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## Activated Carbon Regeneration Technology เทคโนโลยีการคืนสภาพถ่านกัมมันต์

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### บทคัดย่อ

ถ่านกัมมันต์เป็นวัสดุที่มีประสิทธิภาพในการดูดซับสูง พื้นที่ผิวสูง ไม่เป็นพิษ และมีคุณสมบัติทางธรรมชาติเป็นสารที่ไม่ชอบน้ำ จึงถูกนำมาใช้ประโยชน์อย่างกว้างขวางในการกำจัดสารพิษ และมลพิษทางเคมีในน้ำเสียจากโรงงานอุตสาหกรรม การทำน้ำ อากาศ และสารอื่น ๆ ให้บริสุทธิ์ โดยเฉพาะอย่างยิ่งเพื่อบำบัดน้ำเสียให้เป็นไปตามข้อกำหนดทางสิ่งแวดล้อม ในมุมมองของต้นทุนการผลิต และความต้องการของตลาดที่สูง การนำถ่านกัมมันต์ที่ใช้แล้วกลับมาใช้ใหม่ จึงเป็นเรื่องที่มีความเป็นไปได้ ด้วยเหตุผลดังกล่าว การคืนสภาพของถ่านกัมมันต์ที่ใช้แล้วจึงเป็นประเด็นที่สำคัญเพื่อที่จะกำจัดสิ่งอุดตัน ทำให้กลับมาใช้สภาพเหมือนเดิม เพิ่มประสิทธิภาพของที่ใช้แล้ว เป็นการใช้ทรัพยากรทางธรรมชาติอย่างประหยัดอีกทาง และยังช่วยลดมลพิษในการกำจัดทิ้ง โดยคำนึงถึงผลกำไรในภาพรวมของระดับอุตสาหกรรม เมื่อไม่นานมานี้ มีการนำเทคโนโลยีการคืนสภาพถ่านกัมมันต์มาใช้หลายเทคนิคด้วยกัน เช่น เทคโนโลยีการคืนสภาพด้วยความร้อน สารเคมี ไฟฟ้าเคมี คลื่นไมโครเวฟ กระบวนการออกซิเดชัน และโอโซน เป็นต้น วัตถุประสงค์ของบทความนี้ได้อธิบายถึงความแตกต่าง ข้อได้เปรียบ เสียเปรียบของเทคโนโลยีการคืนสภาพดังกล่าว

**คำสำคัญ:** การคืนสภาพ ถ่านกัมมันต์

## Abstract

Activated carbon, known for its high adsorption capacity, high specific surface, non-toxicity along with its hydrophobic nature, has been widely used for the removal of hazardous material and pollutants from wastewater, purification of water, air, and other materials and for the treatment of pollutants in different media, especially industrial water effluents to meet the environmental legislation. In view of the high production cost and market needs of activated carbon, the economics and feasibility of the adsorption process greatly depends on the reuse of the exhausted activated carbon. For this reason, the regeneration of exhausted activated carbon is an important issue for the removal of the adsorbate and restoration of previous adsorptive capacity of the original activated carbon. It helps increase the efficiency, economize the natural resources, reduce the secondary pollution and produce considerable economic profit of the overall process on an industrial scale. Recently many regeneration technologies have been applied to deal with exhausted activated carbon such as thermal, chemical, electrochemical, microwave, advance oxidation process regeneration, and steam regeneration, among others. The purpose of this paper is to review the differences, advantages and disadvantages of these regeneration technologies.

**Keywords:** Regeneration, Activated Carbon

## Introduction

Activated carbon is porous carbonaceous material with a large surface area, high adsorption capacity, non-toxicity, and with a hydrophobic nature that is typically produced from coal, wood species and agricultural by-products such as rice husk shell, coconut shell, nut shell, corncob, sawdust, bagasse, coffee residue, Litchi Chinensis shell and seeds, etc. (Antal, et al., 2000: 4026; Babu and Chaurasia, 2003: 2140; Cheung, Porter, and Mckay, 2002: 652; Laowachirasuwana, 2009: 118; Laowachirasuwana, 2011: 90). Activated carbon has been widely used for the removal

of hazardous materials and pollutants from wastewater, the purification of water, air, and other materials and for the treatment of pollutants in different media, especially industrial water effluents to meet the environmental legislation. In view of the high production cost and market needs for activated carbon, the economics and feasibility of the adsorption process greatly depends on the reuse of the exhausted activated carbon. The objective of the regeneration of exhausted activated carbon is removal of the adsorbate and restoration of previous adsorptive capacity of the original activated carbon. Exhausted activated carbon

can be regenerated by a variety of methods, but the process fundamentals are essentially the same. In most processes, regeneration is accomplished by subjecting the exhausted activated carbon to conditions that shift the adsorption equilibrium in favor of desorption, which may be physical or chemical desorption. For physisorption, this shift can usually be accomplished by heating, under an oxidizing atmosphere, lowering the pressure, or washing with a solvent (to remove the adsorbed pollutant from the activated carbon surface). In the case of chemisorption, a supply of energy greater than the sorptive force is required to break the strong ionic or covalent bonds. Many regeneration technologies have been applied to deal with exhausted activated carbon, such as thermal, chemical, electrochemical, microwave, advance oxidation process regeneration, and steam regeneration, etc.

