



New Generation Super Adsorbents – A Review

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Abstract

An increasing worldwide concern has recently been raised about detection and removal of toxic pollutants, harmful elements, organic impurities and inorganic contaminants along with colored substances being released excessively into the natural water reservoirs from various sources. The potential toxicity of dyes being a very serious environmental concern has been taken into account by employing economically feasible and potentially reusable super adsorbent materials. The aim of this review is to compile the scattered available information about new super adsorbent materials based on functional polymeric particles for rapid and efficient removal of coloured compounds from aqueous media, as well as usage of different techniques involved in preparation of these materials. It covers recently used and prospected methods for synthesis and modification of such types of super adsorbents. Considering the simple synthetic processes and outstanding adsorption performance of super adsorbent materials, this review provides an effective approach to prepare high-performance super adsorbents. Furthermore, this article shows that super adsorbents are fully efficient and highly effective for removal of dyes in comparison with the conventional adsorbents due to their high adsorption capacity. Porous materials with enhanced surface area, hydrogels, resins, grafted polymers and carbon nanotubes can be employed as super adsorbents for removing toxic pollutants and dyes from water. Starch grafted/AA/Na-Montmorillonite, a hydrogel showed an adsorption capacity of 2237 mgg⁻¹ for removal of Safranin T dye. This value is quite higher in comparison with traditionally used adsorbents. This review also provides a brief outlook of future prospects on super adsorbent and their synthesis for wastewater application.

Key words: Dyes, Super Adsorbents, Resins, Hydrogels, Carbon Nanotubes, Grafted Polymers, Safranin T dye

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1. Introduction

Now-a-days, the term "functional" is often used in combination with newly prepared materials to indicate their potential for certain applications or simply to attach some more importance to them. Indeed, the term "functional material" has already been applied to a large number of different compounds, ranging from liquid crystals [1], organo-gels [2], biomaterials [3-4], block copolymeric nanocomposites [5] and inorganic-organic hybrids [6] to silicates and zeolites [7], metal oxides [8-9], semiconductors [10] and metals [11]. The definition is certainly justified for all these materials as almost every material could somehow be designated as a functional one actually it is much harder to imagine a material which does not exhibit any kind of function or functionality. A functional material could be defined as being prepared from a "target-motivated" approach, that is, all its properties are adjusted and optimized to serve a specific purpose.

To exhibit function, a material has to possess certain chemical or physical functionalities. Examples of the former are acidity/basicity or ability to coordinate with

metals while typical examples of physical functionalities include electrical and optical properties. Furthermore, it should be noted that many materials show their function only when they exist or are assembled into a certain structure or morphology. Two examples of such kind of materials are liquid crystals and semiconductor nanoparticles (e.g. "quantum dots"). The introduction of porosity into a material so as to maximize its accessible surface area is another way to enhance its function. Indeed, useful properties can arise when small pores and thus high surface areas are introduced into a material which can lead to a number of applications. Porous materials are used as catalysts or catalyst supports [12] for the purpose of sorption.

Polymers are natural or synthetic compounds whose structure consists of chains of basic repeating molecular units (monomers). They are classified as macromolecules, due to their high molecular weight. Schematically, the polymeric macromolecules can be divided into following categories (a) natural polymers such as proteins are composed of amino acids (b) synthetic

polymers are traditional plastics such as polyethylene and polyvinyl chloride and (c) biopolymers such as PHA. Cellulose, starch and chitin, proteins and peptides, DNA and RNA are all examples of natural polymers produced by living organisms. The term "biopolymer" is actually used as synonym of bioplastics but two different criteria underline its definition: the source of raw materials and biodegradability of polymer. According to these criteria it is possible to differentiate between three classes: (i) biopolymers that are made from renewable raw materials (biobased) that are biodegradable also (ii) biopolymers that are made from renewable raw materials (biobased) and are not biodegradable and (iii) biopolymers that are made from fossil fuels and are biodegradable.

