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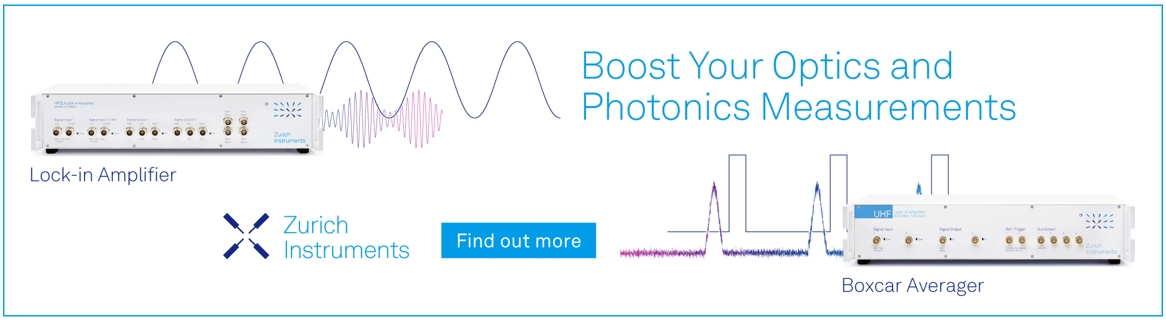

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Activated Carbon Adsorption of Ions in Multi-Ion Solutions: A Review

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Abstract. The factors that influence the adsorption of ions on activated carbon in multi-ion solutions were reviewed. Activated carbon can reduce or remove a particular undesirable ion in multi-ion solutions such as wastewater and seawater. Reducing undesirable ions using activated carbon needs to consider several factors such as the type of ion, the solution pH, and the surface characteristics of the activated carbon. Since the ions will also compete in adsorption on activated carbon, the nature of the water molecule that forms the hydration shell of the ion needs to be considered. Preferable conditions for reducing anion are the basic characteristic of activated carbon and lower pH solution and vice versa for the cation.

INTRODUCTION

Activated carbon is widely used for the removal of various pollutants from air, solids, and liquids. Activated carbon generally most effectively adsorb large and least soluble organic molecules from aqueous solutions [1]. However, activated carbon is also commonly used to adsorb undesirable ions from aqueous solutions. Heavy metal ions such as cadmium, lead, chromium, and mercury that contaminated water can be removed using the adsorption method [2-4]. Activated carbon can reduce or remove those kinds of ions from aqueous solutions. Activated carbon is usually used to adsorb specific undesirable ions. However, the performance of activated carbon to adsorb these ions is reduced due to the presence of several other ions in a solution such as wastewater or seawater.

The activated carbon's ability to adsorb ions may be used to reduce seawater impurity ions, which become the impurities in sea salts. One of the problems of sea salt production is the impurities of the salt. The purity of sea salt is influenced by the impurities present in seawater as the raw material of the salt. The six most abundant seawater ions are sodium, chloride, magnesium, sulfate, potassium, and calcium ions [5]. These ions will form impurities in sea salts, such as calcium sulfate, magnesium chloride, and magnesium sulfate [6]. However, there is potential to reduce the levels of impurities in sea salt by reducing the levels of impurities in seawater. The challenge of ion adsorption on activated carbon of multi-ion solution is the presence of various ions in the solution that compete to be adsorbed by activated carbon [7]. This article will examine the factors that affect the reduction of ions using activated carbon in a multi-ion solution such as seawater.

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ACTIVATED CARBON

Activated carbon is often used as a study material because of several advantages of its properties, such as large pore volume, wide surface area, good thermal stability, excellent mechanical stability, and ease of manufacture [8]. The use of activated carbon is extensive, including the chemical, food, automotive, petrochemical, and environment [9]. The use of activated carbon in the industry is usually as an ingredient for purification, such as water purification, removing unwanted colors, controlling pollution, and others [10-12]. Some of the advantages of activated carbon, such as being non-toxic, chemically stable, and inexpensive, have attracted the attention of many researchers.

Various materials such as wood, coal, coke, and anthracite can be used as activated carbon raw materials. Activated carbon can also be produced from agricultural waste such as rice husks, coconut shells, and bagasse. Compared to activated carbon from coal, activated carbon from agricultural waste contains less ash [13]. Activated carbon with lower ash has a better adsorption capacity [14].

Activated carbon structure consists of parallel stacks of graphite layers composed of sp^2 hybridized carbon atoms forming regular hexagons [15]. Each carbon attaches to the other three carbons by σ-bonds, and the p_z orbitals containing one electron form a delocalized π-bond. Van der Waals forces connect layers of carbon.