The differences, advantages and disadvantages of thermal, chemical, electrochemical, microwave, advance oxidation process regeneration, and steam regeneration are discussed.

### Thermal Regeneration

The most widely used regeneration technique is thermal regeneration, in which adsorbents are desorbed by means of volatilization and oxidation at high temperature.

Thermal regeneration of exhausted activated carbon involves three steps (Duan, et al., 2012: 4). Drying at approximately 105 °C, baking (high temperature desorption and decomposition (500-800 °C) under an inert atmosphere) and reactivation (oxidation in an atmosphere containing a high concentration of steam or CO<sub>2</sub> at elevated temperatures (800-850 °C).

The regeneration process of exhausted activated carbon is conducted using a rotary kiln or multiple hearth furnaces, which process is similar to that used to manufacture the original activated carbon (Cheng, Yang, and Hsieh, 2007: 640; Gutsch and Siata, 2012: 8625). However, it has some important problems as follows: High energy cost is required to keep the regeneration temperature at about 800-850 °C and 10-20% of the carbon is usually lost by attrition, excessive burn-off, and wash-out during each cycle. It needs *ex situ* operation; that is, exhausted activated carbon has to be transported to a reactivation center, regenerated in a furnace at high temperature and transported back to the in – process plant. It may also introduce changes in activated carbon properties (damage the porosity and surface area characteristics). These problems increase with the increase of the regeneration cycles (Berenguer, et al., 2010: 3367; Mourao, et al., 2008: 844-848).

## Chemical Regeneration

Chemical regeneration is an alternative to thermal regeneration. It has a number of significant advantages. Among these are the following (Berenguer, et al., 2010: 3368): It can be done *in situ*, thus unloading, transporting, and repacking of the adsorbent are eliminated. The loss of carbon resulting from thermal desorption is eliminated, and recovery of valuable activated carbon is possible. With proper subsequent treatments such as distillation, chemical regenerants can be reused.

The most commonly used regenerants can be categorized into two groups: organic solvents and inorganic chemicals. It has been found that organic regenerants with solubilizing powers are more effective than inorganic regenerants. This technology uses organic solvents to dissolve adsorbed material out of the pores of the exhausted activated carbon, then the solvent is removed by steam. A detailed investigation of the regeneration of activated carbon examined the effects of the molecular solvent into the micropores, which, therefore, displaced the sorbates more effectively. Many researchers used solvents such as *n*-pentane, acetone, methanol, ethanol, formic acid, and acetic acid to regenerate exhausted activated carbon. While methanol and acetone were found to be of limited use, formic acid and acetic acid were effective regenerants (Guo, et al., 2011: 1789; Horng,

et. al., 2008: 366-367; Lu, et al., 2011: 306).

Among inorganic regenerants, sodium hydroxide (NaOH) has been found to be effective in the regeneration of activated carbon. NaOH can weaken the Van der Waals force between the adsorbate and micropore surface, and undermine the chemical bond between adsorbate and surface functional groups so that organic pollution can be eluted. In addition, NaOH can convert most of the organic pollutants to soluble salt, which is easily ionized in water so that the micropore surface of exhausted activated carbon can be cleaned. It has been shown that the desorption of phenol with 4% aqueous solution of NaOH is commercially effective. The main mechanism of regeneration was postulated to be the formation of sodium phenate, which is easily desorbed from the surface of carbon. It was also concluded that the high pH arising from NaOH modified the polarity of surface oxides, thus reducing the force of attraction between phenol and activated carbon. In studying regeneration mechanisms on activated carbon, it is important to remember that adsorption can be either by physisorption or chemisorption (Sun, Jiang, and Xu, 2009: 79-81).

For example, recent research on the adsorption of phenol on activated carbon has shown that the presence of dissolved oxygen in the adsorbate solution induces polymerization reactions on the surface that enhance the

adsorptive capacity of activated carbon for phenolic compounds (Berenguer, 2010: 2736). Although chemical regeneration techniques have been successfully applied to a number of adsorbates, the regeneration efficiency depends mainly on the use of reagents, and the solubility of the adsorbed substances often give incomplete regeneration.

