Activation methods for activated carbon and its application in removal of metals and dyes from industrial wastewater by adsorption on activated carbon

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CERTIFICATE

This is to certify that the dissertation entitled “ACTIVATED CARBON ACTIVATION METHODS AND ITS APPLICATION IN REMOVAL OF METAL IONS AND DYES FROM INDUSTRIAL WASTE WATER BY ADSORPTION ON ACTIVATED CARBON “ submitted to Goa University in partial fulfilment for the award of degree of Master of Science in Chemistry, is a work done by MISS. SNEHAL DESSAI during the year 2021-2022 under the supervision and guidance of MR.VISHNU CHARI.

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DECLARATION

I hereby declare that the work embodied in this report " ACTIVATED CARBON ACTIVATION METHODS AND ITS APPLICATION IN REMOVAL OF METAL IONS AND DYES FROM INDUSTRIAL WASTE WATER BY ADSORPTION ON ACTIVATED CARBON" was carried out by me during the year 2021-2022 under the guidance of Mr.Vishnu Chari. In keeping with the general practice of reporting scientific observation, due acknowledgements have been made wherever the work described is based on the findings of other investigators.

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AKNOWLEDGMENT

The literature review titled: Activation methods for activated carbon and its application in removal of metals and dyes from industrial wastewater by adsorption on activated carbon has been successfully completed under the guidance of Mr. Vishnu Chari during the year 2021-2022 in the partial fulfilment of the requirements for the degree of Master of Science in Chemistry.

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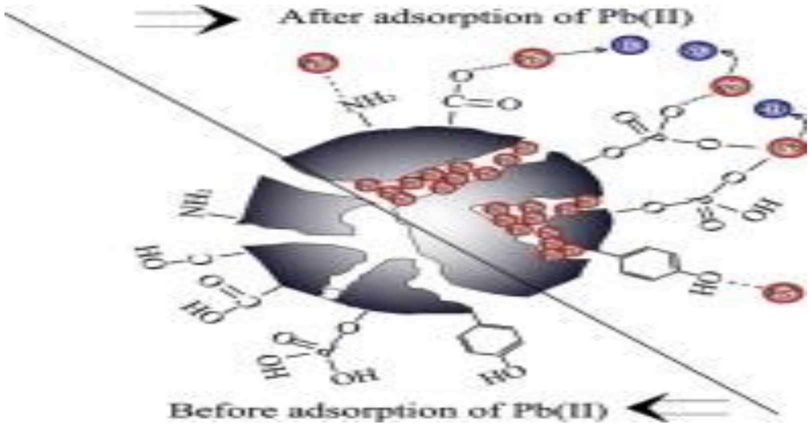
Activation methods for activated carbon and its application in removal of metals and dyes from industrial wastewater by adsorption on activated carbon

Introduction

The activated carbon is highly carbonaceous material[1] with high porosity[2–5] which has high physiochemical stability. Activated carbon has high mechanical strength[6,7] adsorption capacity[8], high degree of surface reactivity[9] with immense surface area. AC is also called as activated charcoal or activated coal and sometimes called activated sponge[10]. AC can be obtained naturally and synthetically[11]. The starting material used and also the precursor plays an important role in deciding quality of the resulting AC[12–15]. AC can be obtained from different types of raw material[16,17]. It can be produced from animals, minerals and vegetables. The raw materials which are used for production of AC depends on its price, purity of raw material, extent of its activation[4]. The agricultural by-product which are used as raw material for production of AC can be converted into AC through pyrolysis under certain controlled conditions[18]. The use of agricultural waste raw material for AC production has been found to be renewable and also less expensive and ultimately could utilise the waste to produce carbon which has many applications[18].Therefore now more focus of AC preparation is from agriculture waste and lignocellulose which are very effective and less expensive[10] such as coconut shel[19]l, olive stone[20], bamboo[21], fruit peels[22] etc.

Natural water contamination is an environmental problem[23]. The release of toxic pollutants in water bodies through disposal from various sources such as agriculture runoff, domestic and industrial wastewater treatment plants causes pollution of water source[24]. The conventional and existing biological processes are often used for water purification[25]. An effective tertiary treatments such as adsorption, is widely used for the treatment of wastewater due to its easy operation, cost effectiveness, energy requirement is less, and its recycling potential[26–28]. Adsorption is a mass transfer phenomenon that involves the sorption of adsorbate, solute particles on the surface of adsorbent which occurs by physisorption and chemisorption[28]. The adsorbent should have simple and scalable route for synthesis, it should be easily available, non- toxic, less expensive, and reusable[29–32]. Activated carbon is associated with low cost, simple method of synthesis, larger specific area and has also shown promising results for waste water treatment[32]. The adsorption process involves the movement of contaminants from waste water bodies to the surface of adsorbent and then within the bulk of adsorbent. The adsorption process is achieved through various processes including pi-pi interaction, hydrogen bonding dipole- dipole, induced dipole and Van der Waals forces[32].



Adsorption of Pb(II) by activated carbon[33]

There are three main types of activated carbon produced

(1) Powdered Activated Carbon

(2) Granular Activated Carbon

(3) Extruded Activated Carbon

Powdered activated carbons generally fall in the particle size range of 5 to 150 A$^{0.}$ Granular activated carbon generally fall in the particle size range of 0.2 mm to 5 mm .