Furthermore, the bioproducts composed by biopolymers can be divided into two broad groups namely biodegradable and non-biodegradable or alternatively into bio-based and non-bio based products. Bioproducts can also be classified on the ways in which they respond to heat as thermoplastics, thermosets or elastomers. Finally, it is noteworthy that bioproducts blends are mixtures of polymers from different origins, while biocomposites are biopolymers or synthetic polymers reinforced with natural fibers and/or fillers and additives [13].

Adsorbent materials are of great scientific and technological interest owing to their ability to interact with specific substances and efficiently separate them from a mixture [14]. Owing to their superior physical and chemical features, including a large specific surface area, unique pore structure and tunable pore surface property, adsorbent materials have found utility in multiple applications such as separation/purification [15] as catalyst supports [16], adsorption [17], drug delivery [18], gas separation/storage [19], electrode materials for electrochemical double layer capacitors and fuel cells [20] and so on. To meet the demand for green chemistry and sustainable development, tremendous endeavors have been devoted to the design and synthesis of advanced adsorbent materials, which is crucial for efficient adsorption, separation and purification. Generally, an effective adsorbent should be a solid material with high mechanical and chemical stability, which makes it suitable for application under severe conditions that is, easy separation, regeneration and reusability. Second, a good adsorbent material should possess a proper porous structure, endowing it with a large contact area and facilitating mass diffusion within the porous media. Third, porous surface should contain a large number of functional groups, which helps to determine its adsorption selectivity and capacity [21-22].

Owing to exponential growth in the field of nanomaterials over the last two decades, we have witnessed rapid development of high-performance nanostructured adsorbents. Numerous nanomaterials with well-defined porosities and controllable surface properties have been designed, synthesized and used as adsorbents for desired applications, including for CO₂ capture [23-24] for the

separation and storage of fuel gas [25] and especially for removal of pollutants from aqueous solutions.

2. Super Adsorbent Polymeric Materials (SAPs)

SAPs are commonly made from starting materials of petrochemical industry more specifically acrylic monomers. However, bio-modified or natural-based SAPs are also being considered to be very interesting owing to the world steadfast decision towards environmental protection. The biopolymer-contained SAPs, however, possess typically higher cost and less performance in comparison with their fully synthetic counterparts. Besides various applications, the most volume of SAP world production (106 tons/year) is yet consumed in hygienic uses for disposable products along with excessive utilization in wastewater treatment [47].

2.1 History and Market of SAPs

The production of the first water-absorbent polymer goes back to 1938 when acrylic acid (AA) and divinyl benzene were thermally polymerized in an aqueous medium. In the late 1950s, the first generation of hydrogels was appeared. These hydrogels were mainly based on hydroxy alkyl methacrylate and related monomers with swelling capacity upto 40-50%. They were used in developing contact lenses which have make a revolution in ophthalmology [48].

2.2 Factors Determining Properties of SAPs

Some important functional features of an ideal SAP material can be listed as follows [49]: (i) SAP should have highest absorption capacity (maximum equilibrium swelling) in saline environment (ii) SAP should have desired rate of absorption (preferred particle size and porosity) depending on the application and requirement (iii) SAP must have highest absorbency under load (AUL) (iv) SAP should have lowest soluble content and residual monomer (v) SAP must be of lowest price (vi) SAP should have highest durability and stability in swelling environment and during storage (vii) SAP must have highest biodegradability without formation of toxic species following the degradation (viii) SAP must have neutral pH after swelling in water (ix) SAP should be colourless, odorless and absolutely nontoxic in nature (x) SAP must be stable to light (xi) SAP should have rewetting capability (if required). The SAP has to be able to give back the imbibed solution or to maintain it; depending on requirement (e.g., in agricultural or hygienic applications).

2.3 Safety and Environmental Issues

Alike each man-made material, some common matters are also primarily questioned about the SAP materials e.g. (a) toxicity and safety of SAPs and (b) environmental fate of end-products of SAPs. These types of materials cannot be returned back to their starting monomers as they are scientifically irreversible to toxic initiating materials. Here, like so many polymers, starting toxic monomers are converted chemically to totally non-toxic product by polymerization reaction. SAPs are organic materials with well-known general structure. For instance, the agricultural SAPs with the name of "cross-linked

acrylamide/potassium acrylate copolymer" has been recorded in the most valid data centre of chemicals, i.e. the Chemical Abstracts with CAS No. 31212-13-2. In the material safety data sheet (MSDS) of the superabsorbent manufacturers, they are also called as "Safe and Non-Toxic Materials" [47]. The conventional SAP materials are neutral and inert in nature. They are moderately bio-degraded in the soil by ionic and microbial media to convert finally to water, carbon dioxide and organic matter.

