

Superadsorbents for Water/Wastewater Treatment

Subjects: **Water Resources**

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An adsorbent's properties, its adsorption chemistry, and treatment efficiency are all interlinked for water/wastewater treatment. Adsorption has been recognized as a prominent strategy to treat contaminated aqueous systems. Researchers focus on superadsorbents possessing ultrahigh adsorption capacities of $\geq 1000 \text{ mg g}^{-1}$ for an efficient water/wastewater treatment. A variety of superadsorbents is reviewed regarding their preparation, characteristics, adsorption chemistries, and mechanistic interactions in the removal of aqueous inorganic and organic contaminants.

water pollutants

pollutant removal

adsorption

1. Preparation Methods

Polymerization [1][2][3][4], cross-linking and co-polymerization processes [5][6], grafting of metal oxide in polymers [7], pyrolysis [8], hydrothermal [9], solvothermal [10], and electrochemical processes [11] have been used to prepare superadsorbents. The ultrahigh adsorption capacity of the superadsorbent depends on the synthesis method, the attributes imparted during its preparation, and the specific reaction conditions. Thus, different materials yield different adsorption performances. Polymerization involves using precursors whereby the inclusion of an initiator, cross-linking species, and oxidant play a significant role in achieving a specific superadsorbent. Salama reported the synthesis of anionic hydrogel prepared by grafting of *p*-(3-sulfopropyl methacrylate) onto carboxymethyl cellulose [12]. Here, *p*-(3-sulfopropyl methacrylate) acted as the monomer, and ammonium persulfate and -*N,N'*-methylenebisacrylamide were the initiator and cross-linker, respectively [12]. The synthesized superadsorbent sorbed methylene blue from aqueous solutions at 1675 mg g^{-1} [12]. In another study, a bioinspired hydrogel-type superadsorbent, which possessed high porosity (specific surface area = $2.8031 \text{ m}^2 \text{ g}^{-1}$ and 5914.66% swelling ratio with a microporous structure), had a high adsorption capacity of 2276 mg g^{-1} for methylene blue because of the presence of nano-layered polydopamine [13]. This ultrahigh adsorption capacity was attributed to the hydrophilicity of polydopamine and constituent functional groups on the superadsorbent [13]. Polymer-type sorbents have received attention because of their unique properties such as ease of synthesis, excellent redox behavior, high adsorptive tendency, and biocompatibility. Ballav et al. [14] reported that an L-cysteine-doped polypyrrole superadsorbent could efficiently remove Hg^{2+} ions from aqueous solutions. In that work, in situ oxidative polymerization of pyrrole and L-cysteine was undertaken in the presence of ammonium persulfate oxidant at 25°C [14]. Elsewhere, a polyaniline/lignosulfonate superadsorbent, prepared by one-step polymerization at $0\text{--}4^\circ\text{C}$, removed Acid Red dye 94 from aqueous solutions at a maximum sorption capacity of 10.56 g g^{-1} [3].

The electrochemical method is one of the most promising techniques because of its mild reaction conditions, high yield of products, low-cost equipment, and high efficiency in energy consumption. In this method, factors such as concentration of electrolytes, physicochemical nature of anodic and cathodic electrodes, and amount of applied current density or potential difference play important roles. Batch or small-scale electrochemical synthesis of adsorbent is being entertained more than pilot-scale production. This is due to issues related to electrode material stability, adsorption capacity, and regeneration of sorbent normally encountered at the pilot scale. Jung et al. [15] reported the electrochemical synthesis of a novel magnetic $\text{Fe}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ hybrid composite using Fe-Al electrodes. The applied current density was 24.87 mA cm^{-2} . After electrolysis, the prepared samples were pyrolyzed at 873 K for 1 h [15]. The superadsorbent thus prepared had the highest adsorption capacity of 1501 mg g^{-1} (Sips isotherm model) at $25 \text{ }^\circ\text{C}$ for Acid Black 1 [15]. Similarly, a two-dimensional MoS_2 superadsorbent was synthesized by ultrasound-assisted electrochemical exfoliation where the natural molybdenite was the cathode, Pt the anode, and aqueous Na_2SO_4 the electrolyte. This adsorbent could chemisorb aqueous Pb^{2+} ions at 1479 mg g^{-1} [11].