There are basically two methods for production of activated carbon

(1) Physical activation

(2) Chemical activation[34]

Physical activation consists of two different steps. First step is Carbonisation or Pyrolysis of starting raw material. It is used done at high temperature range between 700-900 ^{0}C under an inert atmosphere which prevents combustion of carbonaceous material. Carbonisation is a process that produces elementary stable structure with partially developed porosity. In this step heteroatoms and volatile substances are removed converting raw material into bio char with high carbon content. Second step is gasification; in this step removal of most reactive carbon atoms is done that generate characteristic porosity of activated carbon. Usually gasification agents used are CO_2 or O_2 with temperature range of 700-900 ^{0}C. When pure O_2 is used temperature should be low due to its high reactivity[35–38]

The second method of synthesising activated carbon is Chemical Activation. First step is impregnation of raw material with activating agent[35,36] . Activating agents generally used are $ZnCl_2$[39] , H_3PO_4[40] , KOH[41] , NaOH[41] , $FeCl_3$[42]. Second step is thermal treatment in an inert atmosphere, temperature range depends on activating agents used. In this step reactions of de-polymerisation, condensation and dehydration takes place .Next step is washing to remove by products and activating agents used. Last step is drying.

Advantage and disadvantages of Physical and Chemical activation

Physical activation is inexpensive whereas chemical activation is expensive. Physical activation is environmental friendly. Disadvantage of physical activation is it requires high temperature whereas chemical activation requires low activation temperature with shorter time than chemical activation. Activated carbons produced by chemical activation usually have a relatively higher specific surface area and are more mesoporous than those produced by physical activation[43]. The yield of AC obtained by chemical activation are usually higher than those for physical activation, because the chemical agents used generally possess dehydrogenation properties which inhibit the formation of tar and reduce the production of other volatile products[44]. AC are generally have high surface area and pore structure developed is complex resulting from physical and chemical activation processes[34]. Activated carbon with high surface area are used as adsorbent for the adsorption for the adsorption of gaseous and liquid phase. The combination of physical and chemical activation accelerates the chemical changes in the sample and facilitates the removal of hydrogen and oxygen which results in increased amount of carbon[45].

Activated carbon has pores classified into three groups

Micropores, mesopores, macropores. Micropores with 0-2 nm width, mesopores with width 2-50nm and macropores with width greater than 50 nm[46].

The modification of AC’s surface chemistry is taken into consideration as a promising and appealing path towards new applications of AC in several areas. The process of modifying AC entails oxidation and further grafting of functional groups (i.e., carboxylic acid, amine, etc.) and metals (Mn, Cu, Fe, etc.) onto the AC surface through chemical, Electrochemical, plasma, ozone, and microwave methods.

Alkali treatment

The alkaline treatment of AC results in positive surface charges, which leads to adsorption of negatively, charged species in larger quantities. Production of ACs in inert hydrogen and ammonia (NH3) atmosphere at high temperatures yields alkaline surface properties[47]. The surface of AC was modified with NH3 gas to perform the adsorption of phenol from water, which existed in anionic forms. It was observed that NH3 treated AC displayed improved performance for phenol adsorption due to surface modifications[48]. The basicity (hydrophobicity) of the carbon surface and the electron-withdrawing potential of the substituents on the aromatic ring increases the adsorption affinity of phenolic compunds[48]. It was reported that Cr (VI) adsorption was not improved even after alkaline treatment using NaOH, which increased the number of oxygenated surface groups and reduced the SSA. In another study, basic groups and carbonyls on AC surface were also introduced from urea treatment[49] . Further, the adsorption capacity of the AC for phenols was weakened by the presence of surface functional groups. The highest phenol uptake potential was found in urea-treated samples with a basic character and high nitrogen content, followed by nitric acid-treated carbons[49]. In a study, Shaarani and Hameed modified AC using NH3 solution to study the adsorption of 2, 4-dichlorophenol. Ammonia treatment resulted in increased basic nature of the AC and created a more positive surface, which enhanced the phenol uptake capacity by 22.9%. Further, NaOH treatment of AC prepared from corncob resulted in a 44% increase in the qmax for ammonium ions[50].

Acid treatment

Acid treatment of carbon is commonly used to oxidize porous carbon surfaces since it improves the acidic property, eliminates mineral elements, and improves the presence of hydrophilic surface groups (O–H, C=O, C–O, etc.)[51] . Among all the acids used for this purpose, HNO3 and H2SO4 are extensively studied. On the other hand, acidic functional groups (i.e., oxygen functional groups with proton donors) on AC surfaces were extensively used for the treatment of heavy metals because metals tend to form complexes with the negatively charged acidic groups[47]. AC treated with HNO3 was compared with untreated AC for the adsorption of Cd. It was observed that HNO3-treated AC adsorbed 8.7 times more Cd (0.165 mmol/g) than untreated AC (0.019 mmol/g)[52]. Further, modification of AC was done using cetyltrimethylammonium bromide (CTAB), which achieved an adsorption capacity of 555.56 and 625 mg/g for CR and DB-6, respective Further, the adsorption of cationic dyes on tea leaf-derived AC was seen to be effectively enhanced when the AC was modified using sulfonic acid[53]. The qmax for cationic dye (i.e., Rhodamine B (RhB)) was found to increase from 398.4 mg/g to 757.6 mg/g for acid-modified AC. On the other hand, qmax decreased while removing anionic dye (i.e., orange G) from 318.5 mg/g to 105.7 mg/g, suggesting that the surface modifications using sulfonic acid treatment improved cationic dye adsorption. Sulfonic acid treatment enhances the negatively charged surface characteristics of the AC, which in turn, results in enhanced electrostatic interaction between positively charged dye molecules (cationic dye) and negatively charged AC surface. In another study, Anjum et al.[54] used mild oxidizing agents (i.e., citric acid, tartaric acid, malic acid, and salicylic acid) in conjunction with NaOCl to produce oxidizing-AC. Surface modification due to oxidizing agents led to enhanced removal of BTX-compounds i.e., benzene (260.78 mg/g), toluene (263.16 mg/g), and p-xylene (269.55 mg/g). Surface oxidation of AC led to the increased amount of –COOH groups which provide enhanced π-π interactions and hydrogen bonding between AC surface and BTX compounds.