### Electrochemical Regeneration

Electrochemical regeneration appears as a very promising alternative that presents some advantages compared to the conventional methods (Thermal and chemical regeneration). Essentially, it can be conveniently operated *in situ*, with lower energy consumption and short time requirements. The electron is the only reagent, and it requires simple handling and equipment. Moreover, the proper setting of the applied current (or electrode potential) and other operational variables (such as electrolysis time, electrode composition, etc.) can allow for the recovery/modification of organic pollutants into less hazardous compounds, or even complete mineralization (Wang and Wang, 2008: 45-46). In particular cases, it is well-documented that phenol and phenol derivatives can be electro-oxidized both anodically via direct electron transfer or indirect oxygen transfer from hydroxyl radicals coming from water electrolysis, (Garcia-Oton, et al., 2005: 319-323) and cathodically through indirect oxidation by electrogenerated peroxide species (Weng and

Hsu, 2008: 231). In both anodic and cathodic treatments, phenol transformation proceeds through a rather complex mechanism, yielding hydroquinone and benzoquinone as main reaction intermediates. Provided that sufficient electrolysis time is left, these intermediates are further oxidized to a number of less toxic and much more biodegradable organic acids (e.g. maleic, fumaric and oxalic acids), and eventually to CO<sub>2</sub> (Berenguer, et al., 2009: 1019, 2010: 3370; Brown and Roberts, 2007: 1330; Narbaitz and Karimi-Jashni, 2009: 29-33).

Once the adsorptive capacity of the activated carbon bed has been exhausted by the adsorption of pollutant molecules, the carbon is transferred to an electrochemical cell (to either the anode or the cathode) in which electrochemical regeneration can occur. There are several mechanisms by which passing a current through the electrochemical cell can encourage pollutant desorption. Ions generated at the electrodes can change local pH conditions in the divided cell that affect the adsorption equilibrium and have been shown to promote desorption of organic pollutants such as phenols, from the carbon surface. Other mechanisms include reactions between the ions generated and the adsorbed pollutants resulting in the formation of a species with a lower adsorptive affinity for activated carbon that subsequently desorb, or the oxidative destruction of the organics on the carbon surface. It is agreed that the main mechanisms

are based on desorption induced regeneration as electrochemical effects are confined to the surface of the porous carbons, so cannot be responsible for bulk regeneration. The performance of different regeneration methods can be directly compared using the regeneration efficiency equation which is detailed elsewhere (You, et al., 2013: 855).

Cathodic regeneration: the cathode is the reducing electrode and generates hydroxylion ( $\text{OH}^-$ ), which increases the pH conditions. An increase in pH can have the effect of promoting the desorption of pollutants into a solution where they can migrate to the anode and undergo oxidation. Studies on cathodic regeneration have shown regeneration efficiencies for adsorbed organic pollutants such as phenols on the order of 85% based on regeneration times of 4 hours with applied currents between 10-100 mA. However, due to mass transfer limitations between the cathode and anode, there is often residual pollutant left in the cathode unless large currents or long regeneration times are employed.

In anodic regeneration, the anode is the oxidising electrode and as a result has a lower localised pH during electrolysis, which also promotes desorption of some organic pollutants. Regeneration efficiencies of activated carbon in the anodic compartment are lower than that achievable in the cathodic compartment by between 5-20% for the same regeneration times

and currents, however there is no observed residual organic due to the strong oxidizing nature of the anode (Wikipedia free encyclopedia, 2013a).

## Microwaves Regeneration

Research on the regeneration of activated carbon mainly focuses on thermal, chemical and electrochemical methods. Chemical methods demand the use of reagents and often give incomplete regeneration. Electrochemical methods show a promising prospect but their practical application has still to be tested. Thermal regeneration is more commonly employed in practice, but it is time-consuming and after repetitive regenerations the activated carbon becomes seriously damaged. In recent years, microwaves have been successfully applied for the regeneration of activated carbon. Microwaves are a form of electromagnetic energy, wherein the applied energy is converted into heat by mutual interaction between media; the electric field component of the wave with charged particles in the material. Broadly speaking, microwave radiation is the term associated with any electromagnetic radiation in the microwave frequency range from 300 MHz to 300 GHz, which lie in the segment between infrared and radio wave of the electromagnetic spectrum (Tai and Lee, 2007: 300). Depending on the nature of the materials, different heating mechanisms might exist

including dipole rotation (for molecules with a permanent dipole moment) and ionic conduction (for ions or free electrons) (Liu, et al., 2012: 1004).

