

Nanoadsorbents: An Approach Towards Wastewater Treatment

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Abstract

Clean, secure, and adequate water is basic to the endurance of every individual living life frame. Environmental pollutants pose serious threats to freshwater supply, living organisms, and public health, despite their occurrence at low concentration ranges. Thus, treatment of waste water required around the creation. So, nanotechnology is an innovative technique for the treatment of water and wastewater to improve water quality and to improve water supply through safe usage of clean water source. Therefore, in past various techniques utilized for wastewater treatment, for example, adsorption, compound precipitation, sol-gel, solvo-thermal response, and so on, for the incorporation of nanoadsorbents, which can be viably utilized for groundwater treatment. This chapter concentrates on the removal of pollutants from water using a variety of adsorbents such as nanotubes, nanowires, and nanoadsorbents by using adsorption technology, which has turned out to be one of the best technologies for wastewater treatment. The survey will aid the readers to select suitable nanomaterials and to get up further research required for pollutant removal using nanoadsorbents, depending on the characteristics of effluents to be processed, industrial applicability, release standards, cost-effectiveness, regulatory demands, and durable ecological impacts.

Keywords: Nanotechnology, adsorption, nanoadsorbents, effluents

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12.1 Introduction

Creation of unsafe squanders and harmful gas exhaust and smokes into the earth because of the fast pace of industrialization and the resultant by-items have influenced nature. For the treatment of a wide range of natural and lethal squanders different ordinary advances are utilized, for example, adsorption, organic oxidation, compound oxidation and cremation. Supercritical water oxidation (SCWO) has been proposed as an innovation fit for crushing an extensive variety of natural dangerous wastes. It has been attracting consideration because of its capacity to crush a substantial assortment of high-hazard wastes coming about because of weapons disarmament and complex mechanical synthetic handling. In the scope of convergence of 1–20% of natural poisons, SCWO is far less expensive than cremation or active carbon treatment. In parallel, the quick development in nanotechnology has picked up a lot of enthusiasm for the environmental uses of nanomaterials. The high surface territory to a mass proportion of nanomaterials can enormously enhance the adsorption limits of sorbent materials. Because of its diminished size, the surface territories of nanomaterials develop exponentially for an indistinguishable thickness from the breadth shrivels. In view of their decreased size and vast radii of ebb and flow, the nanomaterials have a surface that is particularly responsive (basically because of high thickness of low-planned particles at the surface, edges, and vortex). These one of a kind properties can be connected to corrupt and search poisons in water and air [1]. Nanomaterials in different shapes/morphologies/frames significantly affect water and air quality in a natural environment [2]. Likewise, a few normal and designed nanomaterials have additionally been demonstrated to have solid antimicrobial properties, including chitosan, silver nanoparticles (nAg), photograph synergist TiO_2 , and carbon nanotubes (CNT) [3–7]. Nanotechnology is likewise utilized for discovery of pesticides and substantial metals (e.g., cadmium, copper, lead, mercury, arsenic, etc.). Besides, nanomaterials have improved redox and photocatalytic properties [8–10]. Functionalization process is connected on nanomaterials by covering or substance alteration with a specific end goal to (1) enhance surface and optical properties, (2) evade total, and (3) dispense with association among nanomaterials and biological substance. For instance, doping with a fitting dopant can improve photocatalytic movement and cause red-move in the bandgap of TiO_2 that prompts to have the ability to assimilate light in the visible range [11]. Accordingly, hybrid nanocomposites are manufactured by impregnating or covering the fine particles onto strong particles of bigger size to beat the limitations of NPs. The resultant polymer-based nanocomposite (PNC) holds the innate properties of nanoparticles, while the polymer bolster

materials give higher strength, processability, and enhancements brought on by the nanoparticle–matrix association. Additionally, consolidation of nanoparticles (NPs) into polymeric nanocomposites prompts to improvement of mechanical, electrical and optical properties. NPs-based layers can be manufactured by amassing NPs into permeable membranes [12, 13] or mixing them with polymeric or inorganic layers [14]. Nanofibers can likewise furnish a superior filtration with much littler porosity and capacities for catching much littler contaminants. This paper gives a review of the utilization of nanomaterials in the sanitization of water and air defiled by lethal metal particles, natural and inorganic solutes, microscopic organisms and infections and their execution in environmental remediation, contamination detecting, and detection, cleaner creation, and so on.