Microwave

The ability of microwave radiation to heat materials at the molecular level, resulting in homogeneous and rapid thermal reactions, has attracted a lot of attention in recent years. Microwave heating is more advantageous than traditional heating since microwave energy heats the material from inside out and has rapid heating capability. It eliminates the need of heat convection through a fluid and there is no direct interaction between the microwave heating source and the heated material. Microwave processing systems are small, portable, easy to maintain, and affordable[55]. Accordingly, Wang et al.[56] conducted microwave irradiation (800 W) for 10 min of the chemically activated (using ZnCl2) AC prepared from sewage sludge. The adsorption experiment data revealed that the Langmuir isotherm model provided a good fit for Cu(II) with qmax of 10.56 mg/g. The pH of the solution significantly improved the adsorption behaviour of AC, as an increase in pH led to an increase in adsorption capacity for this study. Further, Puchana-Rosero et al.[57] used tannery waste sludge to prepare AC. The AC was chemically activated using ZnCl2 under microwave heating at 1200 W for 20 min and developed an Specific surface area of 280.01 m2 /g and Vp of 0.286 cm3 /g. Liu isotherm models provided the best fit for the experimental data with qmax of 1108 mg/g and 589.5 mg/g for acid black 210 and acid red 357 dyes, respectively. Dye adsorption on the AC was mainly governed by hydrophobic interactions, hydrogen bonding, π-π interactions, and electron donor-acceptor interactions. Further, Koc et al.[58] used ZnCl2 and H2SO4 to chemically activate the carbon derived from orange, pomegranate, and pineapple peels. The peels were microwave treated at 800 W to obtain AC to remove Zn from the wastewater. Results indicated that all these adsorbents had similar adsorption capacity, i.e., 37.64 mg/g for orange peel 36.99 mg/g for pineapple peel, and 37.17 mg/g for pomegranate peels. Microwave pre-treatment was effective in developing the pore structure of AC.

Ozone treatment

Rivera-Utrilla and Sanchez-Polo[59] studied the adsorption of naphthalene sulphonic acids on AC treated with ozone. It was seen that ozone treatment increases the number of electron-withdrawing oxygenated groups, thus decreases the adsorption capacity of Naphthalene sulphonic acids. Further, an increase in the sulfonic groups in the aromatic ring also decreases the adsorption capacity. The adsorption process depends on pH and is a complex relationship of electrostatic and dispersive interactions. Ozone and heat treatment helps to control the surface chemistry of AC[60], as ozone-treated AC prepared through CO2 and steam activation displayed an specific surface area of 603 and 968 m2 /respectively. Surface modification of AC using ozone has shown that ozone treatment transforms basic sites to acidic sites due to oxidation and decreases the adsorption capacity for MB. In another study, Bohli examined Ouedern AC with O3, which lead more oxygenated functional groups on the surface of AC. Further, the adsorption capacity for CO(II) and Cu(III) using ozone-treated AC were 16.2 and 17.9 mg/g, respectively, which was more than 10.25 and mg/g, respectively, as achieved by unmodified AC. Similarly, AC derived from rice husk using ozone as an activating agent developed an Specific surface area of 380 m2 /g and exhibited removal efficiency of 95% for Cr (VI) [61]. Cagnon et al. [62] used AC modified by O3 to study the adsorption of gallic acid. It was observed that ozone modifies the surface properties of AC as described earlier and thus increases the adsorption capacity by 28% compared to non-oxidized AC. Further, with an increase in ozone exposure time, a decrease in rate constant and adsorption energy was observed. In contrast, a decreased adsorption of phenol, p-nitrophenol, and p-chlorophenol on ozone-treated AC was observed by Alvarez et al.[63] . They further found that π-π interactions of the aromatic compounds and oxygenated surface groups were the main force behind adsorption, but ozone in large amount decreased the adsorption of aromatic compounds.

Biological treatment

Biologically activated carbon (BAC) is generated when the spent activated carbon becomes saturated with organic compounds. The microorganisms utilize the organic matter present in the pores of AC as a source of nutrients and create a biofilm on the surface and in the pores of AC, thus producing BAC. The different contaminants such as organics, inorganics, heavy metals, and EDCs can be effectively adsorbed using BAC. The removal of EDC, i.e., 17 β-estradiol from drinking water, was carried out using BAC. The removal performance of BAC was better than GAC with an effluent concentration of 50 mg/L for 17 β-estradiol[64].
A column study observed that the DOC removal was 64.5% and 81% for BAC developed from steam and chemically activated AC. In addition, BAC columns were also capable of removing total nitrogen efficiently. BAC is extensively used in conjunction with other techniques at different stages of treatment, mainly with filtration units[65]. Sbardella et al.[66] used the BAC-filtration process to remove the pharmaceutically active compounds. The BAC-filtration process achieved the removal efficiency for azithromycin, bezafibrate, ofloxacin, irbesartan, propranolol, and ciprofloxacin, as 63%, 67%, 77%, 79%, 83%, and 86%, respectively. Other researchers have also used BAC systems to adsorb pesticides[67] phenols[68]