Microwave irradiation has attracted the attention of chemists due to its capability of molecular level heating, which leads to homogeneous and quick thermal reaction. In the particular case of carbon materials, the efficiency of applying microwave heating technology to regenerate industrial waste activated carbon has been investigated. The results are very promising due to the rapid heating of the activated carbon by microwave energy. In addition, microwave technology allowed the carbon to be recycled and reused for a large number of times. This technique does not damage the carbon, rather it increases the surface area allowing more contaminants to adhere, thereby increasing the value. The main difference between microwave devices and conventional heating systems are in the way the heat is generated (Foo and Hameed, 2012: 236). In the former approaches thermal regeneration is conventionally performed in rotary kilns or vertical furnaces, the heat source is located outside the carbon bed and the bed is heated by conduction or convection. A temperature gradient is established in the material until a condition of steady state is reached (Jou and Wu, 2008: 114). However, in the microwave device, the microwaves supply

energy directly to the carbon bed. Energy transfer is not by conduction or convection as in conventional heating, but is readily transformed into heat inside the particles by dipole rotation and ionic conduction. When high frequency voltages are applied to a material, the response of the molecules with a permanent dipole moment or an induced dipole to the applied potential field change their orientation in a direction opposite to that of the applied field. The synchronized agitation of molecules then generates heat. When regeneration is performed by conventional techniques, the decrease in micropore volume is accompanied by a downward shift to pores of narrower sizes, suggesting that regeneration treatment introduces some molecular sieve effects into the porous structure of the regenerated activated carbon, most likely due to blocking effects at the entrance of the pores of a larger size. In contrast, in the case of regeneration in the microwave heating, a slow and gradual fall off is observed and the pore width remains almost unaltered, indicating that obstruction of the pores of a larger size, specific surface areas and micropore volumes occur to a lesser extent.

Microwave regeneration offers possible advantages over conventional treatment, including the rapid and precise control of the carbon bed temperature, shorter regeneration time, a more compact furnace, and energy savings. Ania has also found that microwave

regeneration gives rise to a better performance of the activated carbon in terms of ulterior adsorption capacity and rate of adsorption compared to conventional heating (Ania, et al., 2007: 3301). Under conventional heating, the adsorption capacity of the activated carbon is observed to decrease gradually with subsequent regeneration cycles, which is in agreement with the partial desorption of adsorbate molecules and the blockage of the porous structure. In contrast, it is worth noting that after one regeneration cycle, despite the slight deterioration of the porous structure of the parent activated carbons, adsorptive capacities after microwave regeneration are unexpectedly high (Ania, et al., 2005: 11; Yuen and Hameed, 2009: 19-20). Moreover, a strong motive for promoting microwave regeneration of activated carbon is the potential for selectivity of microwave heating between the adsorbate and activated carbon, as well as among the adsorbates of a multicomponent vapor stream. During the regeneration, microwave heating has the potential to control the deposition and distribution of energy in the system, of which the adsorbent material and fittings can consume a significant part of the energy. Microwave heating is also volumetric, whereby all of the infinitesimal volume elements within the object are heated. The selective heating of the adsorbates according to their dielectric properties can allow the separation of the adsorbates during the desorption process

and simplify the post – regeneration processing when treating multicomponent vapor streams.

Even though it appears to be very successful, and apparently can promote the accomplishment of remediation, full-scale application of the microwave-assisted processes is still underway, with most of the superior cases demonstrated on a laboratory scale. A distinct drawback to microwave heating is the lack of uniformity (thermal instability) in material heating (both the magnitude and spatial distribution of energy). Moreover, its applications are limited by the high investment costs and the lack of fundamental knowledge regarding the dielectric properties or equipment design. Consequently, much more dedicated work and further exploration are needed to expand the research area, to improve its performance and to scale-up microwave production (Foo and Hameed, 2012: 238; Yuen and Hameed, 2009: 22).

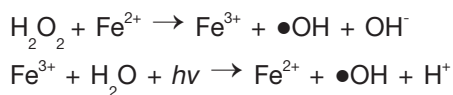
### **Advanced Oxidation Processes (AOPs)**

Advanced oxidation processes (AOPs) have been considered a promising alternative technology for the regeneration of exhausted activated carbon. AOPs are characterized by the production of free radicals, mainly the hydroxyl radical ( $\bullet\text{OH}$ ) that offers a high oxidation potential (2.8 V) and is able to oxidize a wide range of organic compounds. AOPs can be classified according to the different systems



used to generate free radicals, such as:  $O_3$ /UV radiation,  $O_3/H_2O_2$  radiation,  $O_3/H_2O_2/UV$  radiation,  $H_2O_2/UV$  radiation,  $TiO_2/UV$  radiation, and  $Fe^{2+}/H_2O_2$ ,  $Fe^{2+}/H_2O_2/UV$  radiation (Okawa, et al., 2007: 1045; Zhang, et al., 2008: 132).

