnisa et al., 2011), coconut shells (Yang et al., 2010), empty fruit bunch (Zaini and Shaid, 2016), woods, lignite coal, bituminous coal and olive pits (Nowicki, 2016) by chemical or physical activation. Physical activation using oxidizing agents such as steam and carbon dioxide turns the raw material of high carbon content into activated carbon through pyrolysis at high temperature. The specific surface area of activated carbons is usually about 800 m²/g. A large surface area of activated carbon generally reflects a higher adsorption capacity. The intrinsic pore network in the lattice structure of activated carbon enables the elimination of impurities from gaseous and liquid media through a mechanisms known as adsorption. This is mainly attributed to the physical and chemical properties of activated carbon with high surface

area and pore volume, and rich surface chemistry and functional groups (Plaza et al., 2009; Nowicki, 2016).

A rapidly growing production of activated carbon in the present century is due to the stricter environmental regulations on water resources and air quality, and continuous demand for industrial applications such as gas purification, energy storage and conversion, and recovery of chemicals. However, the market price of commercial activated carbon is very expensive that can rise as high as US\$ 1700/ton. Hence, the quest for cheap and abundantly available raw material to synthesize low-cost activated carbon has been escalating over the years. The manufacturing of biomass waste-based activated carbons is foreseen to dominate, and inadvertently replace that of conventional petroleum-based. Agricultural wastes such as wood and coconut shells have been recognized as the precursor to aid in accommodating the world activated carbon production of 300,000 tons/year.

Activation strategies

Wood, coal, bamboo and coconut shells are some common examples of low-cost materials for activated carbon. Generally, carbonaceous material requires activation to boost its surface properties and porous structure before it can be called activated carbon. The methods of activation can be categorized into chemical and physical activation. Physical activation applies a pyrolysis at high temperature, ranging between 700 °C and 1000 °C under oxidizing condition in the presence of

oxygen, steam and/or carbon dioxide. Activation temperature is one of the main factors affecting the development of porous structure. Physical activation requires a high temperature environment because a low temperature would hinder the reaction kinetics as a result of the endothermic nature of activation. Physical activation occurs at the inner surface of carbon, and carbon is eliminated from the pore walls during the course of reaction, developing the channels and making the pores more expand and accessible at the desired temperature. Nevertheless, exceedingly high temperature would activate the reaction at the outer surface of carbon, hence accelerating the burning-off and reducing the yield (Gonzalez et al., 2009).

Oxygen and air are also used as oxidizing agent in physical activation to provide high reactivity to raw material. Often, the activated carbon produced exhibits unsystematic development of porous structure. Nevertheless, this activation strategy renders a large weight loss and produces activated carbon rich in surface oxides, hence minimizing the access to active sites. Thus, oxygen and air may not be appropriate to be employed as activating agent in physical activation of activated carbon. In a related development, a small number of composites such as KOH and K_2CO_3 are used as catalyst to speed-up the physical activation process in industry (Gonzalez et al., 2009). The main benefit of physical activation is a low-cost process in the absence of chemicals and post washing. However, activated carbon by physical activation normally has a specific surface area of smaller than $1000 \text{ m}^2/\text{g}$, and the yield often reduces to 70 % because of high operating temperature. Moreover, the two-step process comprises of carbonization and activation at high temperature implies the energy-consuming of physical activation (Kwiatkowski and Broniek, 2017).

In chemical activation, the carbonaceous material is mixed and impregnated with chemical agents such as phosphoric acid, zinc chloride, potassium tartrate, potassium hydroxide, etc. prior to one-step pyrolysis at temperatures of $400 \text{ }^\circ\text{C}$ to $600 \text{ }^\circ\text{C}$ under inert atmosphere. The dehydrating agents are used in the activation to create the pathways of pores and to prevent the production of tar. Upon activation, the salts left in the pores are eliminated by acid wash. In general, chemical activation is advantageous over physical activation due to the fact that it produces a greater yield of activated carbon with better surface chemistry and textural properties at a lower activation temperature. Nevertheless, cautious should be exercised because the former utilizes chemicals that could be toxic and harmful to the environment.

Generally, the properties of activated carbon are influenced by the period of activation and temperature.