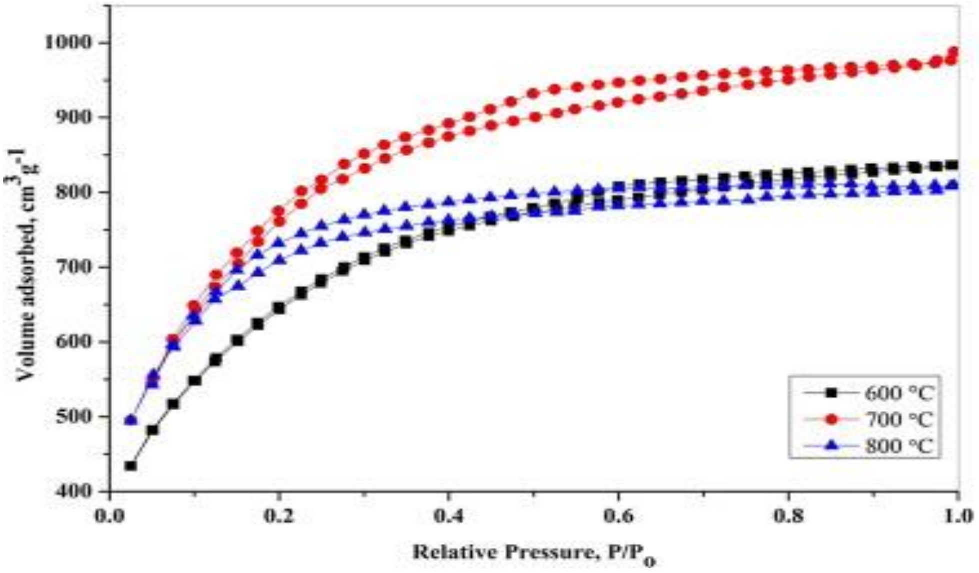
Methods for characterisation of AC

Iodine test

Determination of iodine number is one of the methods commonly used in industry utilizing AC. The iodine number indicates the porosity of activated carbon and it is defined as the amount of iodine adsorbed by 1 g of carbon at the mg level. Higher number indicates higher degree of activation[69]. This method was used to examine the adsorption of iodine on the oxidised active carbons. Ion exchange mechanism involving hydroxyl groups that bind to a positively charged carbon surface by electrostatic interactions as well as specific interaction are the two effects contributing to the iodine adsorption. Other adsorption mechanism has also been proposed. This includes the adsorption of the I_3^- complexes. It was seen that iodine can be adsorbed on activated carbons only in a form of elementary I_2 that results from the oxidation of iodide ions on the surface of carbon[70]. Standard determination of iodine adsorption number comprises the measurement of iodine amount in the adsorption layer of an activated carbon sample. The change of the bulk concentration results in the changes in the interfacial layers, which induces mutual displacement of the solution components from the adsorbed layer. During excess adsorption from the solution there are no unoccupied sites on the surface, which implies that the same iodine amount occupies the same surface in the different carbon samples. The differences concern only the availability of the adsorbent surface or the iodine on the different carbon samples. Such a hypothesis allows to define so called surface area occupied by the iodine atom[70].

BET method

Characterization in terms of specific surface area, pore volume, and pore diameter of the obtained activated carbons was determined by N_2 adsorption with surface area and pore size analyser using BET method. The BET is performed based on the adsorption isotherms of non- reactive gas molecules such as nitrogen at 77K or argon at 87K at a pressure range that covers the monolayer coverage of molecules[71]. The obtained isotherms are transformed into the linearized BET plot, where the monolayer loading can be determined. The ability of BET approach to accurately estimate the accessible surface area can be largely subject to pore size and its distribution in a structure[71].



Nitrogen adsorption isotherm for activated carbon at different temperature[72]