2. Physicochemical Properties

A thorough analysis of the literature shows that the physicochemical characteristics of the adsorbent(s) play an important part in determining their adsorption behavior(s) towards specific pollutants under a specific set of analysis conditions. Moreover, it is equally necessary to highlight that each adsorbent has its own specific set of physicochemical properties. These properties are developed during the synthesis of the adsorbents [16] and can be improved through certain chemical, physical, and/or biological functionalization/modifications [17][18]. Functionalization is performed to introduce the desired changes in the adsorbent material's physico-chemical properties, including surface area, pore size, pore volume, surface charge distribution and behavior [19], surface functional groups [17], and degree of aromaticity [20]. Interestingly, the physicochemical characteristics of adsorbents are highly diverse and depend on the type of adsorbent and its synthesis conditions.

For example, carbonaceous adsorbents have extensively rich porous structures and large specific surface areas, and the latter constitute the essential morphological features of the adsorbent materials [21]. Adequately developed and adsorption-conducive pore size distributions give rise to favorable mass transfer paths, while large surface areas host more active adsorption sites [21] where pollutant molecules can compete and be adsorbed selectively. Another example is layered double hydroxides, which are usually ionic layered materials by reason of their structures consisting of positively charged brucite-like layers and abundant exchangeable anions within their galleries [22]. Yet another class of novel adsorbents are graphene-based materials. The incorporation of oxygen functionalities augments the hydrophilicity of graphene oxide, as a result of which it is rapidly dispersed to form stable colloidal suspensions in aqueous solutions [23]. The significantly large surface area (approximately $2630 \text{ m}^2 \text{ g}^{-1}$), high aspect ratio for modification, and superior colloidal stability than other carbon-type materials make graphene oxide a suitable candidate for sustaining adsorption and surface reaction [23]. Likewise, the adsorption literature is populated with details of many other physicochemical properties of materials exhibiting adsorption potential for aqueous adsorbates. Examples of those properties include surface area [1][13][24], nature and

distribution of functional groups [3][13][14][25][26], the type of crystal structure [27], average pore size [28], degree of exfoliation [29], degree of cross-linking and rigidity of solid network [30], response to a magnetic field and/or the presence of magnetic moieties [16], swelling properties [31], zeta potential [27], variations in the extent of aggregation [32], and ion exchange capacity [17][29].

3. Adsorption Chemistries

The adsorption process is essentially a surface phenomenon whereby an adsorbate is bound to the surface of the adsorbent [33][34]. Adsorption mechanisms are mainly of the following three categories: chemisorption, which is brought about through the formation of chemical bonds [35]; physisorption, which can involve van der Waals forces [35]; and ion exchange [33]. The set of data obtained from adsorption mechanisms is of much significance when designing adsorption systems for handling real-scale process streams [33]. In an overwhelming majority, if not all, of adsorption-related research studies, reasonable attempts have been made to elucidate possible adsorption mechanisms using predefined mathematical models intended to portray the variations of equilibrium adsorption data.

These models can be linear and non-linear [33][36]. They can also be grouped as one-parameter isotherms (Henry's isotherms), two-parameter isotherms (Hill–Deboer model, Fowler–Guggenheim model, Langmuir isotherm, Freundlich isotherm, Dubinin–Radushkevich isotherm, Temkin isotherm, Jovanovic isotherm, Elovich isotherm, Harkin–Jura isotherm, Flory–Huggins isotherm, Hill isotherm, Halsey isotherm, and Kiselev isotherm), three-parameter isotherms (Redlich–Peterson isotherm, Sips isotherm, Koble–Carrigan isotherm, Toth isotherm, Kahn isotherm, Radke–Prausniiz isotherm, Langmuir–Freundlich isotherm, and Jossens isotherm), four-parameter isotherms (Fritz–Schlunder isotherm, Baidu isotherm, Weber–Van Vliet isotherm, and Marczewski–Jaroniec isotherm), and five-parameter isotherms (Fritz and Schlunder derivation which approaches the Langmuir model) [36].

An adsorption isotherm describes the equilibrium relation between the concentration of adsorbate on the adsorbent and the quantity of adsorbate in solution at a constant temperature. An adsorption isotherm is constructed by studying the adsorption at different adsorbate concentrations followed by its mathematical modeling. An adsorption isotherm not only describes the extent of adsorption and the relationship between the concentration of adsorbate in solution and the adsorbent, but can also insignificantly contribute to reveal the underlying mechanisms and interactions between the adsorbate and adsorbent [37].

The pool of data from equilibrium adsorption isotherm models reveal the maximum adsorption capacity of an adsorbent for a specific adsorbate [33]. The maximum adsorption capacity is an essential parameter in the assessment and comparison of the adsorption performance of adsorbents within and across adsorption systems [33]. This is because the adsorption capacity gives an indication of the amount of adsorbate that can be scavenged from a specific volume of contaminated aqueous media.