The activation temperature affects the pore structure and specific surface area of activated carbon. The surface area of activated carbon-derived from green alga by potassium tartrate activation increased when the temperature increases from $500 \text{ }^\circ\text{C}$ to $700 \text{ }^\circ\text{C}$, and then decreased at $900 \text{ }^\circ\text{C}$ (Zhu et al., 2017). The decrease in surface area at higher temperature could be attributed to the expansion and collapse of micropores to mesopores, and the break of cross-linked structure under strong gasification (Yahya et al., 2015). Thus, the activated carbon may become mesoporous when the activation temperature is too high. Similarly, a longer activation can cause the collapse and constriction of pore structure, hence decreasing the pore volume, pore size and surface area of activated carbon (Xu et al., 2014).

Mechanisms of zinc chloride activation

In zinc chloride activation, the liquid chemical is intercalated into the carbon matrix to produce pores at temperature above the melting point of chemical agent. The reaction between the carbon atoms and dehydrating agent is promoted in the extended interlayers of carbon. The application of $ZnCl_2$ in chemical activation generally improves the carbon content through the formation of aromatic graphitic structure. The carbon content of safflower seed press cake increased from 49.5 % to 76.3 % after carbonization and activation with $ZnCl_2$ (Angin, 2013). Yet, a higher amount of $ZnCl_2$ in activation often results in a lower yield. The yield decreased from 42 % to 30 % for a four times increase in the amount of $ZnCl_2$ (Angin, 2013). A high amount of activating agent increases the removal of light and volatile matters through the collapsed of aliphatic and aromatic bonds, thereafter causes the loss in weight. Activation at a higher temperature also results in a lower yield. For agro-waste materials, the cellulose turns into activated carbon due to the decomposition of hemicellulose, splitting-off of cellulose and decomposition of lignin structure at high temperature. The tar-containing phenolic compounds are stripped, hence causing a loss in material weight.

Tomato processing solid waste-based activated carbons were prepared at impregnation ratio of 1:6 (tomato processing solid waste : $ZnCl_2$) at $600 \text{ }^\circ\text{C}$ for 0.5 to 4 h (Saygili and Guzel, 2015). The surface area, pore volume, mesoporosity, average pore diameter were found to increase with increasing activation time from 0.5 h to 1 h. However, the textural properties of activated carbon collapse because some of the pores start to sealed-off as a result of sintering effect due to an extended activation time from 1 h to 4 h (Mohanty et al., 2006; Saygili and

Guzel, 2015). Cashew nut shell was activated using zinc chloride at impregnation ratio of 1.5:1 (cashew nut shell : $ZnCl_2$) at 500 °C. The adsorption capacity increases with the amount of surface acidic functional groups, surface area and pore volume as compared to activation at 400 °C (Spagnoli et al., 2016). The presence of acidic functional groups on activated carbon surface is desirable for the adsorption of charged pollutants. It is believed that the surface functional groups are originated from the nature of raw materials, as there is no evidence of direct relationship with the use of zinc chloride in activation. However, activation at a higher

temperature for a longer period may diminish the existing functional groups. Saygili and Guzel (2015) reported an increase in surface area, pore volume, mesoporosity and pore diameter with increasing activation temperature from 400 °C to 600 °C. The decomposition of primary compounds on the material surface at higher temperature has resulted in the formation of new pores. However, the decrease in pore characteristics above 600 °C might be due to the sintering effect at high temperature followed by the shrinkage of char and realignment of carbon structure which resulted in the decrease of pore area and volume.

Tab. 1. Activation strategies in activated carbon preparation.