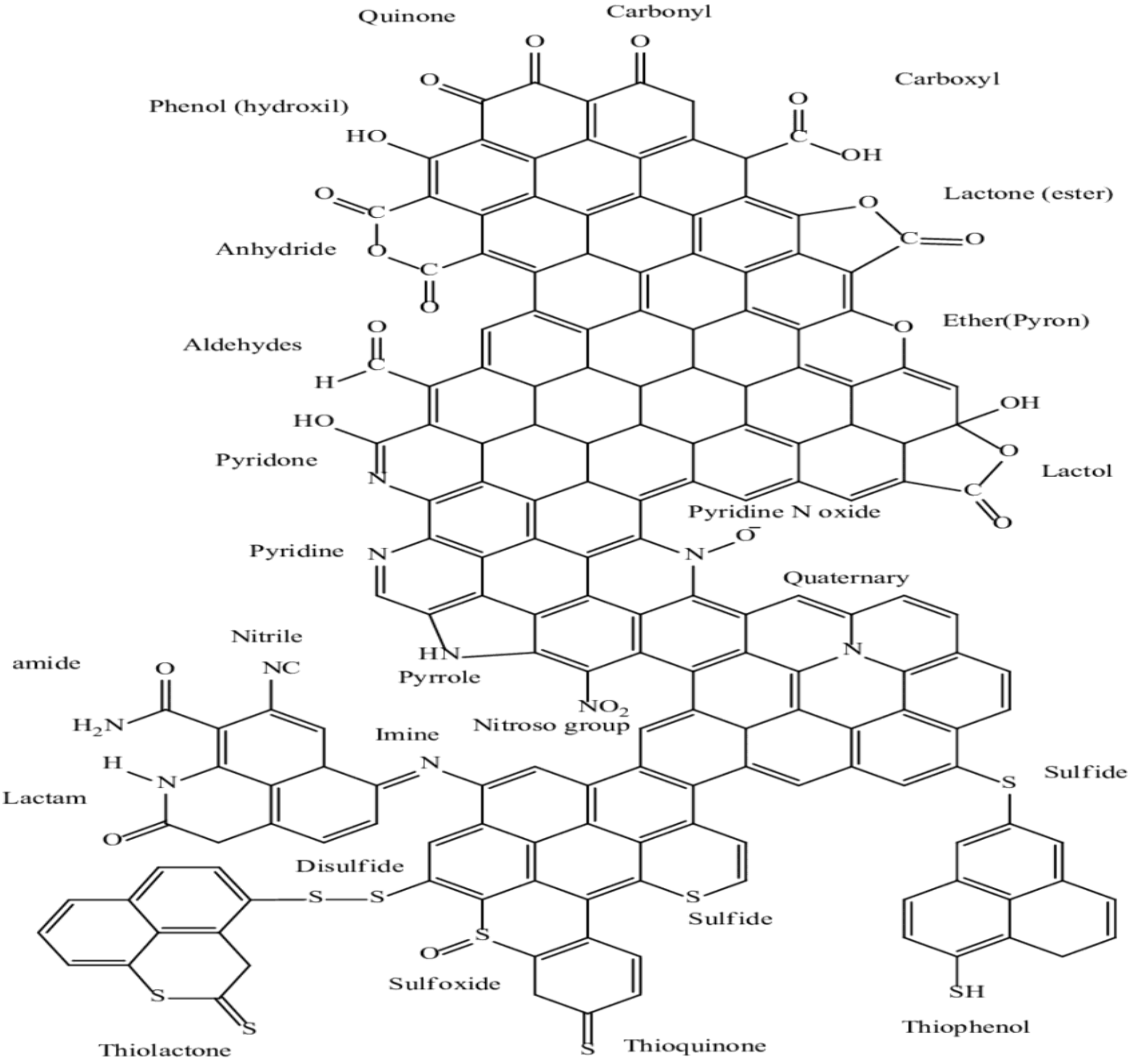
PZC determination

PZC is called as the pH for which the substance under consideration has net neutrality. The pH drift is a quick and reliable method for determination of PZC and is believed to be appropriate for charcoal. The most significant qualities of PZC is that the substance under consideration has a positive charge below PZC and negative charge beyond PZC. This unique feature of having positive and negative charge allows cations and anions to be adsorbed on the surface of charcoal[73,74].

Fourier-infrared spectroscopy

Infrared transmittance measurements of the activated carbons were carried out at room temperature. The surface functional groups of the activated carbon fibres were analysed by FTIR spectrophotometry[74]

Oxygen , Nitrogen and sulphur functional groups on the surface of activated carbon[75]



Activators used for production of activated carbon are divided into three types

(1) Acid activation

(2) Strong base activation

(3) Neutral activation

Acidic activator is H_3PO_4, Basic activator is NaOH, KOH and neutral activator is $ZnCl_2$ and $FeCl_3$.

Activation by H_3PO_4

Phosphoric acid is widely used as an activating agent. It is because it has non-polluting character compared to Zinc chloride and it can be eliminated by leaching with water with the recovered phosphoric acid being recycled for future use[43]. First step of activation of carbon by phosphoric acid is impregnation of raw material. The biomass precursor is taken and mixed with phosphoric acid and kept overnight at room temperature whose concentration is

20 wt% and 50wt% varying precursor and weight ratios of acid solution. Sample after completion of impregnation were further treated thermo chemically which is done in three ways (1) Thermal activation by pyrolysis in inert atmosphere. Samples after impregnation were heated at a heating rate of 3^0C/min in an inert atmosphere of Nitrogen and then final treatment is done at 600^0C for a period of one hour. (2) Activation with consecutive pyrolysis in inert atmosphere and in presence of steam. Steps similar to (1) were first carried out and the samples were then submitted to additional pyrolysis at same temperature 600^0C in a flow of steam for one hour. (3) Third way is activation with steam pyrolysis .This is done after impregnating the sample. Samples were directly pyrolysed at 700^0C in a flow of steam for 2 hour. After cooling the sample, hot water washing was given till pH becomes neutral and finally sample is washed with cold water to remove excessive phosphorus compounds. Sample was dried to obtain product[45].