Those last two processes have been widely studied and known as the so-called Fenton and Photo-Fenton systems, respectively. The Fenton process is a combination of ferrous ions and hydrogen peroxide (Fenton's reagent). Those chemicals produce hydroxyl as follows (Muranaka, et al., 2010: 990):



The Photo-Fenton system ( $Fe^{3+}/H_2O_2$ ) reaction was discovered by Fenton who reported that by using hydrogen peroxide and an iron salt as catalyst, several organic molecules could be oxidized. Hydroxyl radicals are also characterized by a little selectivity of attack, an attractive feature for an oxidant to be used in waste water treatment. Many different organic compounds are susceptible to be removed or degraded by means of hydroxyl radicals. Once hydroxyl radicals are generated, they can virtually oxidize and mineralize almost every organic molecule, yielding  $CO_2$  and inorganic ions (Zhang, et al., 2008: 134).

Recently Fenton oxidation has been successfully applied for the recovery of activated carbon exhausted with chlorinated organic compounds (Toledo, et al., 2003:

1050) and methyl tert-butyl ether (Huling, et al., 2005: 2145).  $H_2O_2/UV$  radiation has also been reported for the regeneration of activated carbon saturated with acetone and isopropyl alcohol (Horng, et al., 2008: 368). Fenton and Photo-Fenton oxidations have been carried out in very mild conditions to destroy adsorbed phenol, selected as the most common model pollutant, and *in situ* regeneration of activated carbon. The two-step process is conducted using either a full batch system (preliminary experiments to study the influence of  $Fe^{2+}$  and  $H_2O_2$  concentrations) or a continuous fixed bed adsorption, followed by a batch circulation of the Fenton's reagent through the exhausted activated carbon bed.

## Supercritical Fluid Extraction (SFE)

The recent interest in supercritical fluid extraction (SFE), including adsorption/desorption phenomena, is due to the unique properties of supercritical fluids. SFE is a powerful technique for regeneration of exhausted activated carbon. This technique that can provide the solvent power of a liquid and the mass transfer characteristics of a gas has some advantages in comparison with other traditional processes. Other properties of the supercritical fluids are also favorable for extraction. Densities are comparable to liquid densities while gas-like viscosities and low surface tension enhance the mass transfer between solid and supercritical fluids. The most employed supercritical solvent

is carbon dioxide (CO<sub>2</sub>) because of its low critical temperature of 304 K and a moderate critical pressure of 73 bar, which are considered ideal to extract substances from a solid matrix as is required for the regeneration of exhausted activated carbon. It is non-flammable, non-toxic, environmentally friendly and low cost. It is often used to replace toxic freons and certain organic solvents. Further, it is miscible with a variety of organic solvents and is readily recovered after processing. It is also a small and linear molecule and thus diffuses faster than conventional liquid solvents (Heidari, Lotfollahi, and Baseri, 2013: 317).

In addition, several other supercritical fluids can be used, but the final choice would depend on the specific application and additional factors such as safety, flammability, phase behavior and solubility at the operating conditions and the cost of the fluid. SFE is an attractive option for contaminant removal from activated carbon and presents several advantages over conventional regeneration methods. The advantage of using supercritical fluids extraction is the ease of separation of the extracted solute from the supercritical fluid solvent by simple expansion. In addition, supercritical fluids have liquid-like densities but superior mass transfer characteristics compared to liquid solvents due to their high diffusion (diffusion coefficients similar to those of gases, excellent transport characteristics),

and very low surface tension that enables easy penetration into the porous structure of the solid matrix to release the solute. There is little loss of surface area compared to thermal regeneration where harsh temperatures and attrition result in a reduction of capacity. Another important aspect in supercritical extraction relates to solvent/solute interactions.