Raw material	Activation strategies	Surface area (m ² /g)	Adsorption capacity, Q_{max} (mg/g)	Reference
Waste rubber tires-based activated carbon for thiophene and dibenzothiophene removal	Mixture of H_2O_2 and HNO_3 , 900 °C for 2 h	62	5.13 (thiophene); 7.40 (dibenzothiophene)	(Swat et al., 2017)
Calcium carbonate-activated sawdust carbon to remove acid orange II	Sawdust : calcium carbonate ratio of 1:1, 800 °C for 2 h	707	389	(Kong et al., 2017)
Pineapple plant leaves-based activated carbon to remove caffeine	Mixture of biomass and H_3PO_4 , 300 °C for 2 h, and 500 °C for 1 h	1031	156	(Beltrame et al., 2017)
Matured tea leaf-based activated carbon to remove rhodamine B and orange G	Matured tea leaf : H_3PO_4 ratio of 1:3, 500 °C for 1 h	1313	398 (rhodamine B), 319 (orange G)	(Goswami and Phukan, 2017)
Green alga-based activated carbon to remove chloramphenicol	Green alga : potassium tartrate ratio of 1:1, 700 °C for 30 min	1692	709	(Zhu et al., 2017)
Phragmites australis-derived activated carbon to remove Pb(II)	Phragmites australis : H_3PO_4 ratio of 2:1, 450 °C for 1 h	1058	167	(Guo et al., 2017)
Mangosteen fruit peel-based activated carbon to remove methylene blue	Mangosteen fruit peel : $ZnCl_2$ ratio of 1:4, 600 °C for 30 min. Activated carbon : sodium alginate ratio of 2:1 in 0.1 M of $CaCl_2$, 60 °C for 24 h	890	230	(Nasrullah et al., 2017)
Cashew nut shell-based activated carbon to remove methylene blue	Cashew nut shell : $ZnCl_2$ ratio of 1:1.5, 500 °C for 2 h	1478	476	(Spagnoli et al., 2016)
Tamarind wood-based activated carbon to remove chromium(VI)	Tamarind wood : $ZnCl_2$ ratio of 1:3, 493 °C for 40 min	1322	28	(Acharya et al., 2008)
Tomato processing solid waste-based activated carbon to remove methylene blue and metanil yellow	Solid waste : $ZnCl_2$ ratio of 1:6, 600 °C for 1 h	1093	400 (methylene blue), 385 (metanil yellow)	(Saygili and Guzel, 2015)

Generally, the porosity of activated carbon depends on impregnation ratio and activation temperature. The release of volatiles due to the dehydrating effect of $ZnCl_2$ at elevated temperature commonly results in the development of pores and channels in the matrix of activated carbon. However, the new pores are prone to collapse and become larger pores at higher temperature, hence decreasing the surface area. This is also true for the excessively used $ZnCl_2$ in impregnation and activation. The boiling point of $ZnCl_2$ (732 °C) is of another concern that worth to be considered in selecting the operating conditions. As the temperature of activation is normally below the boiling point, some portion of the salt may remain on the activated carbon. Consequently, the washing step would drain-off the chemical, hence polluting the environment because of the hazardous nature of $ZnCl_2$ (Lee and

Zaini, 2016). From the process economics point of view, and to minimize the release of $ZnCl_2$ to the environment, the residual activator on activated carbon can be recovered using Soxhlet unit, and reuse for subsequent activation (Zaini et al., 2014; Zaini et al., 2016). However, less attention has been paid in this regard in much of published literature. Table 1 summarizes some studies on chemical activation of activated carbon. The surface area and removal performance of activated carbons are also presented.

Methylene blue adsorption by activated carbons – case studies

Dye is a coloured chemical substance that is widely used in the textile, plastic and paper industries. It is adhered to the material surface via covalent

Tab. 2. Adsorption of methylene blue by activated carbons.

Raw material	Activation strategies	Surface area (m ² /g)	pH	Adsorption capacity (Q_{max} , mg/g)	Reference
Mangosteen fruit peel	Mangosteen fruit peel : zinc chloride of ratio 1:4, 600 °C for 30 min, modified with sodium alginate in $CaCl_2$ solution	890	10	230	(Nasrullah et al., 2018)
Activated carbon-clay composite	Carbon clay : K_2CO_3 ratio of 1:1, 800 °C for 120 min	355	8.5	179	(Marrakchi et al., 2017a)
Fishery waste-based activated carbon	Fishery waste : NaOH ratio of 1:3, 600 °C for 90 min	1867	11	184	(Marrakchi et al., 2017b)
Cashew nut shell-based activated carbon	Cashew nut shell : $ZnCl_2$ ratio of 1:1.5, 500 °C for 2 h	1871	4.4	476	(Spagnoli et al., 2016)
Tomato processing solid waste-based activated carbon	Tomato processing solid waste : $ZnCl_2$ ratio of 1:6, 600 °C for 1 h	1093	5.8	400	(Saygili and Guzel, 2015)
Palm kernel shell-based activated carbon	Palm kernel shell : $ZnCl_2$ ratio of 1:1, 550 °C for 1 h	1058	12	721	(Garcia et al., 2017)
Pineapple waste-based activated carbon	Pineapple waste : $ZnCl_2$ ratio of 1:1, 500 °C for 1 h	914.67	7	288	(Mahamadet al., 2015)
Fox nutshell-based activated carbon	Fox nutshell : $ZnCl_2$ ratio of 1:2, 600 °C for 1 h	2869	11	916	(Kumar and Jena, 2016)
Coated palygorskite-based activated carbon	Coated palygorskite : $ZnCl_2$ ratio of 1:1, 450 °C for 1 h	1201	7	351	(Zhang et al., 2015)
Pongamia pinnata hulls-based activated carbon	Pongamia pinnata hulls : KOH ratio of 1:3, 600 °C for 1 h	828.30	7	239.4	(Islam et al., 2017)