The anthropogenic arrival of overwhelming metals into nature is turning into a worldwide plague [15, 16]. These species can enter natural waters through the arrival of wastewater, mechanical activity [17] and household effluents [18, 19]. Albeit anthropogenic sources cause a significant part of the ecological contamination, substantial metals can likewise be brought into the earth through common sources. These interfacial collaborations, particularly between regular solids and water, can add to the discharge or collection of substantial metals into the earth [20]. The mixture of normal and anthropogenic sources can bring about substantial metals to gather and therefore have lethal impacts to people and other living beings [21–23]. The most poisonous metals are As, Cu, Hg, Ni, Cd, Pb, and Cr [24]. Due to ingestion of these metals, various diseases occurs such as serious seminal and neurological issue that can cause even death. Currently, the most widely recognized techniques to expel substantial metals from water and wastewater are particle exchange [25–27], reverse osmosis [28, 29], compound precipitation [30], electrochemical treatment [31–33], layer filtration [34], floatation [35], and adsorption. The adsorption is most important method to remove these metals from water samples. In creating nations where access to a lot of force and monetary assets can be an issue, this straightforward and shabby process would be a suitable choice. The thoughtless procedure of adsorption permits adaptability in the outline and utilization of the adsorbent. The two most normal strategies utilized for adsorption are the cluster strategy and section or stream technique. A segment or stream strategy utilizes a persistent stream of fluid through a settled bed of the adsorbent. Different isotherms are created, with a specific end goal to gauge and group adsorption frameworks. To depict and recognize the system of adsorption, an isotherm can be utilized between the solute and the substrate surface [36]. There are numerous adsorption isotherms required to discuss the adsorption process, for example, Langmuir and Freundlich isotherms. For the most part, the bend produced from the

Langmuir isotherm demonstrates an underlying slant reliant on the rate of progress of accessible destinations on the molecule with expanding solute adsorbing to the locales. It shows the balance dispersion of particles between the strong and fluid phase [37]. The Freundlich adsorption isotherm experimentally portrays the adsorption qualities for the liquid–solid interface. Because of its ease, proficiency, and reliable nature, adsorption is broadly well known for removal of substantial metals [38]. The biomaterials, polymers, and metal oxides were utilized for the removal of substantial metals from water [39–41]. The nanomaterials are also a good adsorbent due to incorporating upgraded surface territory in contrast with mass particles. This chapter discusses the sorts of inorganic nanoadsorbents and the kind of metal particles being evacuated. For the removal of various pollutants from water, the application of iron oxide (hematite, magnetite, and maghemite), carbon nanotubes (CNT), and metal oxide based (Ti, Mn, Zn), and polymeric nanoadsorbents are analyzed.

It is assessed that more than one billion individuals on the planet need access to safe water and inside couple of decades the flow water supply will diminish by one-third. The event of new/rising microcontaminants (e.g., endocrine disturbing mixes (EDCs)) in contaminated water/wastewater has rendered existing normal water/wastewater treatment plants ineffectual to meet the natural norms. The release of these mixes into the amphibian environment has influenced every living being. The customary materials and treatment advances like initiated carbon, oxidation, nanofiltration (NF), and reverse osmosis (RO) layers are not viable to treat unpredictable and confounded contaminated waters including pharmaceuticals, surfactants, different modern added substances, and various synthetic purported. The traditional water treatment procedures are not ready to address enough the expulsion of a wide range of harmful chemicals and pathogenic microorganisms in crude water. Utilizing better sanitization innovations can decrease issues of water deficiencies, wellbeing, vitality, and environmental change. Physicochemical medicines, for example, coagulation, flocculation, or lime softening turned out to be insufficient for evaluating diverse EDCs and pharmaceutical mixes in different studies [42–44]. Membrane processes like microfiltration, ultrafiltration, NF, and RO, which are weight-driven filtration procedures, are considered as some new very powerful processes [45–50]. These are considered as option strategies for expelling immense measures of natural micropollutants [51–53]. For the removal of micropollutants, NF and RO have proved to be quite effective filtration technologies [54, 55]. RO is moderately more compelling than NF; however, higher vitality utilization in RO makes it less alluring than NF where expulsion of toxins is brought about by various instruments including convection, dissemination (sieving), and

charge impacts [56]. Despite the fact that NF-based film procedures are very successful in evacuating huge masses of micropollutants [57], advanced materials and treatment methods are required to treat newly emerging micropollutants. This is especially critical to accomplish a significant consumable water investment funds through reuse of wastewater notwithstanding handling the step by step compounding nature of drinking water. Nanotechnology has been viewed as successful in taking care of water issues identified with quality and amount [58]. Nanomaterials (e.g., carbon nanotubes (CNTs) and dendrimers) are adding to the improvement of more productive treatment forms among the propelled water frameworks [59]. This chapter gives a remarkable viewpoint on essential research of nanotechnology for water/wastewater treatment and reuse by concentrating on difficulties of future research.