Characteristics of carbon activated by acid activator

The oxygen content of sample which was treated by pyrolysis in steam was found to be higher. The samples which was pyrolysed in steam alone and the sample which was pyrolysed in steam as well as in inert atmosphere was having high carbon content, means they have undergone effective carbonisation. The chemically activated carbon sample which is pyrolysed in inert atmosphere of nitrogen has lowest pH 4.5. The samples activated by both physical and chemical activation that is activation in steam and nitrogen has pH 5.9. The sample which is activated in steam alone has highest pH 6.5. This helps to determine the surface properties of the carbon and hence their quality as ion exchangers, catalysts and catalysts supports. Iodine number is used to determine adsorption capacity of activated carbon prepared by impregnation with H_3PO_4. Pyrolysis of sample done only in nitrogen has low iodine number than those which is pyrolysed only in steam and other sample which is pyrolysed consecutively in nitrogen and steam. Also increasing the concentration of H_3PO_4 from 20 wt% to 50 wt% increases the adsorption capacities. BET surface area is more of then carbon activated by pyrolysis in steam than other two samples which is chemically and physically pyrolysed. Steam activation promotes narrower micro pore formation and has lower iodine number. This is due to lower access of iodine in narrower pores. Phosphoric acid with steam pyrolysis has positive effect, because surface area of the sample is increased and has well developed porous structure and favours adsorption properties of carbon. The presence of steam has also helped to remove phosphor from product and has good adsorption capacity to remove metal ion during water treatment.

The role of phosphoric acid in activation process is phosphoric acid combine with organic species to form phosphoric linkage, such as phosphate and phosphate esters that resulted in broader porous structure in activated carbon[76]. Increasing the amount of phosphorus leads to an increase in the volumes of micro and mesoporosity[77].

Activation by $FeCl_3$

$FeCl_3$ has low cost and it causes no harm to the environment while other activating agents like KOH, NaOH and H_3PO_4 are either strong acids or bases. In case of $ZnCl_2$, ions of Zn and its oxides are toxic[78]. There are two methods for activation of carbon by $FeCl_3$ .In physical activation pyrolysis or carbonisation of the carbonaceous precursor at high temperature between 700-900 ^{0}C; it is done under an inert atmosphere to avoid combustion of carbonaceous matter. Next step is gasification. Temperature around 700-900^{0}C is used with vapours of water or carbon dioxide gasification. In chemical activation first step is impregnation. In impregnation carbonaceous material is mixed with $FeCl_3$. It is either performed in aqueous solution or by physically mixing between precursors and activating agent $FeCl_3$. In physical mixing it avoids the drying step but in aqueous solution it requires drying step before pyrolysis. After drying pyrolysis or thermal treatment is carried out to get activated compound[79].

Characteristics of Carbon activated by $FeCl_3$

The activated carbon prepared by using $FeCl_3$ are found to be micro porous from higher percentage obtained of S_{mic}/S_{BET} parameter where S_{mic} is micro pore surface area and S_{BET} is BET surface area. Activation temperature required is 700-900 ^{0}C .$FeCl_3$ activated carbon has surface area up-to 1700 m^2g^{-1}. The surface area values are higher than those activated by $ZnCl_2$ or H_3PO_4, However Porosity developed via $FeCl_3$ is less than obtained by KOH. FTIR analysis suggests presence of acidic group on the surface of activated carbon. From magnetic hysteresis curve which showed low coercivity and negligible magnetic hysteresis cycle, confirms that it has super-paramagnetic behaviour which can be used to remove pollutants from aqueous medium[79].

NaOH / KOH

Chemical activation using bases like KOH and NaOH is an effective method for preparation of AC. Both hydroxides are efficient. Disadvantage of this bases are they are more expensive and requires additional washing. Hydroxides are also corrosive in nature.

Characteristics of carbon activated by basses

Chemical activation using chemicals like hydroxides are more useful than physical activation in the development of highly porous structure. It is also found to be selective than physical activation. Pore size distribution of AC prepared by using KOH are found to be narrower than obtained by using NaOH, But NaOH develops more porosity than KOH.

Applications

Activated carbon when added to water it develops charge on the surface and exhibit amphoteric properties. Surface groups present on carbon are responsible for adsorption of metal ions from waste water and release of H^+ ions. The presence of surface charge leads to increase in number of counter ions near the charged surface, forming electrical double layer. Adsorption of cation of metal is totally dependent on the pH of the solution[80].

The well- known application of activated carbon is adsorption[81]. Activated carbon derived from lignocellulosic products and activated by treatment with phosphoric acid are usually used to decolourise or remove organic pollutants from liquids[43]

Methylene blue dye adsorption

MB has serious attention due to its positive and negative aspects. High blood pressure, irritation of the skin with redness and itching, irritation of throat, mouth, oesophagus, and stomach, gastrointestinal pain, nausea, vomiting, diarrhoea, dizziness, headache, and fever are some general problems associated with dye[82]

Adsorption of dye using $FeCl_3$ has become popular especially MB because of its super-paramagnetic behaviour and the surface of dye activated by $FeCl_3$ has acidic nature and its point of zero charge (pH_{PZC}) value is less than 5. When the pH of the solution is higher than (pH_{PZC}) , the surface of absorbent becomes negatively charged and this attracts positively charged methylene blue molecules whose pka is 0.04 towards its surface, and increases its adsorption capacity. Maximum adsorption capacities between 163 and 192 $mg.g^{-1}$ were obtained increasing saturation capacity with adsorption temperature $25\text{-}55^0C$[79]. The adsorption process is spontaneous and endothermic and occurs through interaction between positively charged Nitrogen of methylene blue molecule and $COOH^-$ group on surface of activated carbon[83]. The low cost and effective carbon adsorbents derived from pumpkin peels for removal of Methylene blue dye has found to be sustainable solution for removal of methylene blue dye from waste water. It was activated by natural antioxidants present in beetroot extracts. It has been explored as a green approach which eliminates the use of toxic chemicals. The clearly visible macro pores present on surface of BAC helps in easy mobility and diffusion of dye molecules into the micro porous structure and facilitates the higher adsorption of MB molecules. The functional group present in BAC are C-O of alcohol, ether, ester, carboxylic acid and anhydride. C=C Aromatics, OH group of aldehyde, ketone, carboxylic acid, NH deformation. BAC showed type VI isotherm behaviour. This shows incomplete reversibility and desorption plot lying above the adsorption isotherm with hysteresis existing between them attributed to the presence of slit shaped pores. BAC showed highest adsorption capacity 198.15 $mg.g^-$ for MB at 200 $mg.L^{-1}$ at pH 7[84].