Normally the interactions between the solid and the solute determine the ease of extraction, i.e., the strength of the adsorption isotherm is determined by interactions between the adsorbent and the adsorbate. However, when supercritical fluids are used, interactions between the solvent and the solute affect the adsorption characteristics due to large negative partial molar volumes and partial molar enthalpies in supercritical fluids. The thermodynamic parameters that govern the extraction are found to be temperature, pressure, the adsorption equilibrium constant and the solubility of the organic particles in supercritical fluid. Similar to the retrograde behavior of solubility in supercritical fluids, the adsorption equilibrium constants can either decrease or increase with an increase in temperature at isobaric conditions. This is primarily due to the large negative partial molar properties of the supercritical fluids. In addition to the above factors, the rate parameters like the external mass transfer resistances, the axial dispersion in the fluid phase, and

the effective diffusion of the organics in the pores also play a crucial role in the desorption process. A thorough understanding of these governing parameters is important in the modeling of the supercritical fluid extraction process and in the design, development and future scale-up of the process (Sovová, 2005: 35-38). Due to strict environmental regulations, supercritical fluids are used as replacements for conventional hazardous chemicals such as hexane. Supercritical fluid extraction has been proposed as an alternative technique for activated carbon regeneration. Over 99% of a majority of organics can be removed from contaminated activated carbon. Carbon dioxide has also been used with entrainers for the extraction of highly polar compounds (Liang, Liang, and Lin, 2012: 462).

### Ultrasonic Regeneration

A new ultrasonic method for regeneration of exhausted activated carbon was developed. Currently, one of the regeneration ways that is considered is the desorption by ultrasound. Experimental results showed that the method was effective. The operation time and type of ultrasound, the kind of adsorbate, and the size of granular carbon were investigated in the process of ultrasonic regeneration. The ultrasonic regeneration has many advantages, such as lower energy consumption, simpler process equipment, lower carbon loss, higher recovery of valuable substances, etc. (Liu, Yu,

and Han, 2007: 748).

The ultrasound study was used as an alternative method to regenerate granular activated carbon saturated with *p*-chlorophenol. Desorption experiments of exhausted activated carbon have been conducted in the presence of ultrasound of different frequencies (21,800 and 1660 kHz) and in silent conditions with stirring. The desorption rates were significantly increased by ultrasound. The ultrasonic effects increase with increasing acoustic intensity at frequencies of 21 and 800 kHz. The rates of desorption of *p*-chlorophenol from activated carbon appreciably increases by increasing the temperature. In all cases, this rise is more noticeable as ultrasonic power increases. The stability of activated carbon was not affected until an ultrasonic power of 38.3W was used, showing the adsorbent stiffness towards ultrasonic application. The addition of NaOH to the desorption system causes an enhancement in the amount of *p*-chlorophenol desorbed, especially in the presence of ultrasound. The rate of desorption was significantly increased by the addition of ethanol to the regenerating solution. This behaviour was higher in the presence of ultrasonic irradiation, with the exception of that at 1,660 kHz. In general, a synergetic enhancement of the desorption rate was observed when ultrasonic irradiation was coupled with chemical regeneration (Lim and Okada, 2005: 277-279; Zhang, Wang, and Liu, 2003: 59-60).

## Steam Regeneration

Steam regeneration is widely popular. Even though steam is readily available in industry it can also be generated by skid mounted boiler units which are available at relatively low cost (Gu and Bart, 2005: 297; Shah, Pre, and Alappat, 2013: 1078). Steam works especially well with hydrophobic organics, such as chlorinated solvents. Hydrophobic adsorbates have an added advantage in that they can be separated from the condensed water by gravity. Steam is less useful for hydrophilic contaminants such as alcohols, aldehydes, or ketones. If steam is used for these types of contaminants, the contaminants can be separated from the condensate by distillation. However, distillation raises the operation and maintenance costs of the system. Hydrophobic adsorbate desorbs at a temperature approaching steam distillation temperature and hydrophilic adsorbate desorbs at a temperature approaching their boiling points. After regeneration of an adsorbent bed, the condensed adsorbate can be recovered by separation techniques, multiplying benefits of steam regeneration (Pelech, Milchert, and Wróblewska, 2005: 519).

Steam regeneration has been repeatedly shown to be very effective and economic to regenerate active carbons. Heating and purging properties of steam are important for regeneration and contribute equally to

the regeneration of adsorbents. The source of energy for regeneration is the heat of the steam and the heat of adsorption of water. The heat generated by adsorption of water cannot be neglected as a driving force for regeneration of adsorbents. During steam regeneration, unlike purge gas regeneration, the temperature doesn't drop significantly along the length of bed as the heat released due to adsorption is uniform throughout the bed. In steam regeneration, the high heat of condensation of steam allows the bed to be heated rapidly, allowing for a faster desorption from the adsorbent; the desorbate is however only swept out of the bed when the latter is hot enough such that at least some steam remains in gaseous form and can sufficiently purge the adsorbate. Steam also activates adsorbent and does not cause polymerization of adsorbate (Alley, 2007: 111). The superiority of steam over nitrogen as a purging gas for low thermal desorption processes is already established. The temperature of the adsorbent bed is critical in steam regeneration. Upon contact with a cold bed, the inlet steam immediately condenses and the system pressure drops, however after some time the desired conditions roll back, during this process the heat of condensation leads to rapid but brief heating. Sometimes the bed is preheated to avoid condensation (Pelech, Milchert, and Wróblewska, 2005: 521).