12.2 Classification of Nanomaterials as Nanoadsorbents

Due to the inborn surface property and outside functionalization of nanomaterials, these are essentially separated into groups considering their part in adsorption applications. Gold NPs, metallic oxide NPs, nanostructured mixed oxides, and magnetic NPs are the main categories of nanoparticles. Carbonaceous nanomaterials (CNMs) are other imperative groups in spite of adsorbent properties. Different carbonaceous nanomaterials such as, carbon nanotubes (CNTs), carbon nanoparticles (CNPs), and carbon nanosheets (CNSs) have been used as adsorbents. Correspondingly, silicon nanotubes (SiNTs), silicon nanoparticles (SiNPs), and silicon nanosheets (SiNSs) are included in a class of silicon nanomaterials (SiNMs). Nanofibers (NFs) are also a kind of nanomaterials for adsorption procedures. Nanoparticles have huge effect in the field of science, gadgets, solution science, and material sciences with a size of roughly 1–100 nm [60–71]. For the developing field of nanomaterials, the outline, combination, portrayal, and uses of nanostructures are basic viewpoints. The expression “group,” which had been broadly utilized as a part of the synthetic writing in previous years, is at present used to assign small nanoparticles in the sizes with 1 nm. As of late, NPs have been utilized as adsorbents because of their better natural properties, for example, concoction action and fine article estimation, as contrasted and the vast materials including ordinary scale TiO_2 , Al_2O_3 , and so on [72–74]. To acquire another specific strong stage extractant, NPs can be synthetically adjusted by a reagent for the preconcentration of metal particles [75–77]. The TiO_2 , Al_2O_3 , ZrO_2 , SiO_2 , and ZnO nanoparticles showed high capacity to absorb eluent from water samples [78–82]. They give

promising outcomes when utilized for tracemetal investigation of different sorts of water and arrangements of high virtue soluble base salts [83–89]. Because of their little measurement and high scattering, the detachment is difficult of these particles from aqueous medium [90]. Vassileva *et al.* described the adsorption capacity relies on upon pH conditions [91].

12.3 Importance of Nanomaterials in the Preconcentration Process

Overwhelming metal particles are progressively discharged into the earth, especially thus of industrialization, prompting to genuine contamination. Some trace metals, for example, cobalt, are basic to people; however, the day by day prerequisite is just a couple of milligrams. The metal substance, sediments, plants, and creatures can likewise give fundamental data on the levels of pollution in the earth [92]. Test pretreatment techniques, for example, division or potentially preconcentration before the instrumental location, have grown quickly because of the expanding requirement for exact and exact estimations at to a great degree low levels of analytes in different networks. Test readiness forms, including partition and preconcentration, directly affect exactness, accuracy, and recognition limits for some explanatory strategies. This procedure is additionally the deciding stride of the systematic method [93]. It is apparent from the literature [94] that other than division of meddling network segments and separation of toxic level of analytes, connected specimen pretreatment plans ought to suggest various advantages, for example, high effectiveness regarding test throughput or examining recurrence, diminished specimen and reagent utilization and waste generation, enhanced accuracy, low cutoff points of measurement (LOQs), negligible danger of test sullying, potential change of selectivity through active separation under synthetically nonequilibrated conditions, and computerization. Nonetheless, drawbacks, for example, critical concoction added substances, dissolvable misfortunes, complex gear, huge auxiliary waste, prefiltration issues, and tedious systems, constrain the use of the vast majority of these procedures. These issues could be tended to by the advancement of secluded and minimal procedures that give sufficient detachment and preconcentration without complex procedures. Strong stage extraction (SPE) is a decent apparatus to take care of these issues. This system has a few favorable circumstances over other preconcentration strategies in perspective of (1) basic planning of strong stage, (2) bring down cost and less tedious, (3) simple utilize, (4) low utilization of reagents, (5) safety regarding hazardous specimens, (6) advanced selectivity, (7) simple