Activated carbon has a large surface area, high porosity, and high surface reactivity. These characteristics can be grouped into two to describe its adsorption ability: the morphology of the pores (surface area and pore structure) and surface chemical properties [16]. Activated carbon material, activation process, and further treatment affect the morphology of the pores and surface characteristics [17-18]. In addition, the adsorption ability of activated carbon is also influenced by several environmental conditions such as pH, the influence of salt, ionic strength, and the presence of anions, cations, and other organic materials [19].

In activated carbon, there are several types of pores based on the width: macropores (more than 50 nm), mesopores (from 2 to 50 nm), and micropores (less than 2 nm) [20]. The pore size is influenced by the raw materials and methods used to manufacture activated carbon. Micropores can be further subdivided into primary micropores (less than 0.8 nm) and secondary micropores (from 0.8 to 2 nm) [21]. Micropores are located between layers of carbon. The existence of mesopores and macropores depends on the activated carbon material. Micropores are effectively used for the adsorption of small molecules, especially for gases whose size is usually between 0.4 nm to 0.9 nm. In contrast, it is more efficient to use mesopores for larger molecules.

Adsorption occurs in the pore structure of activated carbon through two different mechanisms: chemical and physical adsorption [22]. In physical adsorption, molecules are bound to the carbon surface by van der Waals forces. The intermolecular forces are very weak and decrease as the distance between the adsorbate molecule and the carbon surface increases. Since the weak attraction highly depends on distance, physical adsorption occurs mainly in pores having a radius only a few times larger than the diameter of the adsorbed molecule. Chemical adsorption is a direct reaction of the adsorbed molecule with the active region on the carbon surface and results in a chemical bond between the carbon surface and the adsorbate. The chemical adsorption is called chemisorption if the adsorbed molecule is chemically bonded to the carbon surface (shared electrons) and catalytic conversion if the adsorbed molecule is only temporarily on the carbon surface, picks up an electron, and then leaves the carbon surface.

The active regions on the carbon surface involved in chemisorption are mainly functional groups that contain oxygen and change the electron balance on the carbon surface. The surface of a carbonaceous material consisting mostly of sp^2 hybridized carbon atoms is not homogeneous. The surface consists of the faces of graphene sheets and edges of such layers. The edges, where groups of atoms such as oxygen and hydrogen are located, are much more reactive than the atoms inside the graphene sheet [23].

The group of atoms chemically bonded in various functional groups gives the carbon surface acidic, basic, and neutral properties [24]. These functional groups can be formed during the carbon activation process and added afterward through a particular treatment process to obtain the desired chemical properties.

The acidic surface of activated carbon mainly has functional groups containing oxygen and is located on the edge of the carbon basal planes. These functional groups contribute to the surface chemical properties of activated carbon. The acidic surface is associated with several functional groups such as carboxyl, lactone, phenol, and lactol [25]. Other functional groups that are also acidic are carboxylic anhydrides, lactones, and phenolic hydroxyls. Functional groups that are acidic at a certain pH are effective for binding cations [26].

The basic surface of activated carbon is affected by electrons forming delocalized bonds in the basal planes that attract protons and functional groups that can bind protons [25,27]. Functional groups containing basic oxygen proposed are chromene, ketones, and pyrones [24]. The surface's basic nature can also occur by adding nitrogen-containing functional groups to the carbon [24,28]. Functional groups derived from nitrogen include amide, amine, lactone, pyrrole, and pyridine [28]. These functional groups can interact with acid molecules through hydrogen bonds, dipole-dipole, covalent bonds, and others [29].

However, the basic nature of activated carbon mainly comes from the electrons forming bonds delocalized in the basal planes. The simplest aromatic ring model is benzene. Benzene is a model system that has no permanent dipole moment because the contribution of the weak polar carbon-hydrogen bond is removed due to the symmetrical shape of the molecule. However, the electron-rich system above and below the benzene ring has a partial negative charge. The negatively charged quadrupole region can interact with something positively charged or called the cation-π interaction [30].

The negatively charged basal planes on the surface of activated carbon can interact with hydronium ions (H_3O^+) through cation-π interactions where the aromatic ring acts as a hydrogen bond acceptor [25]. It makes the surface of the basal planes positively charged and will be neutralized by anions in the solution [27]. However, the basic strength in the carbon basal plane is not as strong as that of functional groups such as pyrone.

The morphology of activated carbon is affected by the method of activating the carbon material [8]. The activation method can increase the number of pores and enlarge the pore size so that some pore sizes change from micropores to mesopores [31]. The treatment of activated carbon to obtain the characteristics of specific functional groups also affects the morphology of the activated carbon, such as increasing the acidic functional groups to reduce the porosity of the activated carbon [2]. The functional groups also influence the performance of pores in the adsorption process [32].