3. Types of Super Adsorbent Materials

There are different types of super adsorbent materials that are widely used for number of fruitful applications in agriculture or wastewater treatment. Some of these materials include (i) porous super adsorbent materials that are prepared by sol gel method (ii) hydrogels that are also manufactured by polymerization reactions, ionizing radiations, physical interactions, cross linking, bulk polymerization, solution polymerization and suspension polymerization (iii) grafted polymerization through surface-initiated atomic transference aided by radical polymerization (iv) resins and (v) carbon nanotubes.

3.1 Porous Super Adsorbent Materials

Currently, research interest in adsorbent development is mainly concentrated on the functionality of the pore surface and the design of pore size and geometry [21-22]. To endow the porous materials with high selectivity and adsorption capacity, a relatively high density of functional groups should be grafted onto pore surface [50-51]. Mesoporous silica functionalized with a high density of carboxylate groups can serve as an efficient adsorbent for the selective removal of basic dyes [52]. In addition to the content of functional groups, the appropriate pore structure also has a crucial role. The pore structure of conventional adsorbents is mainly composed of micropores which are not applicable for dye molecules with large size. To overcome the disadvantage of micropores, adsorbents with mesopores or even hierarchically porous structures have been designed (for example, bimodal macrostructure–mesostructure and multilevel porous structures) [53-54]. The micropores and mesopores provide the adsorbent with a large specific surface area combined with a high density of functional groups, leading to a high adsorption capacity. Meanwhile, the presence of macropores and interconnected mesopores enables the fast diffusion of molecules into the internal pores (especially for large molecules), which greatly improves the adsorption rate [55-56]. However, the tedious preparation procedures for the hierarchically porous adsorbents greatly hinder their practical applications. Furthermore, there are still some inaccessible binding sites in such materials leading to binding efficiencies far below 100% (relative to the molar amount of the functional groups).

3.1.1 Sol-Gel Method

A novel multifunctional microsphere with a large pore size mesoporous silica shell and a magnetic core (Fe_3O_4) has been successfully synthesized via a facile two-

step sol–gel method. In the synthesis process, CTAB was first dissolved in water to form spherical micelles, then added to the mixture in which $\text{Fe}_3\text{O}_4@SiO_2$ was dispersed in ethanol, next dropping TEOS to form $\text{Fe}_3\text{O}_4@SiO_2@CTAB/SiO_2$ composites. This approach helps to form mesoporous silica shell with a large pore size, which is propitious to the modification of much more amino groups in order to enhance the adsorption capacity of heavy metal ions. The metal-loaded multifunctional microspheres can be easily removed from aqueous solution by magnetic separation and regenerated easily by acid treatment [57].

3.2 Hydrogels

In recent years, functional hydrogels have emerged as effective adsorbents for the removal of water-soluble contaminants. Compared with conventional adsorbents having porous structures, hydrogels present several advantages. For instance, the 3D network of the hydrogel is formed through the physical/chemical crosslinking reactions of various monomers and precise control of functionality can be achieved through structure design at a molecular level. Functional groups in the 3D network can equivalently conjugate with target molecules, leading to unique selectivity and remarkable adsorption capacities [58-59]. However, for amorphous soft materials such as hydrogels, relatively long period of time is required in order to reach a saturated state of adsorption. Meanwhile, difficulties associated with the regeneration and disposal of hydrogel adsorbents constitute major obstacles for their practical applications.