computerization, (8) high separation calculate, (9) eco-accommodating techniques, (10) adsorbent reusability, and (11) more adaptable to consolidate with other present day recognition methods in an on the web or disconnected mode. These prompt to various elements that improve the selectivity and affectability of the technique, in particular, high surface zone, dynamic sorption locales, and substance action. In any case, adjustment of the adsorbents' external surface is regularly fundamental. Wang and Hansen [95] expressed that, keeping in mind the end goal to plan SPE pressed sections, as a standout among the most as often as possible utilized example pretreatment procedures, various variables impacting the execution of the segment division or preconcentration framework ought to be considered. Consequently, to achieve affectability and exactness is of astonishing vitality, the part of strong stage adsorbents in test pretreatment techniques. The exploration for new adsorbents is of significance keeping in mind the end goal to enhance diagnostic parameters, for example, selectivity, partiality, and limit in SPE techniques [96]. Researchers show an increased interest in science and engineering, due to unique physical and chemical properties of nanoparticles, in the use of nanoparticles for drinking water quality. The essential contaminants in drinking water are lead, cadmium, and copper metals, which are found in e-squander and different sources. The fundamental target of this chapter is to survey not just the characteristics, components, and conduct of nanomaterials in fluid frameworks and test arrangements, additionally the real readiness strategies, either straightforward procedures done in labs or confounded instrumental methods, showed in various unique papers or audit articles.

12.4 Properties and Mechanisms of Nanomaterials as Adsorbents

In this analysis, the uses of the nanoadsorbents examined to a great degree subordinate upon on their inborn surface properties. These occur because of being close to the edge of the nanometric scale, and in addition, on their outer functionalization, which is interpreted now and then as an indistinguishable course for the selectivity and affectability of the utilized preconcentration and detachment technique.

12.4.1 Innate Surface Properties

The properties of NPs such as physical, material, and substance are straightforwardly identified with their inherent synthesis, apparent volumes, and

irrelevant structures of surface [97]. Deciding the nature and dispersion of dynamic destinations on nanostructured surfaces is a critical analysis. Additionally, the adsorption capacity increases due to area of the most particles in the surface, high surface territory, high synthetic action, high adsorptive limit, absence of internal diffusional resistance, and high surface restricting vitality. Notwithstanding utilizing surface instruments, it can here and there be hard to portray the way of the real nanoparticle surfaces [98]. While metal oxide and metal nanoparticles have got to be distinctly amazing optimistic as adsorbents in test readiness forms and can beneficially trade ordinary sorbents for partition and preconcentration courses. Different morphologies of nanomaterials present new adsorption properties and qualities, similar to strong stage extraction and strong stage microextraction processes.

12.4.2 External Functionalization

In the surface properties of nanomaterials, various changes rise utilizing the different useful groups. The mixing of a variety of nanomaterials will bring about incredible adsorption properties with various outside functionalization techniques. The selectivity of NPs increases due to advance functionalization of the surface. The properties of variety of nanoparticles may significantly affect due to planned coatings. The adsorbents have high adsorption limit and quick desorption quality due to the functionalized groups on their surface [99]. To enhance analytical parameters such as selectivity, affinity, and adsorption limit the functionalized groups is a significant constituent. For the separation of metals, amino and oxygen groups are known to have the capacity through electrostatic collaborations. For the removal of Cd(II) from water, Vukovic *et al.* [100] synthesized MWCNT with ethylene diamine oxidized CNT surface. The adsorbent showed good selectivity and adsorption capacity. When the pH of the oxidized CNT is over the isoelectric point, these groups can hold a variety of metals. Such oxidation procedures can build the surface range by expelling polluting influences and presenting surface imperfections that empower the presentation of oxygen-containing useful groups [101]. Various types of nanomaterials are examined here as indicated by their properties and conduct as a sorbent. In spite of the fact that the assortment of nanomaterials utilized by scientists for expository reasons and adsorption procedures is boundless and a few of nanoadsorbents have been presented lately, we will concentrate on the most understood nanomaterials in view of their significance and long haul applications.