HSAB CONCEPT ON ACTIVATED CARBON

Alfarra et al. [33] offered the concept of hard soft acid base (HSAB) on the adsorption of metal ions on activated carbon. It is based on their observations of many published data which showed that some of the ions adsorbed by activated carbon did not depend on the micro texture of the carbon and only depended on pH, the number of functional groups, and the concentration of the solution. It shows that the adsorption by activated carbon is only bound to the functional group. While in some other ions, such as heavy metals, the adsorption of ions by activated carbon does not depend on the number of functional groups and pH because it is only dependent on the surface characteristics and porosity of the carbon. It means that the ions are more attached to the carbon basal planes. Some other ions are adsorbed by activated carbon either by functional groups or by carbon basal planes.

The HSAB concept was proposed based on the Lewis acid-base principle, which Pearson [34] categorized into acids/bases as hard and soft. Hard bases prefer to react with hard acids, and soft bases prefer to react with soft acids. The preference here is relative, meaning that acid can pair with one of two bases, but there is a tendency for the acid to prefer one base over the other [35]. The definition of the hardness of an acid/base is not related to the strength of the acid/base. The strength of an acid is affected by the ease with which it can lose a proton, and the strength of a base is affected by its ability to attract a proton. Meanwhile, hardness is influenced by differences in ionization energy and electron affinity. The higher the difference, the higher the hardness.

Some acids and bases have relative hardness or softness [33]. Some bases such as water and the chloride, fluoride, sulfate, carbonate, and hydroxide anions are classified as strong bases, and some acids such as carbon dioxide and the sodium, potassium, magnesium, calcium, proton, and hydronium cations are classified as hard acids. Meanwhile, some bases such as benzene, carbon monoxide and anions like iodide and hydride are categorized into soft bases and those included in soft acids are platinum, silver, palladium and mercury ions. Included in the borderline bases are pyridine and nitrite ions, while those included in the category of borderline acids are ferrous, cobalt, and cadmium cations.

In activated carbon, the functional groups are hard regions that interact with hard ions, and the surface area of the carbon basal planes is soft and can attract soft ions. There are two reasons for determining the hard and soft regions in activated carbon. The first is the difference between carbon-oxygen and carbon-carbon bonds. In general, C=O or C–O bonds are more polar and less polarized, hence harder, than C=C or C–C bonds, so it can be concluded that electronegative heteroatoms on the edges of activated carbon are harder than the graphene layer surface. The second is the strong delocalization of MO in the carbon basal planes and donor or acceptor groups. The hardness of polyaromatic hydrocarbon decreases when the number of rings increases. Therefore, the softness is very high on the surface of the activated carbon layer, especially high distance from the heteroatom edges.

The hard region in activated carbon depends on the number of functional groups, while the soft region is influenced by the texture characteristics of the activated carbon. In addition to ions that are hard acids/bases and soft acids/bases, some ions are in the intermediate region (borderline). The adsorption mechanism for ions in the intermediate region is in the functional groups and the carbon basal planes.

EFFECT OF PH ON ION ADSORPTION

The functional groups in activated carbon are acidic and basic and affect the adsorption of ions on activated carbon. For example, acidic functional groups such as lactone, lactol, and phenol in solution affect the adsorption of cations such as lead ions (Pb^{2+}) [2]. Meanwhile, for anions such as nitrate (NO_3^-), strengthening basic functional groups affects the absorption of the nitrate ion [36].

Some research explained the effect of increasing and decreasing pH on the adsorption of cations and anions. The research found that as the pH increases, the competition between metal ions and protons at the surface decreases, and hence the positive surface charge decreases, resulting in lower coulomb repulsion of metal ions [37]. Other research explained that the reason for the excellent reduction of nitrate anion at low pH was because the negative charge on the surface was reduced due to excess protons in the solution [31]. According to another research, at a low solution pH, electrostatic repulsion occurred between the positively charged carbon surface and metal cations [4]. In addition, a higher concentration of H^+ in the solution will compete with cations for adsorption on activated carbon. An increase in pH will cause the positive charge on the activated carbon surface to decrease and the negative surface charge to increase to attract metal cations.

