



## New generation super adsorbents – A review

Farwa Nadeem<sup>1\*</sup>, Zubia Sajid<sup>1</sup>, Muhammad Idrees Jilani<sup>1,2</sup>, Ahmad Raza<sup>1</sup> and Fazal Abbas<sup>1</sup>

<sup>1</sup>Department of Chemistry, University of Agriculture, Faisalabad-38040-Pakistan and <sup>2</sup>School of Chemistry and Molecular Biosciences, University of Queensland, Australia

### 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<sup>-1</sup> 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

**Full length article** \*Corresponding Author, e-mail: [farwa668@gmail.com](mailto:farwa668@gmail.com)

### 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 CO<sub>2</sub> 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 ( $\text{Fe}_3\text{O}_4$ ) 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  $\alpha$ -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 <sup>-1</sup> )	References
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @meso-SiO <sub>2</sub> -R2-NH <sub>2</sub> Microsphere	Cu (II)	523.6	[57]
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @meso-SiO <sub>2</sub> -R2-NH <sub>2</sub> Microsphere	Cd (II)	446.4	[57]
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @meso-SiO <sub>2</sub> -R1-NH <sub>2</sub> Microsphere	Pb (II)	880.6	[57]
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @meso-SiO <sub>2</sub> -R1-NH <sub>2</sub> Microsphere	Cu (II)	628.3	[57]

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

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

Hydrogels	Adsorbate	Adsorption Capacity (mgg <sup>-1</sup> )	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 <sup>-1</sup> )			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 <sup>-1</sup> )	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

*Nadeem et al., 2016*

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<sup>-1</sup> 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.

## References

- [1] S.W. Tam-Chang, D. Mahinay, L.M. Huang In *Multifunctional Materials via Molecular Self-Organization into Liquid-Crystalline Phase*, Advanced Materials Research, 2008; Trans Tech Publ: 2008; pp 165-168.
- [2] D. Bardelang, M.B. Zaman, I.L. Moudrakovski, S. Pawsey, J.C. Margeson, D. Wang, X. Wu, J.A. Ripmeester, C.I. Ratcliffe, K. Yu. (2008). Interfacing supramolecular gels and quantum dots with ultrasound: smart photoluminescent dipeptide gels. *Advanced materials*. 20(23): 4517-4520.
- [3] E.A.A. Neel, D.M. Pickup, S.P. Valappil, R.J. Newport, J.C. Knowles. (2009). Bioactive functional materials: a perspective on phosphate-based glasses. *Journal of Materials Chemistry*. 19(6): 690-701.
- [4] X.D. Liu, M. Yamada, M. Matsunaga, N. Nishi, Functional materials derived from DNA. In *Functional Materials and Biomaterials*, Springer: 2006; pp 149-178.
- [5] M.R. Bockstaller, R.A. Mickiewicz, E.L. Thomas. (2005). Block copolymer nanocomposites: perspectives for tailored functional materials. *Advanced materials*. 17(11): 1331-1349.
- [6] K. Matsukawa. (2005). Development of photo-functional materials from organic/inorganic nano-hybrids. *Journal of Photopolymer Science and Technology*. 18(2): 203-210.
- [7] K.B. Yoon. (2007). Organization of zeolite microcrystals for production of functional materials. *Accounts of chemical research*. 40(1): 29-40.
- [8] R. Schöllhorn. (1996). Intercalation systems as nanostructured functional materials. *Chemistry of Materials*. 8(8): 1747-1757.
- [9] G.E. Fryxell. (2006). The synthesis of functional mesoporous materials. *Inorganic Chemistry Communications*. 9(11): 1141-1150.
- [10] W.T. Yao, S.H. Yu. (2008). Synthesis of Semiconducting Functional Materials in Solution: From II-VI Semiconductor to Inorganic–Organic Hybrid Semiconductor Nanomaterials. *Advanced Functional Materials*. 18(21): 3357-3366.
- [11] P. Liu, K. Liang. (2001). Review Functional materials of porous metals made by P/M, electroplating and some other techniques. *Journal of materials science*. 36(21): 5059-5072.
- [12] A. Taguchi, F. Schüth. (2005). Ordered mesoporous materials in catalysis. *Microporous and mesoporous materials*. 77(1): 1-45.
- [13] A. Alexander, M. Ajazuddin, M. Swarna, M. Sharma, D. Tripathi. (2011). Polymers and permeation enhancers: specialized components of mucoadhesives. *Stamford Journal of Pharmaceutical Sciences*. 4(1): 91-95.
- [14] M.E. Davis. (2002). Ordered porous materials for emerging applications. *Nature*. 417(6891): 813.
- [15] J.-R. Li, R.J. Kuppler, H.-C. Zhou. (2009). Selective gas adsorption and separation in metal–organic frameworks. *Chemical Society Reviews*. 38(5): 1477-1504.
- [16] Y. Zhang, S.N. Riduan. (2012). Functional porous organic polymers for heterogeneous catalysis. *Chemical Society Reviews*. 41(6): 2083-2094.
- [17] S.M. Kuznicki, V.A. Bell, S. Nair, H.W. Hillhouse, R.M. Jacubinas, C.M. Braunbarth, B.H. Toby, M. Tsapatsis. (2001). A titanosilicate molecular sieve with adjustable pores for size-selective adsorption of molecules. *Nature*. 412(6848): 720.
- [18] M. Vallet-Regí, F. Balas, D. Arcos. (2007). Mesoporous materials for drug delivery. *Angewandte Chemie International Edition*. 46(40): 7548-7558.
- [19] H. Furukawa, O.M. Yaghi. (2009). Storage of hydrogen, methane, and carbon dioxide in highly porous covalent organic frameworks for clean energy applications. *Journal of the American Chemical Society*. 131(25): 8875-8883.