Eriochrome black T adsorption

Negatively charged Eriochrome black T can also be adsorbed by $FeCl_3$ activated carbon due to changes in attraction repulsive forces between carbon and dye molecule it follows opposite trend to pH[85]. Sewage sludge activated by Fenton's reagent and calcinated to form activated carbon. SAC had a porous structure and high specific area due to presence of uniform abundant tiny pores. Graphite like structures is present on SAC and numbers of functional groups are also present. Therefore prepared SAC can be used as adsorbents for EBT removal from water bodies and it was found to exhibit excellent adsorption properties. Through adsorption isotherm, kinetic, and thermodynamic studies, it was found that the adsorption capacity of SAC was greatly improved by Fenton reagent activation. Adsorption capacity was found to be 178.2 $mg.g^{-1}$ in 48 h at temperature of 318K and pH 6. The adsorption of EBT onto Fenton activated SAC was naturally endothermic and spontaneous, and exhibits multilayer adsorption, and involves both physical and chemical processes[86]

Metal ions adsorption

Chromium

Chromium is introduced to the environment due to improper discharge of chromium-containing effluent of industries such as electroplating, battery, dying, petroleum refining[87]

Adsorption of heavy metals from water on $FeCl_3$ activated carbon has found to be successful. Adsorption of Cr (VI) at pH 2 was found effective. Adsorption proceeds through electrostatic attraction, reduction, complexation. At adsorption pH, the mainly negatively charged Cr(VI) species (chromate, CrO_4^{-2}, and hydrogen chromate, $HCrO_4^-$) have strong electrostatic attraction through the positively charged surface of the activated carbon (Ph_{Pzc}=2.56). In the positively charged surface of the carbon adsorbent, the adsorbent, the adsorbed Cr(VI) is reduced to Cr(III) by the pi electrons of the aromatic rings of carbon[23,88]

Fluoride

Many industries are involved in discharge of fluoride in surface water and ground water. These industries are semiconductor manufacturing factories , pharmaceuticals companies , beryllium extraction plants, fertilizer industries[89]. The adsorption of Fluoride by $FeCl_3$ activated carbon with maximum adsorption capacity close to 10 $mg.g^{-1}$ was found to be spontaneous and endothermic. ln case of $pH<pH_{PZC}$, the adsorbent surface charge is positive whereas when $pH > pH_{ZPC}$, the surface charge is negative. The activated carbon was found to have more acid active groups than basic components on their surface. This is due to minimisation of acidic groups with increase in carbonisation temperature, and accordingly, the loss of significant acidic groups such as phenolic, carboxylic, or lactonic groups is also enhance. The thermal activation caused liberation of acidic, metal oxides on the material surfaces. In contrast, the number of basic groups increases with increase in carbonisation temperature. The pH_{PZC} study showed that positive charge behaviour will be favourable for the adsorptive removal of anionic pollutant such as fluoride when pH is less than pH_{PZC}[89].

Activated carbon treated quaternary ammonium salts Decyltrimethylammonium can be effectively used for Fluoride adsorption. The electrostatic interaction between F^- and the N^+ head due to electrostatic interaction and hydrogen bonding between F^- and hydrogen atoms on the quats chain were responsible for the enhanced adsorption of fluoride from aqueous solution. Surface modification increased positive surface charge and fluoride adsorption capacity[90].

Mercury

Mercury is environmentally toxic element. It bio accumulates in the aquatic environment and then reaches the human beings through food chains especially through fishes. It causes various neurological disease and disorders. Activated carbon are found to be effective sorbents for gas phase mercury adsorption

The removal of mercury using a $FeCl_3$ activated bio-char was reported by Yang et al. Work proposed two active sites for adsorption/oxidation of Hg^0, namely Fe^{+3} and oxygen rich functional groups specially C=O groups. Impregnation of bio char derived activated carbon by halides has known to remove mercury from aqueous medium effectively. Activated carbon impregnated by iodide was most effective (98-100%). The gas molecule reacts with surface iodides forming mercury iodide by chemisorption. The conversion of mercury to mercury iodide is thermodynamically favoured. This shows its high efficiency in mercury adsorption. Increasing the temperature from 25 to 135^0C, the mercury removal efficiency is increased to 90-100%[10]..

Nickel

Contamination of water bodies by nickel from electroplating industries is major cause of concern[91] . Nickel can be removed from water by activated carbon obtained from bamboo. It accounts for removing 98.7% of nickel from electroplating industry waste water at an optimum adsorbent dosage of 1.5g/L. From FTIR analysis alkanes, carboxylic acids, aldehydes functional groups in bamboo activated carbon contributed for removal of Nickel. The weak acid ion exchange character of bamboo activated carbon is effectively used for removing various ions present in any waste water. Silica activated carbon composite (2:3) found to show greatest removal percentage for 30 and 100 ppm Nickel. From SEM images it was found that AC was a micro particle with an average size of 25 micrometre, while Silica was nanoparticles having an average size of 12 nm. IR spectra metals adsorbed of Silica/AC were reflected in the shifts in wave number from 796.6 to 854.47 cm^{-1} for Nickel ions. This shifts indicated that there were binding processes taking place on the s Silica/AC (2:3) composite was the most effective micro particle for nickel removal and it is highly recommended to be used in water treatment to remove nickel. Surface of activated carbon and the greater the shift stronger the bond between AC and Nickel ions[92]

Copper

Copper is commonly found in industrial wastewater. It has been widely used in semiconductors, electronic product manufacturing, and electroplating. Copper poisoning can cause nausea, diarrhoea, liver and kidney failure due to long term exposure to copper through contaminated food and water sources.