A wide variety of adsorption isotherms have been applied for these superadsorbents. Among them, Langmuir and Freundlich adsorption isotherms were widely used for the superadsorbents. Though both of these models are two-parameter adsorption isotherms, they have different applications. The Langmuir isotherm model is assumed to be applicable for monolayer adsorption on homogenous sites. On the other hand, the Freundlich isotherm model is mainly applied to multilayer adsorption on heterogeneous sites. However, Langmuir adsorption isotherms were also found to fit better than Freundlich isotherms for the adsorption of cationic malachite green and anionic Congo red on calcium-rich biochar, having a heterogeneous surface [38]. Therefore, it is necessary to select appropriate models considering the system's complexity.

Besides adsorption isotherm modeling, adsorption kinetics analysis based on predefined mathematical equations has been frequently used to further understand the chemistry of an adsorbate–adsorbent interaction [39]. Adsorption kinetics data, particularly at initial time points, are highly important for accurate modeling and to derive logical conclusions [37]. Kinetic studies are intended to identify an appropriate contact time for an optimum equilibrium and adsorption process. The affinity between the adsorbate and adsorbent dictates the adsorption rate. For example, the adsorption of Pb^{2+} proceeded at a high rate, reaching equilibrium in 20 min on two-dimensional molybdenum disulfide [11], or may take 720 min when adsorbed onto esterified hydroxyapatite [40].

The kinetic models can be lumped as reaction-controlled kinetics or diffusion-controlled kinetics [39]. Typically, kinetic adsorption constant can be mathematically described by applying pseudo-first-order, pseudo-second-order, intraparticle diffusion, and Elovich models [37]. The adsorption kinetics for a majority of the cited superadsorbents were better fitted by the pseudo-second-order model than the pseudo-first-order model. However, few studies reported that adsorption kinetics followed the intraparticle diffusion model [10][41]. Additionally, the significance of the intraparticle diffusion has been highlighted in few adsorption kinetics as the rate-limiting or rate-determining step [14][41][42][43]. For example, intraparticle diffusion has been noted as a rate-limiting process in the adsorption of amaranth dye onto Cu_2O nano-composite, while the pseudo-second-order model exhibited the best fit for the adsorption kinetics [43].

Adsorption kinetic model elucidation for a specific adsorbate–adsorbent interaction has an important bearing in the design and scale-up of adsorption units [44][45]. For example, the effects of initial adsorbate concentration, adsorbent particle size, and stirring rate on the adsorption kinetics of methylene blue onto silica have been studied [44]. Among the many parameter-dependent kinetics findings, it was found that stirring rate and mass transfer coefficient shared a linear relationship [44]. Various kinetic models (such as the Yoon–Nelson model, Thomas model, and Bohart–Adams model) have been used in the analysis of laboratory-scale adsorption systems operated in the column configuration [45]. It should be noted that batch experiments allow optimizing the experimental conditions, while column studies, though complicated, are recognized as better representatives of field applications [46]. Based on the kinetic data compiled from such systems, the scale-up design of continuous adsorption columns can be worked out based on the breakthrough curve approach [45].

With these concepts in mind, the adsorption isotherm analysis, adsorption kinetics analysis, and adsorption selectivity analysis of the superadsorbents considered are highly important components of adsorption studies. In

fact, 'selectivity' is a relatively fresh aspect involved in the study of adsorption processes in aqueous media [47]. In a recent work, it has been indicated that the adsorption selectivity and capacity of electro-spun nanofibrous membranes, for example, for heavy metals depend significantly on the type and abundance of functional groups on the membranes' surface [48]. In general, a high abundance of functional groups can be associated with higher adsorption capacity [48]. Yet, the extent to which the adsorption capacity of an adsorbent can shoot for a specific adsorbate will be determined by the specific interactions of the actual functional groups of the adsorbent with those of the adsorbate [49].

4. Mechanistic Interactions

It is important to adequately elucidate and understand the binding mechanism and nature of molecular interactions of a pollutant adsorbate onto a specific adsorbent. Being able to track the sequence of rate-limiting and non-rate-limiting steps at specific points within the adsorption process can plausibly allow the identification of areas of optimization of potential large-scale adsorption systems. As described elsewhere, the '*mechanism of adsorption*' depicts the pathway by which the actual attachment of the pollutant species takes place onto the adsorption sites of the adsorbent, irrespective of molecule/ion diffusion [39]. 'Attachment' by way of an adsorptive route occurs spontaneously because the associated free energy is negative [39]. The force sustaining the attachment of the pollutant adsorbate is the total of many other forces which make up the total free energy of adsorption. Those driving forces can include intramolecular interactions and intermolecular interactions [39]. These interactions can also occur as a result of electrostatic attractions. These electrostatic attractions can be in the form of Coulombic attraction, covalent bonding, and dipole interactions. Surface complexation, oxidation reduction, isomorphic substitution, inner-sphere complexes, and ion exchange can also be other (competing) adsorbate uptake mechanisms [39][41][50][51].