The solution pH has an essential role in the adsorption of anions and cations, as described by the surface complex formation model (SCF) [38]. Based on this model, the functional groups on activated carbon can be modeled as a single weak diprotic acid and can be illustrated by the following surface reaction:

$$SOH_2^+ \leftrightarrow SOH + H_S^+$$

$$SOH \leftrightarrow SO^- + H_S^+$$

where, the symbol (SO^-) represents the surface active site and Hs^+ is the proton activity on the solid surface. Therefore, increasing the pH of the solution releases protons from the surface, giving rise to a more negative surface (SO^-) to bind more cations. Conversely, a decrease in pH causes the surface to attract protons, causing a more positively charged surface on the carbon to attract more anions. An increased pH decreases anion adsorption due to high competition with other anions such as OH^- [39].

THE ROLE OF WATER MOLECULES ON ION ADSORPTION

Most of the content of the aqueous solution is water molecules. Water molecules play a role in the mechanism of ion adsorption on activated carbon. The water molecule is often described as having four approximately tetrahedral sp^3-hybridized electron pairs, two of which are linked by covalent bonds with the hydrogen atom leaving the remaining two electron pairs. In a perfect tetrahedral arrangement, the bond angles, single-bond pairs, and single-lone pairs would all be 104.5°, and such a tetrahedral bond pattern is found in condensed phases such as hexagonal ice [40].

The water molecule is polar, with a partial positive charge on hydrogen and a partial negative charge on oxygen. A bent water geometry structure causes it. The unequal charge distribution in the water molecule indicates the lower electronegativity of hydrogen relative to oxygen. Due to its polarity, water can build electrostatic interactions (charge-based charges) with ions and other polar molecules. Ions and polar molecules interact with the water's partially negative and partially positive ends, with negative charges attracting positive charges. When there are many water molecules relative to the solute molecules, as in an aqueous solution, this interaction forms a three-dimensional sphere of water molecules around the solute. This formation is called a hydration shell, which allows the particles to be dispersed evenly in the water.

However, the hydration shell also causes the electrostatic force of the ions in the solution to decrease [41]. Ions in solution have an ionic charge, forming an electric field around the ion. Ions with a smaller radius and higher valence have a greater surface charge density, which creates an electric field to polarize the water molecules on the surface of the ion. Usually, the stronger the electrical polarization, the more water molecules bound to the surface of the ion, so the larger the hydration shell of the ion. Ions with a smaller ionic radius will either have a larger hydration shell or a larger hydration radius. The hydration shell decreases the strength of the electrostatic forces on the ions.

The concept of the hydration ratio, which is the ratio between the hydration radius to the ion radius, has been proposed [42]. The concept was proposed based on observations of some research. In a solution with many cations and anions, the ions compete with each other to be attracted by a charged material such as activated carbon. The results showed that monovalent ions with a smaller hydration radius were easier to remove from the solution. However, divalent ions such as Ca^{2+} are easier to remove from solution than Na^{+} even though calcium ion has a larger hydration radius than monovalent sodium ion. Another study showed that ions with almost the same hydration radius but the ability to be removed from the solution had a significant difference. From the research results using the concept of the hydration ratio, it was found that the greater the hydration ratio, the greater the reduction in electrostatic forces on the ions.

For example, sodium and potassium ions have the same valency, but the radius of sodium ions (0.95 Å) is lower than that of potassium ions (1.33 Å), therefore, the hydration radius of sodium ions (3.58 Å) is larger than the hydration radius of potassium ions (3.31 A). The hydration ratio of sodium ions (3.77) is higher than potassium ions (2.49) so that sodium ions have a lower electrostatic force than potassium ions. Nitrate ions have a hydration radius (3.35 Å) almost the same as chloride ions (3.32 Å) however, since the radius of nitrate ions (2.64 Å) is higher than chloride ions (1.81 Å) the hydration ratio of nitrate ions (1.27) is lower than chloride ions (1.83) which causes the nitrate ion to have a higher electrostatic force.

Therefore, the electrostatic force on the ions in the solution will be affected by the radius of the ion and its hydration radius. Based on this concept, when adsorption of an ion using activated carbon in a multi-ion solution, it is necessary to consider the hydration ratio of the ion. The lower the hydration ratio, the greater the opportunity for these ions to be adsorbed on activated carbon.

CONCLUSION

There is an opportunity to remove or reduce ions in multi-ion solution such as seawater. Ion removal or reduction using activated carbon is generally influenced by the type of ion (cations or anions), surface characteristics of activated carbon, pH of the solution, and water molecules. For example, when the ions of concern to be reduced or removed are anions, it is necessary to pay attention to basic functional groups, a lower pH solution, and the hydration ratio of the other anions. On the other hand, if the ions of concern to be reduced or removed are cations, more attention should be put to acidic functional groups, solutions with higher pH, and hydration ratios of other cations.

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