- [20] C. Liu, F. Li, L.P. Ma, H.M. Cheng. (2010). Advanced materials for energy storage. *Advanced materials*. 22(8): E28-E62.
- [21] A.G. Slater, A.I. Cooper. (2015). Function-led design of new porous materials. *Science*. 348(6238): aaa8075.
- [22] A. Thomas. (2010). Functional materials: from hard to soft porous frameworks. *Angewandte Chemie International Edition*. 49(45): 8328-8344.
- [23] W. Zhang, T. Liu, H. Wu, P. Wu, M. He. (2015). Direct synthesis of ordered imidazolyl-functionalized mesoporous polymers for efficient chemical fixation of CO<sub>2</sub>. *Chemical Communications*. 51(4): 682-684.
- [24] P. Nugent, Y. Belmabkhout, S.D. Burd, A.J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, L. Wojtas. (2013). Porous materials with optimal adsorption thermodynamics and kinetics for CO<sub>2</sub> separation. *Nature*. 495(7439): 80.
- [25] T.A. Makal, J.-R. Li, W. Lu, H.-C. Zhou. (2012). Methane storage in advanced porous materials. *Chemical Society Reviews*. 41(23): 7761-7779.
- [26] C. Namasivayam, M.D. Kumar, K. Selvi, R.A. Begum, T. Vanathi, R. Yamuna. (2001). 'Waste'coir pith—a potential biomass for the treatment of dyeing wastewaters. *Biomass and Bioenergy*. 21(6): 477-483.
- [27] C. Namasivayam, D. Kavitha. (2002). Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. *Dyes and Pigments*. 54(1): 47-58.
- [28] C. Namasivayam, R. Radhika, S. Suba. (2001). Uptake of dyes by a promising locally available agricultural solid waste: coir pith. *Waste management*. 21(4): 381-387.
- [29] R. Sivaraj, C. Namasivayam, K. Kadirvelu. (2001). Orange peel as an adsorbent in the removal of acid violet 17 (acid dye) from aqueous solutions. *Waste management*. 21(1): 105-110.
- [30] G. Annadurai, R.-S. Juang, D.-J. Lee. (2002). Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. *Journal of hazardous materials*. 92(3): 263-274.
- [31] N. Kannan, M.M. Sundaram. (2001). Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—a comparative study. *Dyes and Pigments*. 51(1): 25-40.
- [32] P.K. Malik. (2003). Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of Acid Yellow 36. *Dyes and Pigments*. 56(3): 239-249.
- [33] M.M. Mohamed. (2004). Acid dye removal: comparison of surfactant-modified mesoporous FSM-16 with activated carbon derived from rice husk. *Journal of Colloid and Interface Science*. 272(1): 28-34.
- [34] Y. Guo, S. Yang, W. Fu, J. Qi, R. Li, Z. Wang, H. Xu. (2003). Adsorption of malachite green on micro-and mesoporous rice husk-based active carbon. *Dyes and Pigments*. 56(3): 219-229.
- [35] F. Banat, S. Al-Asheh, L. Al-Makhadmeh. (2003). Evaluation of the use of raw and activated date pits as potential adsorbents for dye containing waters. *Process Biochemistry*. 39(2): 193-202.
- [36] B. Hameed, M. El-Khaiary. (2008). Batch removal of malachite green from aqueous solutions by adsorption on oil palm trunk fibre: equilibrium isotherms and kinetic studies. *Journal of hazardous materials*. 154(1-3): 237-244.
- [37] B. Hameed, H. Hakimi. (2008). Utilization of durian (*Durio zibethinus* Murray) peel as low cost sorbent for the removal of acid dye from aqueous solutions. *Biochemical Engineering Journal*. 39(2): 338-343.
- [38] V. Ponnusami, S. Vikram, S. Srivastava. (2008). Guava (*Psidium guajava*) leaf powder: novel adsorbent for removal of methylene blue from aqueous solutions. *Journal of hazardous materials*. 152(1): 276-286.
- [39] F.D. Ardejani, K. Badii, N.Y. Limaee, S.Z. Shafaei, A. Mirhabibi. (2008). Adsorption of Direct Red 80 dye from aqueous solution onto almond shells: Effect of pH, initial concentration and shell type. *Journal of hazardous materials*. 151(2-3): 730-737.
- [40] B. Hameed, D. Mahmoud, A. Ahmad. (2008). Sorption of basic dye from aqueous solution by pomelo (*Citrus grandis*) peel in a batch system. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 316(1-3): 78-84.
- [41] B. Hameed, M. El-Khaiary. (2008). Sorption kinetics and isotherm studies of a cationic dye using agricultural waste: broad bean peels. *Journal of hazardous materials*. 154(1-3): 639-648.
- [42] M.Ş. Tanyildizi. (2011). Modeling of adsorption isotherms and kinetics of reactive dye from aqueous solution by peanut hull. *Chemical Engineering Journal*. 168(3): 1234-1240.
- [43] B.K. Suyamboo, R.S. Perumal. (2012). Equilibrium, thermodynamic and kinetic studies on adsorption of a basic dye by *Citrullus lanatus* rind. *Iranica Journal of Energy & Environment*. 3(1): 23-34.
- [44] A.S. Sartape, A.M. Mandhare, V.V. Jadhav, P.D. Raut, M.A. Anuse, S.S. Kolekar. (2017). Removal of malachite green dye from aqueous solution with adsorption technique using *Limonia acidissima* (wood apple) shell as low cost adsorbent. *Arabian Journal of Chemistry*. 10: S3229-S3238.