Mechanisms of adsorption are dependent on the nature of the pollutant and that of the adsorbent material. For example, adsorption can take less time to reach equilibrium onto non-porous adsorbents than porous materials owing to the different adsorption mechanisms [37]. Porous adsorbents rely mainly on pore filling along with other mechanisms including electrostatic attraction, surface precipitation, hydrogen bonding, cation exchange, π - π interactions, and n - π interactions. Likewise, Agathian et al. [24] highlighted the involvement of electrostatic interaction, hydrogen bonding, and complexation in the adsorption of Cr(VI) and Rhodamine 6G onto cotton fiber modified using poly-caprolactone/oxydianiline/ V_2O_5 nano-particles. The super-loading of Pb^{2+} on 2D molybdenum disulfide was also attributed to the complexation of Pb^{2+} with intrinsic S or O atoms (as $—S—Pb$ and $—O—Pb$ complexation) together with electrostatic adsorption of positively charged Pb^{2+} onto negatively charged adsorbent [11]. Indeed, the nature of functional groups on adsorbent's surface plays a vital role in determining the adsorption mechanism. For example, the higher adsorption of Hg^{2+} has been linked to the electrostatic interactions between positively charged Hg^{2+} and electron-rich functionality ($—SH$, $—NH_2$ and $—COOH$) on the surface of L-cysteine-doped polypyrrole adsorbent [14]. These functional groups can strongly bind cationic pollutants. In another study, the FTIR characterization of GO intercalated layered double hydroxide after Pb^{2+} adsorption revealed an increase in the intensity of peaks [41]. This corresponded to 1120 cm^{-1} (C—O alkoxy group), 3460 cm^{-1} (O—H of $COOH$

and/or H_2O), and 1635 cm^{-1} ($\text{C}=\text{O}$ and/or $\text{O}-\text{H}$ bending), while the intensity of the peak corresponding to 791 cm^{-1} ($\text{M}-\text{O}$ stretching vibration) decreased [41]. This has been attributed to the formation of $-\text{O}-\text{Pb}$ -type complexation of Pb^{2+} with the carboxylic, epoxy, and hydroxyl groups in adsorbent structure. However, the involvement of different functional groups in adsorption in ion exchange was highlighted during the comparative adsorption of metal ions (Cd^{2+} , Cu^{2+} , Hg^{2+} and Pb^{2+}) onto hyperbranched polyethylenimine functionalized carboxymethyl chitosan composite [52]. Moreover, FTIR spectral changes indicated the reaction of CN group with Hg^{2+} whereas the interaction of other three metal ions (Cd^{2+} , Cu^{2+} , and Pb^{2+}) were prominent with $-\text{COO}-$ group.

Thus, adsorption mechanisms can also vary according to the nature of the target pollutants. For example, Li et al. used maleylated-modified hydrochar to adsorb methylene blue and Cd^{2+} [9]. Their findings revealed that the adsorption of methylene blue occurred mainly through the $\pi-\pi$ interaction, electrostatic interaction, and hydrogen bonding. However, predominant mechanisms for Cd^{2+} adsorption included surface complexation and ion exchange. Additionally, the co-existing ions and solution pH have substantial effects on adsorption extent and mechanisms, as reported by Qiu et al. [6] when two gels, namely sodium alginate/Ca/fiber hydrogel and cellulose nanofiber/chitosan aerogels, were used for the adsorption of methylene blue. Using a solution with pH lower than the point of zero charge led to the development of positive charges on the surface of the adsorbents repelling the pollutant. Here, the adsorption mechanism mainly involved the H-bond interactions between the nitrogen atoms in methylene blue and hydroxyl groups on the gels. However, when the solution pH was greater than the point of zero charge, gels' surfaces were negatively charged, which led to electrostatic interactions as the adsorption mechanism. The solution pH can also affect the protonation/deportation of surface functional groups which could change the adsorption mechanisms [51]. However, recognizing the interactions at the adsorbent/adsorbate interface and the resultant adsorption mechanisms is a challenging task. Moreover, various mechanisms can be involved simultaneously and, therefore, identifying the extent of simultaneously involved interactions can also be a major challenge. To correctly depict the adsorption mechanisms, it would be highly rewarding to use sophisticated spectroscopic techniques along with an adequate interpretation of kinetic modeling.

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