Discovery of low molecular weight hydrogels is a recently emerging field of current scientific researches [60]. Hydrogels produced by self-assembly of small organic molecules are exquisitely interesting due to numerous applications of hydrogels. They can be used for tissue engineering [60], pollutant capture and removal [61], drug delivery vehicles [62] and other applications [63]. Low molecular weight hydrogelators are structurally diverse and over the past few years different types of molecules, such as bis-urea [64], bis-amides [65] and tris-amides [66], azo-benzene-based sugar derivatives [67], de-novo designed α -hairpin-forming oligo-peptides [68], short peptide derivatives [69], 2'-deoxyuridine derivatives [70], tripodalcholic acid-based compounds [71], bile acid-based compounds [72], peptide-based amphiphiles [73], derivatives of vancomycin and others have been discovered to be low molecular weight (LMW) hydrogelators. Low molecular weight pH-responsive hydrogelators belongs to a unique class of hydrogelators in which the change of pH plays a vital role in modulating sol-gel phase transition and this property can be nicely exploited to develop new soft materials for encapsulation and slow release of biologically important molecules like vitamins [74]. Pollutants including water-soluble toxic dye molecules can also be removed from wastewater using organo gel scaffold [75]. Though metal ions, sensitive organo-gels have been studied extensively [76] and examples of metal-ion-induced hydrogels are quite

few in number [77]. Here, we present metal-ion-induced, pH-responsive hydrogel formation using amino acid-based bola-amphiphilic molecule containing phenylalanine residues and the application of these gels to remove rapidly different types of water-soluble dyes to purify contaminated water. One of these metallo-hydrogels can also trap vitamin B12 molecules and release slowly the vitamin molecules by changing the pH of the system and this property may be utilized to carry vitamin B12 molecules at target site [58].

3.2.1 Preparation of Hydrogels

In the most succinct sense, a hydrogel is simply a hydrophilic polymeric network cross-linked in some fashion to produce an elastic structure. Thus, any technique which can be used to build a cross-linked polymer can be used to produce a hydrogel. Copolymerization/cross-linking free-radical polymerizations are commonly used to produce hydrogels by reacting hydrophilic monomers with multifunctional cross-linkers. Water-soluble linear polymers of both natural and synthetic origin are cross-linked to form hydrogels in a number of ways [85] such as (i) linking polymer chains via chemical reactions (ii) using ionizing radiation to generate main-chain free radicals which can recombine as cross-link junctions and (iii) physical interactions such as entanglements, electrostatics and crystallite formation. Any of these various polymerization techniques can be used to form gels, including bulk, solution and suspension polymerization.

(A) Bulk Polymerization

Many vinyl monomers can potentially be used for the productions of hydrogels. Bulk hydrogels can be formed with one or more types of monomers. The wide variety of monomers enables one to prepare the hydrogel with desired physical properties for a given application. Usually, small amount of cross-linking agents are usually added in any hydrogel formulation. The polymerization reaction is normally initiated with radiation, ultraviolet or chemical catalysts whereas choice of a suitable initiator depends upon the type of monomers and solvents being used. The polymerized hydrogel may be produced in a wide variety of forms including films and membranes, rods, particles and emulsions.

Bulk polymerization is simplest technique which involves only monomer and monomer-soluble initiators. High rate of polymerization and degree of polymerization occur because of the high concentration of monomer. However, the viscosity of reaction increases markedly with the conversion which generates the heat during polymerization. These problems can be avoided by controlling the reaction at low conversions [86]. The bulk polymerization of monomers to make a homogeneous hydrogel produces a glassy, transparent polymer matrix which is very hard. When immersed in water, the glassy matrix swells to become soft and flexible.

(B) Solution Polymerization/Cross-Linking

In solution copolymerization or cross-linking reactions, the ionic or neutral monomers are mixed with

multifunctional cross-linking agent. The polymerization is initiated thermally by UV-irradiation or by a redox initiator system. The presence of solvent serving as a heat sink is the major advantage of the solution polymerization over the bulk polymerization. The prepared hydrogels need to be washed with distilled water in order to remove the monomers, oligomers, cross-linking agent, initiators, soluble and extractable polymer and several other impurities. Phase separation occurs and the heterogeneous hydrogel is formed when the amount of water during polymerization is more than the water content corresponding to the equilibrium swelling.

Typical solvents used for solution polymerization of hydrogels include water, ethanol, water-ethanol mixtures and benzyl alcohol. The synthesis solvent may then be removed after formation of gel by swelling the hydrogels in water [85].