bonds or forming complexes with salts or metals, by physical and mechanical retention (Bafana et al., 2011). Generally, dye is composed of a group of atoms known as chromophores, that is responsible for the colour. The chromophores with centres of functional groups include azo, anthraquinone, methine, nitro, arilmethane, carbonyl, etc. The electrons withdrawing/donating group known as auxochromes is responsible to strengthen the colour of chromophores. Examples of common auxochromes are amine, carboxyl, sulfonate and hydroxyl (Ming-Twang et al., 2015).

Nearly 200,000 tons of dyes from textile industry are loss to sewage every year. Due to high loads and inefficient treatment, dyes may find their way into water receiving bodies. The presence of small amount of dyes in water is enough to impart colour and diminishes the aesthetic quality and transparency of water bodies, causing the deterioration of aquatic environment. Dye in water decreases light penetration and photosynthetic activity, leading to oxygen deficiency to aquatic creatures therein. Dye chemicals are also toxic to human and may cause eye burn, cyanosis, skin irritation and other health implications (Ming-Twang et al., 2015). Methylene blue is an example of the commonly used dye in textile industry and has been extensively studied as model pollutant in adsorption. Figure 1 shows the molecular structure of methylene blue. Table 2 summarizes the methylene blue adsorption studies using various activated carbons.

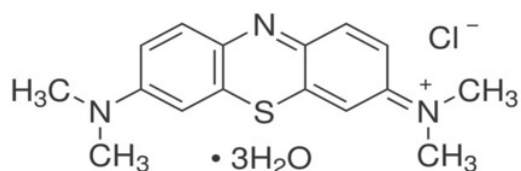


Fig. 1. Molecular structure of methylene blue.

Fox nutshell was activated using ZnCl_2 at a ratio of 1:2 (material : activator) to yield activated carbon with a high surface area of $2869 \text{ m}^2/\text{g}$ (Kumar and Jena, 2016). Activated carbon with a higher surface area normally exhibits a greater methylene blue adsorption capacity. The development of pores and textural properties of activated carbon relies on various factors, such as the solid structure and carbon content of the precursor, and the selection of activator and operating conditions. Raw materials with a high carbon content of more than 45 % are normally required to produce activated carbon. Apart from the specific surface area and pore texture of activated carbon, the solution pH can also affect the removal capacity of methylene blue.

Methylene blue dye dissociates in water as cationic molecule (Figure 1). Therefore, the adsorbate is more attracted to the surface of activated carbon through electrostatic attraction when the surface is negatively charged. As such, a basic environment should be introduced to deprotonate the activated carbon. Nevertheless, the adsorption of methylene blue could be pH-independent as the role of surface chemistry outweighs the change in solution pH on adsorbent (Mahamad et al., 2015).

The pH-dependent adsorption can largely be associated to the class and ionic state of functional groups, and adsorbate chemistry in solution. The negatively charged adsorbate species bind through electrostatic attraction to the positively charged functional groups if the adsorption takes place at low pH. While, activated carbon with functional groups carrying a net negative charge tends to repulse the anions at high pH. Hence, the adjustment of pH could be of considerable importance to boost the adsorption performance. In addition, physical deposition, subsidiary substances and hydrogen bonding play substantial part in the adsorption process, wherein they could be of pH-independent. Sulfonic acid-modified activated carbon exhibits pH-dependent removal for rhodamine B (Goswami and Phukan, 2017). The solution pH can alter the electrostatic interaction between the adsorbent and adsorbate. The adsorption capacity slowly increases when the solution pH increased to pH 6, while the uptake slightly decreases with further increased in pH. At low pH, rhodamine B retains its cationic properties and may readily lodged onto the pores of adsorbent. The surface becomes negatively charged at high solution pH, rendering a favourable environment for cationic dye adsorption. However, it also triggers the switch of cations into zwitterions. The dimerization of molecules, consequently complicates the pore filling as a result of molecules aggregation. Furthermore, the pH-dependent adsorption could be associated with the pH_{PZC} of activated carbon. For example, the surface becomes negatively charged at a solution pH higher than pH_{PZC} for prospective cationic dyes removal thru electrostatic interaction. Beltrame and co-workers (2017) demonstrated a tailor-able surface charge of pineapple leaves-derived activated carbon as protonated and de-protonated by pH adjustment. Concentration, contact time, solution pH and temperature of the system are among the contributing factors in dye adsorption. Apart from that, the pore volume and particle size of adsorbent, the solubility of solute (adsorbate), the size of adsorbate molecules with respect to the size of pores, the degree of ionization of adsorbate molecules and the affinity of solute towards adsorbent show