- [45] A. Aygün, S. Yenisoý-Karakaş, I. Duman. (2003). Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties. *Microporous and mesoporous materials*. 66(2-3): 189-195.
- [46] B. Hameed, M. El-Khaiary. (2008). Removal of basic dye from aqueous medium using a novel agricultural waste material: Pumpkin seed hull. *Journal of hazardous materials*. 155(3): 601-609.
- [47] M.J. Zohuriaan-Mehr, K. Kabiri. (2008). Superabsorbent polymer materials: a review. *Iranian polymer journal*. 17(6): 451.
- [48] U. Dayal, S.K. Mehta, M.S. Choudhary, R.C. JAIN. (1999). Synthesis of acrylic superabsorbents.
- [49] M. Zohuriaan-Mehr. (2006). Super-absorbents. *Iran Polymer Society, Tehran*. 228.
- [50] Y. Chen, M. He, C. Wang, Y. Wei. (2014). A novel polyvinyltetrazole-grafted resin with high capacity for adsorption of Pb (II), Cu (II) and Cr (III) ions from aqueous solutions. *Journal of Materials Chemistry A*. 2(27): 10444-10453.
- [51] S. Nayab, A. Farrukh, Z. Oluz, E.I. Tuncel, S.R. Tariq, H.u. Rahman, K. Kirchoff, H. Duran, B. Yameen. (2014). Design and fabrication of branched polyamine functionalized mesoporous silica: an efficient absorbent for water remediation. *ACS applied materials & interfaces*. 6(6): 4408-4417.
- [52] Z. Yan, S. Tao, J. Yin, G. Li. (2006). Mesoporous silicas functionalized with a high density of carboxylate groups as efficient absorbents for the removal of basic dyestuffs. *Journal of Materials Chemistry*. 16(24): 2347-2353.
- [53] X.-Y. Yang, A. Léonard, A. Lemaire, G. Tian, B.-L. Su. (2011). Self-formation phenomenon to hierarchically structured porous materials: design, synthesis, formation mechanism and applications. *Chemical Communications*. 47(10): 2763-2786.
- [54] W. Shi, S. Tao, Y. Yu, Y. Wang, W. Ma. (2011). High performance adsorbents based on hierarchically porous silica for purifying multicomponent wastewater. *Journal of Materials Chemistry*. 21(39): 15567-15574.
- [55] Y. Liang, Z. Li, R. Fu, D. Wu. (2013). Nanoporous carbons with a 3D nanonetwork-interconnected 2D ordered mesoporous structure for rapid mass transport. *Journal of Materials Chemistry A*. 1(11): 3768-3773.
- [56] L. Meng, X. Zhang, Y. Tang, K. Su, J. Kong. (2015). Hierarchically porous silicon-carbon-nitrogen hybrid materials towards highly efficient and selective adsorption of organic dyes. *Scientific reports*. 5: 7910.