(C) Suspension Polymerization or Inverse-Suspension Polymerization

Dispersion polymerization is an advantageous method since the products are obtained as powder or microspheres (beads) and thus grinding is not required. Since water-in-oil emulsion process is chosen instead of the more common oil-in-water emulsions, polymerization is referred to as "inverse-suspension". In this preparation technique, monomers and initiators are dispersed in hydrocarbon phase as a homogenous mixture. The viscosity of monomer solution, agitation speed, rotor design and dispersant type, mainly governs the particle size and shape of resin [87]. Some detailed discussions on hetero-phase polymerizations have already been published [88-89]. The dispersion is thermodynamically unstable and requires both continuous agitation and addition of a low hydrophilic-lipophilic-balance (HLB) suspending agent.

3.3 Grafting Polymers

A number of studies have demonstrated that adsorbents modified with polymers containing functional groups which can enhance the adsorption capacity because of their highly coordinating capabilities with metal ions [57]. As a result, several methods have been proposed for grafting polymers onto the surfaces of adsorbents, such as chemisorption of reactive polymer onto the surface [90], grafting a polymer chain through a monomer covalently linked to surface [91] and grafting a polymer chain from a surface modified with polymerization initiators [92]. Among these methods, latter can achieve maximum structural control and is called as "grafting" method.

3.3.1 Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP)

This method has attracted considerable attention for the preparation of functional grafted materials, as this method can endow the adsorbent with high capacity. Zong *et al.* grafted poly-acrylonitrile onto the surface of cross-linked polystyrene (PS) via surface-initiated ATRP and followed the reaction with $\text{NH}_2\text{OH}\cdot\text{H}_2\text{O}$ to prepare a high-capacity resin for mercury removal [93]. Deng *et al.*

prepared an aminated PS resin for the removal of Cu(II), Pb(II) and Cr(VI) by grafting of poly(glycidyl methacrylate) (PGM) via ATRP and a subsequent amination reaction [94]. Modified PGM-grafted PS beads with iminodiacetic acid are incorporated into a chelating resin for metal ion removal. Therefore, new adsorbents can be prepared by grafting polymers with new functional groups via atomic transfer radical polymerization.

3.4 Resins

In polymer chemistry and materials science, resin is a solid or highly viscous substance of plant or synthetic origin that is typically convertible into polymers [95]. Resins are usually found to be a mixture of numerous organic compounds.

3.5 Carbon Nanotubes

Diverse techniques have been developed for the synthesis of CNTs but they are mainly produced by arc discharge, laser ablation and catalytic chemical vapor

deposition (CVD) methods [100-101]. The latter one, in comparison with the other methods, is the easiest, simplest and scalable way to produce CNTs which generally employs gas phase hydrocarbons. In the CVD method, presence of amorphous carbon on supported catalysts can be a challenge which affects the yield, purity and quality of final products since the catalytic activity and lifetime of catalyst are limited by the amorphous carbon [102]. CNTs are promising materials for the environmental pollution management due to their large specific surface area, highly porous structure and strong interaction between functionalized carbon and target species [103-104]. In view of environmental application, CNTs have been extensively used as adsorbents for the removal of a number of heavy metal ions including cadmium, chromium, lead, nickel, mercury, arsenic and so on [105].