an interplay in governing the adsorption process. A large surface area of adsorbent generally reflects a high adsorption capacity. Adsorbent with small particle size is preferred in adsorption as it decreases the internal diffusion and mass transfer resistance for the penetration of adsorbate towards rapid equilibrium. Dye solubility may compromise the removal capacity if the substance is too soluble in water/solvent. A large dye molecule may not be possible to enter a small pore for adsorption, even though the surface area is large. Normally, the pore width should be in the order of twice as much as the size of adsorbate. Also, the highly ionized adsorbate molecules are adsorbed to a smaller degree as compared to the neutral molecules because of the possible electrostatic repulsion from the adsorbent surface. The degree of ionization of a species is influenced by the solution pH. The affinity of slightly polar solute towards the surface of activated carbon is minimal because of the hydrophobic nature of activated carbon.

A rapid adsorption at initial adsorption stage is possible because of high concentration gradient between the adsorbate in solution and vacant sites. The increase in adsorption capacity, and hence the attainment of equilibrium is due to the unrestricted mass transfer of dye molecules from the bulk liquid to the external surface of activated carbon. Further, a slower internal mass transfer within the particles as the contact time is prolonged decreases the rate of adsorption upon reaching the equilibrium. The percentage of adsorption decreased with increasing feed concentration indicates that the surface sites have already been occupied, and increasing the concentration might certainly increase the residual concentration, hence decreasing the removal percentage. A high concentration of dye increases the effective contact area with adsorbent and offers essential driving force to overcome the mass transfer resistance on the interface, hence increasing the adsorption capacity. Also, the increase in initial concentration increases the competition among dye molecules, and improves the adsorption leading to surface saturation.

Pineapple leaves-derived activated carbon showed a methylene blue capacity of 39.7 mg/g and reaches a saturation at 120 min (Mahamad et al., 2015). The driving force to overcome the mass transfer resistance on the adsorbent phase is due to the concentration of methylene blue. After a period of time, it is assumed that the rate of adsorption is equal to the rate of desorption, i.e., the state of equilibrium. However, a longer contact time is needed to remove a more concentrated methylene blue and reach the equilibrium. Generally, the mechanisms of methylene blue removal onto activated carbon can

be assumed to follow four steps, 1) migration of dye from the bulk solution to the surface of adsorbent, 2) diffusion of dye through the boundary layer to the surface of adsorbent, 3) adsorption of dye at the active sites on the surface of adsorbent and 4) intraparticle diffusion of dye into the interior pores of adsorbent. The mass transfer resistance at the boundary layer affects the rate of adsorption; an increase in contact time while the resistance is minimal increases the fluidity of dye during the adsorption process for high adsorption capacity.

Concluding remarks

The textural properties of activated carbon are tuneable according to impregnation ratio, activation period and temperature. The yield and pore texture of activated carbon rely upon the selection of activation conditions, where excessive temperature at longer activation time may result in lower yield and surface area. Activated carbon has been widely applied to remove dye from water. A greater adsorption capacity is normally reflected by a higher surface area of activated carbon. Notwithstanding that, the pore size of activated carbon also plays an important role in adsorption as a smaller pore size may not be able to be entered by dye molecules even though the surface area is huge. Apart from the inherent properties of activated carbon, the performance of activated carbon in dye adsorption could also be prompted by external factors such as solution pH, ionic strength, temperature, foreign matters, etc. Despite the fact that zinc chloride activation is a mature domain of research in activated carbon production, there are still rooms for improvement in overcoming the zinc chloride toxicity and recyclability upon activation.

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