- [57] S.-H. Wu, C.-Y. Mou, H.-P. Lin. (2013). Synthesis of mesoporous silica nanoparticles. *Chemical Society Reviews*. 42(9): 3862-3875.
- [58] S. Ray, A.K. Das, A. Banerjee. (2007). pH-responsive, bolaamphiphile-based smart metallo-hydrogels as potential dye-adsorbing agents, water purifier, and vitamin B12 carrier. *Chemistry of Materials*. 19(7): 1633-1639.
- [59] S. Deng, H. Xu, X. Jiang, J. Yin. (2013). Poly (vinyl alcohol)(PVA)-enhanced hybrid hydrogels of hyperbranched poly (ether amine)(hPEA) for selective adsorption and separation of dyes. *Macromolecules*. 46(6): 2399-2406.
- [60] M. De Loos, B.L. Feringa, J.H. van Esch. (2005). Design and application of self-assembled low molecular weight hydrogels. *European Journal of Organic Chemistry*. 2005(17): 3615-3631.
- [61] S. Kiyonaka, K. Sugiyasu, S. Shinkai, I. Hamachi. (2002). First thermally responsive supramolecular polymer based on glycosylated amino acid. *Journal of the American Chemical Society*. 124(37): 10954-10955.
- [62] B. Xing, C.-W. Yu, K.-H. Chow, P.-L. Ho, D. Fu, B. Xu. (2002). Hydrophobic interaction and hydrogen bonding cooperatively confer a vancomycin hydrogel: a potential candidate for biomaterials. *Journal of the American Chemical Society*. 124(50): 14846-14847.
- [63] Z. Yang, K. Xu, L. Wang, H. Gu, H. Wei, M. Zhang, B. Xu. (2005). Self-assembly of small molecules affords multifunctional supramolecular hydrogels for topically treating simulated uranium wounds. *Chemical Communications*. (35): 4414-4416.
- [64] M. de Loos, A. Friggeri, J. van Esch, R.M. Kellogg, B.L. Feringa. (2005). Cyclohexane bis-urea compounds for the gelation of water and aqueous solutions. *Organic & biomolecular chemistry*. 3(9): 1631-1639.
- [65] K. Hanabusa, M. Yamada, M. Kimura, H. Shirai. (1996). Prominent gelation and chiral aggregation of alkylamides derived from trans-1, 2-diaminocyclohexane. *Angewandte Chemie International Edition in English*. 35(17): 1949-1951.
- [66] A. Heeres, C. van der Pol, M. Stuart, A. Friggeri, B.L. Feringa, J. van Esch. (2003). Orthogonal self-assembly of low molecular weight hydrogelators and surfactants. *Journal of the American Chemical Society*. 125(47): 14252-14253.
- [67] H. Kobayashi, A. Friggeri, K. Koumoto, M. Amaike, S. Shinkai, D.N. Reinhoudt. (2002). Molecular design of "super" hydrogelators: understanding the gelation process of azobenzene-based sugar derivatives in water. *Organic letters*. 4(9): 1423-1426.