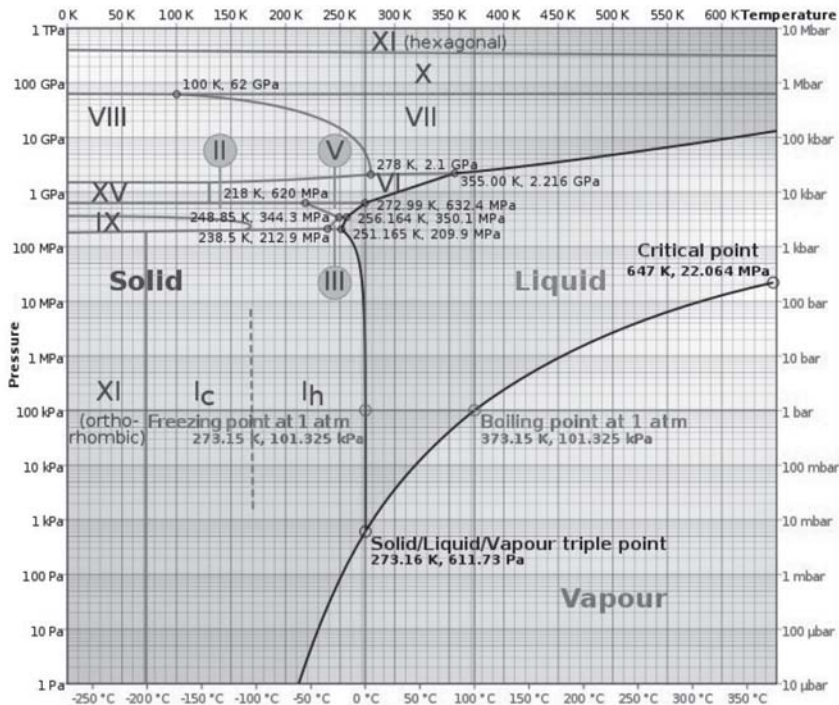
Time of regeneration is an important design parameter and also directly linked to energy consumption and thus cost of regeneration. Time of steam regeneration needs to be optimized as a prolonged time of regeneration causes over reactivation and leads to gasification of adsorbent, and damages porous networks of adsorbents. Regeneration is expected to be complete when effluent gas temperature reaches the regeneration temperature, although this is not applicable to adiabatic systems. Regeneration time is also defined as time at which effluent gas concentration reaches 1% of feed gas concentration (Cabal, et al., 2009: 1290). Five elementary processes take place during steam regeneration of exhausted activated carbon (Urano, Yamamoto, and Takeda, 1982: 181). (I) Thermal decomposition of activated carbon, (II) Oxidizing decomposition of activated carbon with steam, (III) Vaporization or sublimation of adsorbate, (IV) Thermal decomposition and carbonization of adsorbate, and (V) Oxidizing decomposition of carbonized matter with steam.

Different types of activated carbon respond differently to steam regeneration depending upon their composition and manufacture. In steam regeneration, additional adsorbate is introduced to the system as water, which is not desired in either phase and must be removed from adsorber as a re-adsorption

step. Hence, there arises a need for an energy intensive drying step. Despite this complexity, steam is the classical regeneration process for activated carbon. Steam regeneration can be high or low temperature. High temperature steam regeneration is carried in an inert environment in order to prevent an oxidative reaction of steam with adsorbent, and an adsorbate that may also cause char formation and result in deterioration of the porous network of the adsorbent. For the same reason low temperature steam regeneration can be carried in air flow, which is cheaper than inert flow. During the heating stage, the carbon passes through the following steps: drying (evaporation of water), thermal desorption (desorption of volatile compounds, 100-260 °C), pyrolysis and carbonization (pyrolysis and carbonization of non-volatile compounds, 200-650 °C) and gasification of pyrolytic residue at high temperature (650-850 °C) in the presence of limited amounts of oxidant such as water vapour, oxygen, etc. The selection of steam temperature depends upon the heat capacity of the adsorbent and the boiling point of organic adsorbate and solvency of inorganic adsorbate. For organic compounds, temperature of steam is generally taken 30-50 °C above the boiling point of adsorbate. The process of steam regeneration can be divided into the following three steps (Shah, Pre, and Alappat, 2013: 1079): (I) Desorption, (II) Drying and (III) Cooling.