Table 1 Conventional adsorbents for efficient removal of dyes

| Adsorbent | Dyes | Max. Adsorption Capacity | References |
|--|------------------------|--------------------------|------------|
| Coir Pith | 1. Basic violet 10 | 2.56 mg/g | [26] |
| | 2. Direct red 28 | 6.72 mg/g | [27] |
| | 3. Acid violet | 8.06 mg/g | [26] |
| | 4. Basic violet 10 | 94.73 mg/g | [28] |
| Orange Peel | 1. Acid violet 17 | 19.88 mg/g | [29] |
| | 2. Methyl Orange | 20.5 mg/g | [30] |
| | 3. Basic blue 9 | 18.6 mg/g | [30] |
| | 4. Basic violet 10 | 14.3 mg/g | [30] |
| Banana Peel | 1. Basic blue 9 | 20.8 mg/g | [30] |
| | 2. Methyl Orange | 21 mg/g | [30] |
| | 3. Basic violet 10 | 20.6 mg/g | [30] |
| Rice Husk | 1. Basic blue 9 | 19.83 mg/g | [31] |
| | 2. Acid yellow 36 | 86.9 mg/g | [32] |
| | 3. Acid blue | 50 mg/g | [33] |
| | 4. Basic green | 511 mg/g | [34] |
| Straw | 1. Basic blue 9 | 19.82 mg/g | [31] |
| Date Pit | 1. Basic blue 9 | 17.3 mg/g | [35] |
| Oil Palm Fibre | 1. Malachite green | 149.35 mg/g | [36] |
| Durian | 1. Methylene blue | 289.26 mg/g | [37] |
| Guava | 1. Methylene blue | 185.2 mg/g | [38] |
| Almond Shell | 1. Direct red 80 | 90.09 mg/g | [39] |
| Pomelo (<i>Citrus grandis</i> peel) | 1. Methylene blue | 344.83 mg/g | [40] |
| Broad Bean Peel | 1. Methylene Blue | 192.7 mg/g | [41] |
| Peanut Hull | 1. Reactive dye | 55.5 mg/g | [42] |
| <i>Citrus lantus</i> Rind | 1. Crystal violet | 11.9 mg/g | [43] |
| Wood Apple (<i>Limonia acidissima</i>) | 1. Malachite green dye | 35.48 mg/g | [44] |
| Hazelnut Shell | 1. Basic blue 9 | 8.82 mg/g | [45] |
| Pumpkin Hull Seed | 1. Methylene Blue | 141.92 mg/g | [46] |

Table 2 Sorption capacities of various adsorbents for removal of different metals

| Adsorbents | Adsorbate | Adsorption Capacity (mgg ⁻¹) | References |
|---|-----------|--|------------|
| Fe ₃ O ₄ @SiO ₂ @meso-SiO ₂ -R2-NH ₂ Microsphere | Cu (II) | 523.6 | [57] |
| Fe ₃ O ₄ @SiO ₂ @meso-SiO ₂ -R2-NH ₂ Microsphere | Cd (II) | 446.4 | [57] |
| Fe ₃ O ₄ @SiO ₂ @meso-SiO ₂ -R1-NH ₂ Microsphere | Pb (II) | 880.6 | [57] |
| Fe ₃ O ₄ @SiO ₂ @meso-SiO ₂ -R1-NH ₂ Microsphere | Cu (II) | 628.3 | [57] |

| | | | |
|---|---------|-------|------|
| Fe ₃ O ₄ @SiO ₂ @meso-SiO ₂ -R1-NH ₂ Microsphere | Cd (II) | 492.4 | [57] |
|---|---------|-------|------|

Table 3 Sorption capacities of various hydrogels for removal of different organic dyes

| Hydrogels | Adsorbate | Adsorption Capacity (mgg ⁻¹) | References |
|--|----------------------------------|--|------------|
| Hydroxypropyl Cellulose (HPC) Immersed with Graphene Oxide | Methylene Blue | 118.483 | [78] |
| Carboxymethyl Cellulose Immersed with Acrylic Acid | Methyl Orange | 1111.11 | [79] |
| Carboxymethyl Cellulose Immersed with Acrylic Acid | Disperse Blue | 1090.0 | [79] |
| Carboxymethyl Cellulose Immersed with Acrylic Acid | Malachite Green Chloride | 509.1 | [79] |
| Poly-acrylic Acid Immersed with Bentonite Nanocomposite Hydrogel | Crystal Violet | 300 | [80-81] |
| Maize Starch Grafted AA Immersed with Aam Hydrogel | Direct Brown 2 Direct Blue 21 | 35.97 95.24 | [80] |
| Poly(AA-co-AMPS)/MMT Immersed with Monotrillionite | Methylene Blue | 192.31 | [82] |
| Starch Grafted/AA Immersed with Na-Montmorillonite | Safranin-T | 2237 | [83] |
| Starch Cellulose Immersed with Nano-Whiskers | Methylene Blue | 2050 | [84] |