- [68] D.J. Pochan, J.P. Schneider, J. Kretsinger, B. Ozbas, K. Rajagopal, L. Haines. (2003). Thermally reversible hydrogels via intramolecular folding and consequent self-assembly of a de novo designed peptide. *Journal of the American Chemical Society*. 125(39): 11802-11803.
- [69] V. Jayawarna, M. Ali, T.A. Jowitt, A.F. Miller, A. Saiani, J.E. Gough, R.V. Ulijn. (2006). Nanostructured hydrogels for three-dimensional cell culture through self-assembly of fluorenylmethoxycarbonyl-dipeptides. *Advanced materials*. 18(5): 611-614.
- [70] S.M. Park, Y.S. Lee, B.H. Kim. (2003). Novel low-molecular-weight hydrogelators based on 2'-deoxyuridine. *Chemical Communications*. (23): 2912-2913.
- [71] S. Mukhopadhyay, U. Maitra. (2004). Chemistry and biology of bile acids. *Current Science*. 87(12): 1666-1683.
- [72] P. Terech, N.M. Sangeetha, B. Demé, U. Maitra. (2005). Self-assembled networks of ribbons in molecular hydrogels of cationic deoxycholic acid analogues. *The Journal of Physical Chemistry B*. 109(25): 12270-12276.
- [73] J. Kisiday, M. Jin, B. Kurz, H. Hung, C. Semino, S. Zhang, A. Grodzinsky. (2002). Self-assembling peptide hydrogel fosters chondrocyte extracellular matrix production and cell division: implications for cartilage tissue repair. *Proceedings of the National Academy of Sciences*. 99(15): 9996-10001.
- [74] S.L. Zhou, S. Matsumoto, H.D. Tian, H. Yamane, A. Ojida, S. Kiyonaka, I. Hamachi. (2005). pH-responsive shrinkage/swelling of a supramolecular hydrogel composed of two small amphiphilic molecules. *Chemistry—A European Journal*. 11(4): 1130-1136.
- [75] V. Bekiari, P. Lianos. (2006). Ureasil gels as a highly efficient adsorbent for water purification. *Chemistry of Materials*. 18(17): 4142-4146.
- [76] S.-i. Kawano, N. Fujita, S. Shinkai. (2004). A coordination gelator that shows a reversible chromatic change and sol-gel phase-transition behavior upon oxidative/reductive stimuli. *Journal of the American Chemical Society*. 126(28): 8592-8593.
- [77] M. Suzuki, M. Yumoto, H. Shirai, K. Hanabusa. (2005). L-Lysine-based supramolecular hydrogels containing various inorganic ions. *Organic & biomolecular chemistry*. 3(16): 3073-3078.
- [78] X. Liu, Y. Zhou, W. Nie, L. Song, P. Chen. (2015). Fabrication of hydrogel of hydroxypropyl cellulose (HPC) composited with graphene oxide and its application for methylene blue removal. *Journal of materials science*. 50(18): 6113-6123.