Desorption is carried by steam at the desired temperature depending upon solubility of inorganic adsorbate or boiling point of organic compound. If the boiling point of the compound is less than 200 °C effective

regeneration can be achieved using steam. Once the temperature for regeneration is fixed, the combination of temperature and pressure is selected using phase diagram of water (Figure 1).



**Figure 1** Pressure-temperature Phase Diagram of Water. The Roman numerals indicate various ice phases (Choukrouna, and Grasset, 2007; Wikipedia free encyclopedia, 2013b)

The criteria selected for the mass flow rate of steam is the bed pressure drop and is generally kept the same as during the adsorption step. However, maintaining a minimum flow rate is essential to reduce the partial pressure of adsorbates in the vapour phase and to transfer the solvent out of the bed (Gu and Bart, 2005: 299).

The amount of steam required for regeneration will depend on the interaction between solvent and activated carbon. Küntzel, Ham, and Melin, on the comparison of two different steam flow rates, concluded that to achieve same degree of regeneration the same amount of steam will be utilized, and for high steam flow rate regeneration time will

be less and for low steam flow rate time of regeneration will be more (Küntzel, Ham, and Melin, 1999: 993). Steam consumption during the desorption step can be quantified either as grams of steam used per gram of adsorbate desorbed, grams of steam used per gram of adsorbent regenerated or the number of bed volumes of steam consumed to regenerate a single bed of spent adsorbent.

Generally, consumption of steam would be 3-5 kg of steam per kg of organic compound desorbed (Woods, 2007: 118). Drying of the bed is important as moisture left un-removed in the bed can drastically affect the adsorption capacity and other operational performances. Drying ensures that leftover removable moisture as well as adsorbate is removed in order to bring the bed back to identical defined starting condition as much as possible. Drying can be fast with heating or slow without heating. Drying is also fast at the beginning, when the bed is still warm, and it is slow after the bed has cooled to ambient temperature. Drying is the most time and energy consuming step in steam regeneration. The drying phase should be designed considering time and cost. In fact, in real situations in industry where steam is mostly available, drying is the only step in steam regeneration where the cost implication is very high. The drying gas used is generally air or inert gas like nitrogen (Gu and Bart, 1999: 860; Shah, Pre, and Alappat, 2013: 1081).

Adsorption is a very important unit process for pollution abatement. The efficiency of the adsorption process, its diverse applicability and its operator friendliness make it a more desirable process in industry for compliance and recovery purpose. However, disposal of spent adsorbents is still a topic of debate. With strict legislation surfacing for treatment and storage of spent adsorbent, many industries would like to shift to regeneration. This review presented various technical aspects of steam regeneration of adsorbents. Owing to availability and familiarity of steam in industry, it is highly beneficial to utilize steam for regeneration. However, drying a steamed bed is an energy intensive process and more research is required so as to minimize steam consumption and drying time during the regeneration cycle. Moreover, steam adsorbate reactivity needs to be studied to ensure thermal stability of the material during regeneration (Shah, Pre, and Alappat, 2013: 1082).

## **Conclusion**

Selection of a method of regeneration depends upon the priority of regeneration. If adsorbate or both adsorbent and adsorbate recovery is desired, physical means of regeneration are generally employed, e.g. thermal, pressure and microwave, etc. If adsorbent recovery or adsorbent recovery with destruction of adsorbate is required,

then oxidative or chemical regeneration may be preferred. However, this is not a hard and fast rule but techno-economics generally dominates the selection of procedure for regeneration. Regeneration has been also referred to as reactivation. A literature survey suggests that regeneration is a better term for the reuse of adsorbents as it includes both desorption and activation. In the best case, the agent of desorption is also a candidate for activation and hence the activation step is skipped and thus regeneration can be explained as a combination of desorption and activation. In the regeneration process, the following factors influence the effectiveness of the installation performance: the degree of solution purification, the separation of a mixture into the components, adsorbent stability, the degree of recovery of adsorbed components and energy consumption. The chosen regeneration method should ensure.

- The highest possible degree of desorption of the adsorbed compound.
- The least possible erosion and mechanical destruction of used adsorbent.
- Easy access and the ecological safety of used regeneration agent.
- Ease of separation of recovered or removed compounds from desorbate.
- Invariable qualitative composition of desorbed components.

However, the efficiency and performance of the different regeneration methods cannot be directly compared to each other if the regenerated carbon materials, the adsorbate, and/or uptake are different. It is well-known that both the adsorption and regeneration capacities of activated carbon strongly depend upon their unique physicochemical properties, mainly determined by the carbon precursor nature and the activation procedure. Therefore, a comparison among different regeneration methods has to be performed for the same saturated activated carbon.

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