Table 4 Sorption capacities of various grafted polymers for removal of different organic dyes

| Adsorbents | Adsorbate | Adsorption Capacity | References |
|---|-----------|---------------------|------------|
| Polyacrylic Acid Sodium (P(AA-Na)) Immersed with Grafted Cotton | Cu (II) | 2.45 mmol/g | [91] |
| Polyacrylic Acid Sodium (P(AA-Na)) Immersed with Grafted Cotton | Pb (II) | 2.44 mmol/g | [91] |

Table 5 Sorption capacities of adsorbents for removal of Cu(II), Pb(II) and Cr(VI)

| Adsorbents | Adsorption Capacities (mmolg ⁻¹) | | | Equilibrium Times | pH | References |
|------------|--|--------|--------|-------------------|-----|------------|
| | Pb(II) | Cu(II) | Cr(II) | | | |
| PVT-g-PS | 1.52 | 2.65 | 3.36 | 90-120 minutes | 5.0 | [50] |

Table 6 Sorption capacities and equilibrium time of various resins for removal of metals

| Adsorbents | Adsorbate | Adsorption Capacity (mmolg ⁻¹) | Equilibrium Time | References |
|--|-----------|--|------------------|------------|
| Aminated Resin via SI-ATRP | Pb(II) | 0.97 | 6-20 Hours | [94] |
| Aminated Resin via SI-ATRP | Cu(II) | 2.6 | 6-20 Hours | [94] |
| Commercial 732-CR Resin | Pb(II) | 1.92 | 200 Minutes | [96] |
| Diphonix Resin | Pb(II) | 0.555 | 30 Minutes | [97] |
| Diphonix Resin | Cu(II) | 0.925 | 30 Minutes | [97] |
| Poly(vinyl pyridine-ethylene glycoldimethacrylate) Resin | Pb(II) | 0.09 | - | [98] |
| Poly(vinyl pyridine-ethylene glycoldimethacrylate) Resin | Cu(II) | 0.29 | - | [98] |
| Poly(vinyl pyridine-ethylene glycoldimethacrylate) Resin | Cr(II) | 0.33 | - | [98] |
| N,N-Di(carboxymethyl) dithiocarbamate Chelating Resin | Pb(II) | 1.88 | 30 Minutes | [99] |
| N,N-Di(carboxymethyl) dithiocarbamate Chelating Resin | Cu(II) | 1.57 | 30 Minutes | [99] |

4. Conclusions

Super adsorbents have attained special attention in the field of wastewater treatment due to their excellent properties like high adsorption capacity, fast kinetics and reusability. Potential toxicity of organic dyes being a very

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serious environmental problem has been taken into account by employing economical and reusable super adsorbents. The review focuses on utilization of different raw materials for the synthesis of novel super adsorbent materials for dye removal. Development of technologies for decolorization of

wastewaters effectively and efficiently is the dire need of the hour. Porous materials with enhanced surface area, hydrogels, resins, grafted polymers and carbon nanotubes can be employed as super adsorbents for removing toxic pollutants and dyes from water. Adsorption on polymers and hydrogels is cheaper and popular methods for the removal of pollutants from wastewater. There cycling of adsorbents and least probability of toxic residues makes the technique economically important and commercially viable. Hence, in a general sense, if we look out at the systems which different researchers have investigated into and subsequently brought into the light, use of recyclable different hydrogels, polymers (grafted), resins and porous substances is in reality a best available system to study and explore. In conclusion, super adsorbents could be easily synthesized for employing as a superior adsorbent to remove toxic metals and dyes from water. The adsorbent put forward in this review has the main advantages over other adsorbents previously reported the fast saturation time and capability of reuse. Starch grafted/AA/Na-Montmorillonite, a hydrogel showed an adsorption capacity of 2237 mgg⁻¹ for removal of Safranin T dye from aqueous media. Therefore, hydrogel composite presents outstanding capacity to be employed in the remediation of dye contaminated wastewaters. These materials simultaneously provide convenient separation capability, fast removal rate, high uptake capacity, superior adsorption selectivity and favorable reusability for adsorbing dyes from water. In comparison from conventional adsorbents, super adsorbents showed higher values for adsorption capacity.

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