- [79] G. Zhang, L. Yi, H. Deng, P. Sun. (2014). Dyes adsorption using a synthetic carboxymethyl cellulose-acrylic acid adsorbent. *Journal of Environmental Sciences*. 26(5): 1203-1211.
- [80] A. Hashem, E. Abdel-Halim, H. Sokker. (2007). Bi-functional starch composites prepared by  $\gamma$ -irradiation for removal of anionic and cationic dyes from aqueous solutions. *Polymer-Plastics Technology and Engineering*. 46(1): 71-77.
- [81] B. Bethi, S.H. Sonawane, I. Potoroko, B.A. Bhanvase, S.S. Sonawane. (2017). Novel hybrid system based on hydrodynamic cavitation for treatment of dye waste water: A first report on bench scale study. *Journal of environmental chemical engineering*. 5(2): 1874-1884.
- [82] H. Hosseinzadeh, N. Khoshnood. (2016). Removal of cationic dyes by poly (AA-co-AMPS)/montmorillonite nanocomposite hydrogel. *Desalination and Water Treatment*. 57(14): 6372-6383.
- [83] E. Al, G. Güçlü, T.B. İyim, S. Emik, S. Özgümüş. (2008). Synthesis and properties of starch-graft-acrylic acid/Na-montmorillonite superabsorbent nanocomposite hydrogels. *Journal of Applied Polymer Science*. 109(1): 16-22.
- [84] R.F. Gomes, A.C.N. de Azevedo, A.G. Pereira, E.C. Muniz, A.R. Fajardo, F.H. Rodrigues. (2015). Fast dye removal from water by starch-based nanocomposites. *Journal of colloid and interface science*. 454: 200-209.
- [85] E.M. Ahmed. (2015). Hydrogel: Preparation, characterization, and applications: A review. *Journal of advanced research*. 6(2): 105-121.
- [86] S. Kiatkamjornwong. (2007). Superabsorbent polymers and superabsorbent polymer composites. *Sci. Asia*. 33(1): 39-43.
- [87] T. Ogata, K. Nagayoshi, T. Nagasako, S. Kurihara, T. Nonaka. (2006). Synthesis of hydrogel beads having phosphinic acid groups and its adsorption ability for lanthanide ions. *Reactive and Functional Polymers*. 66(6): 625-633.
- [88] D. Hunkeler. (1992). Synthesis and characterization of high molecular weight water-soluble polymers. *Polymer international*. 27(1): 23-33.
- [89] N. Watanabe, Y. Hosoya, A. Tamura, H. Kosuge. (1993). Characteristics of water-absorbent polymer emulsions. *Polymer international*. 30(4): 525-531.
- [90] P. Auroy, L. Auvray, L. Leger. (1992). Silica particles stabilized by long grafted polymer chains: from electrostatic to steric repulsion. *Journal of colloid and interface science*. 150(1): 187-194.
- [91] Y. Zheng, S. Deng, L. Niu, F. Xu, M. Chai, G. Yu. (2011). Functionalized cotton via surface-initiated atom transfer radical polymerization for enhanced