Activated carbon oxidised by nitric acid and adding iminodiacetic acid to the carbon has modified the activated carbon in such a way that it has high affinity for copper present in waste water due to oxygen containing groups on activated carbon. Because of high affinity between iminodiacetic acid and metal ion it can easily remove copper ions from low concentration solution and retain high adsorption capacity in high ionic strength. They are cost effective highly potential adsorbents for water treatment[93].

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Cadmium

Cadmium is introduced in water bodies from smelting, metal plating, agricultural by-products. Cadmium present in waste water can be removed by powdered activated carbon. The fraction of cadmium removal is found to increase from zero to one over a relatively narrow pH range (2-3). The agricultural waste C. pentandra hulls were found to be economical and useful for the economic treatment of wastewater containing cadmium metals. From FT-IR spectrum additional peaks at 1457 and 1118 cm^{-1} indicated the presence of C-H and S=O groups. The C=O and S=O functional groups show very high coordination with heavy metals. Hence, the good sorption properties of adsorbent towards cadmium. With increasing pH beyond PZC (5.7) the negative charge on the surface of adsorbent increases there by enhancing the cadmium adsorption[93,94].

Arsenic

Long term exposure to Arsenic can cause cancer of bladder, lungs, skin, kidney, liver prostate. Sources of Arsenic include industrial waste, mining, agriculture. Activated carbon oxidised chemically and then loading with iron has greatly improved its arsenic adsorption capacity from waste water. Iron preloaded carbon has better adsorption capacity than virgin carbon. Nitric acid and Sulphuric acid oxidation of carbon achieved more iron loading than oxidation with nitric acid alone. Iron contents plays important role in arsenic adsorption, therefore Iron is loaded in such a way that much of the Iron is available to adsorb Arsenic. The magnetite activated carbon fibre was able to reduce As (v) concentration below its maximum contaminant level regulated by the US EPA for drinking water in a wide pH range without formation of more poisonous As (III). Kinetic experiments indicated that the diffusion of As(V) within the pores of magnetite activated carbon was more rapid than that of simple activated carbon and the surface reaction was the dominant step in the adsorption of As(V) onto MACF. Compared to raw AC , the MACF had a wider applicable pH range from 2 to 8 for As(V) uptake[81].

Lead

A toxic heavy metal, lead is generated by various industries such as metal plating, metal finishing, battery manufacturing, and electronic industries[95]. The constant exposure to lead is can cause liver, kidney damage, infertility and abnormalities in pregnant women. Lemna minor using one- step H_3P0_4 activation is used for Pb (II) removal. LACs possess high mesoporosity and surface area according to BET analysis. FTIR analysis and XPS analysis showed the presence hydroxyl, carbonyl, amide and phosphate functional groups on the surface which lead to binding of Pb(II) on the surface through strong chemisorptive bonds or through ion exchange. LACs could serve as an inexpensive, environment friendly and efficient adsorbent[33].

Conclusion

In recent handling of hazardous and poisonous adsorbents has become a challenging task because of their toxicity towards the environment and their carcinogenic effects on living organisms. In such cases, modification of AC has proved to be efficient approach.

Chemical activation is found to be more economical than physical activation due to high carbon efficiency, requires low activation temperature, short processing time and develop more porous activated carbon structure.

The selectivity of activating agent depends on precursor and adsorption application.

ACs derived from shells, leaves, and other agricultural sources may be effectively used for dyes, heavy metals, organics removal.

Modification of activated carbon by acid adds acidic functional groups to AC and metal species attraction is enhanced. It may decrease BET surface area. Organic uptake is affected.

Microwave assisted heating develops a better pore structure, which enhances the adsorption ability. Organic uptake is enhanced. Good activation and yield can be achieved.

Biological treatment of AC aids utilisation of spent acid. Bacterial action in conjunction with adsorption increases contaminant removal. Microbes may block active adsorption sites

Ozone treatment of AC controls acidic and basic nature of AC. May deter the adsorption of phenol. Organic and heavy metal uptake are enhanced.

Alkali modification of AC generates positive surface charges. Increased adsorption of negatively charged species. Organic uptake is enhanced. Metal ion uptake may reduce.

Impregnation of AC using metals such as Fe facilitates selective removal of contaminants.

H_3PO_4 activation found to be safer than $ZnCl_2$ as it has less toxicity and requires low activation temperature compared to KOH.

An effective activated carbon not only based on activating agent but also precursor and optimum parameters used such as activating agent concentration, impregnation ratio, residence time and activated temperature.

The surface of AC prepared by using chemical activator is less damaged than AC obtained by physical activation for a high porosity development.

For alkali activation KOH is more preferable than NaOH as it develops greater surface area more than 3000 m^2g^{-1}

In microwave treatment of AC increasing activation time of AC increases the adsorption potential by the production, but further increasing time kills or widens micropore structure..

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