- sorption of Cu (II) and Pb (II). *Journal of hazardous materials*. 192(3): 1401-1408.
- [92] J. He, X. Yang, J. Mao, F. Xu, Q. Cai. (2012). Hydroxyapatite–poly (l-lactide) nanohybrids via surface-initiated ATRP for improving bone-like apatite-formation abilities. *Applied surface science*. 258(18): 6823-6830.
- [93] G. Zong, H. Chen, R. Qu, C. Wang, N. Ji. (2011). Synthesis of polyacrylonitrile-grafted cross-linked N-chlorosulfonamidated polystyrene via surface-initiated ARGET ATRP, and use of the resin in mercury removal after modification. *Journal of hazardous materials*. 186(1): 614-621.
- [94] L. Niu, S. Deng, G. Yu, J. Huang. (2010). Efficient removal of Cu (II), Pb (II), Cr (VI) and As (V) from aqueous solution using an aminated resin prepared by surface-initiated atom transfer radical polymerization. *Chemical Engineering Journal*. 165(3): 751-757.
- [95] A. Wilkinson, A. McNaught. (1997). *IUPAC Compendium of Chemical Terminology*, (the "Gold Book"). International Union of Pure and Applied Chemistry: Zürich, Switzerland.
- [96] H. Guo, Y. Ren, X. Sun, Y. Xu, X. Li, T. Zhang, J. Kang, D. Liu. (2013). Removal of Pb<sup>2+</sup> from aqueous solutions by a high-efficiency resin. *Applied surface science*. 283: 660-667.
- [97] D. Kołodyńska. (2010). Diphonix Resin® in sorption of heavy metal ions in the presence of the biodegradable complexing agents of a new generation. *Chemical Engineering Journal*. 159(1-3): 27-36.
- [98] A. Duran, M. Soyulak, S.A. Tuncel. (2008). Poly (vinyl pyridine-poly ethylene glycol methacrylate-ethylene glycol dimethacrylate) beads for heavy metal removal. *Journal of hazardous materials*. 155(1-2): 114-120.
- [99] X. Jing, F. Liu, X. Yang, P. Ling, L. Li, C. Long, A. Li. (2009). Adsorption performances and mechanisms of the newly synthesized N, N'-di (carboxymethyl) dithiocarbamate chelating resin toward divalent heavy metal ions from aqueous media. *Journal of hazardous materials*. 167(1-3): 589-596.
- [100] W. Li, H. Wang, Z. Ren, G. Wang, J. Bai. (2008). Co-production of hydrogen and multi-wall carbon nanotubes from ethanol decomposition over Fe/Al<sub>2</sub>O<sub>3</sub> catalysts. *Applied Catalysis B: Environmental*. 84(3-4): 433-439.
- [101] P. Zarabadi-Poor, A. Badieli, A.A. Yousefi, B.D. Fahlman, A. Abbasi. (2010). Catalytic chemical vapour deposition of carbon nanotubes using Fe-doped alumina catalysts. *Catalysis Today*. 150(1-2): 100-106.
- [102] N. Yoshihara, H. Ago, M. Tsuji. (2007). Chemistry of Water-Assisted Carbon Nanotube Growth over Fe– Mo/Mgo Catalyst. *The Journal of Physical Chemistry C*. 111(31): 11577-11582.
- [103] H. Alijani, Z. Shariatinia. (2017). Effective aqueous arsenic removal using zero valent iron doped MWCNT synthesized by in situ CVD method using natural  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> as a precursor. *Chemosphere*. 171: 502-511.
- [104] H. Alijani, M.H. Beyki, Z. Shariatinia, M. Bayat, F. Shemirani. (2014). A new approach for one step synthesis of magnetic carbon nanotubes/diatomite earth composite by chemical vapor deposition method: application for removal of lead ions. *Chemical Engineering Journal*. 253: 456-463.
- [105] A. Abbas, A.M. Al-Amer, T. Laoui, M.J. Al-Marri, M.S. Nasser, M. Khraisheh, M.A. Atieh. (2016). Heavy metal removal from aqueous solution by advanced carbon nanotubes: critical review of adsorption applications. *Separation and Purification Technology*. 157: 141-161.