12.5 Nanoparticles for Water and Wastewater Remediation

12.5.1 Nanoparticles of Metal Oxide

12.5.1.1 Al_2O_3 Nanoparticles

The nano-sized alumina have high surface territory, mechanical quality, level of surface reactivity, and low temperature modification, and due to this, the nano-sized alumina depicted a solid adsorption limit and porosity [102]. The colloidal conduct of aluminum oxide NPs has been investigated by Ghosh *et al.* [103] as a component of pH. On the addition of humic acid, which is a natural matter, the surface charge of the Al_2O_3 NPs likewise was found to decrease. The Al_2O_3 NPs moved toward point of zero charge (PZC) where van der Waals forces command over electrostatic repulsion tended to total as the pH of the suspension. It was observed that the colloidal suspension of NP can be stable in pH values far from PZC [104]. The weak bonding between these natural compounds and the hydrophilic surface of alumina is not quantitative characteristic to the retention in non-modified alumina NPs.

12.5.1.2 ZnO Nanoparticles

Different physical and compound properties have been shown by nanoscale ZnO in comparison to microscale ZnO. The large surface area and high catalytic activity of ZnO nanostructures are responsible to a great advantage applied toward a catalytic reaction process. According to the precursor's content, the morphologies, particle sizes, and surface areas of ZnO NPs are different. The PZC for ZnO nanoparticles from ζ -potential experiments was obtained by Rupasinghe [105], sizes 4, 7, and 15 nm. By the use of linear extrapolation, pH_{PZC} value (8.75) was found between pH 8 and 10 for 4 nm ZnO nanoparticles. The surface of ZnO nanoparticles below pH 8.75 is positively charged due to the reason that acidic water donates more H^+ ions than OH^- below the pH_{PZC} . On the other hand, as a result of dominant OH^- ions, the surface is negatively charged above this pH. Zinc oxide NPs has been utilized as a catalyst in the photodegradation of many organic pollutants. In various organic reactions, ZnO is an inexpensive and highly efficient catalyst as a consequence of its high zinc content (80%) and highly predictable reaction kinetics and adsorption capacity. ZnO is a good adsorbent for the removal of dangerous, toxic, and corrosive gases from water samples. Consequently, for solid waste disposal, ZnO sorbent is

generally considered nonhazardous and provide a wide range of potential applications in various industries [106].

12.5.1.3 *TiO₂ Nanoparticles*

Generally, because of high photocatalytic action, prominent potential of photogenerated electrons, nontoxic nature, and relatively expensive property, TiO₂ is favored in anatase frame. For certain specialized applications, the execution of TiO₂ influenced by its crystallite measure, stage structure, surface territory, contaminating agents, and concentration [107]. TiO₂ exhibits very favorable ligand sorption properties, through inner-sphere complex formation and electrostatic interaction and hydrogen bonding between TiO₂ and organic polar side groups [108]. The NPs may build the general natural proficiency of water treatment procedures to evacuate metals by creating appropriate proclivity, limit, and selectivity for contaminants [109]. For the metal adsorption onto TiO₂ anatase nanoparticles, the Langmuir isotherm is the most appropriate model. Adsorbed species associated with autonomous adsorbate surface adsorption locales wherein dynamic destinations can be involved by just a single particle at an opportunity to shape a monolayer on the adsorbent [110]. The adsorption property of titanium dioxide depends on the pH. At high pH, the adsorption of cations is favored because of the protected surface of titanium dioxide with OH⁻ aggregates [111]. Besides, at pH < 6.2, adsorption of anions is favored because of protected surface of the titanium dioxide with hydroxonium groups. According to Qian *et al.* [112], the colloid has the accompanying points of interest as another adsorbent contrasted and nanometer-estimate TiO₂ powder: (1) It has a more grounded adsorption capacity, a higher adsorption rate, a littler grain measure, and a more particular surface. (2) It is steadier and more dispersive without agglomeration, giving it a higher adsorptive repeatability. (3) With slurry inspecting, the elution step could be discarded so high example tainting and loss of analyte are maintained a strategic distance from.

12.5.2 **Metallic Nanoparticles**

12.5.2.1 *Au Nanoparticles*

For the utilization of Au NPs in future advancements, these are gradually pulling in a lot of consideration, including catalysis, biosensors, tranquilize transporters, optical materials, electronic gadgets, and high complexity cell imaging [113–116]. Because of their size-dependent electrical

properties, high electrocatalytic action, and useful similarity with atoms and polymers, Au NPs have been broadly utilized as a part of scientific methods [117]. Additionally, biomolecules can be adsorbed suddenly onto gold surfaces containing thiol (SH) or amino (NH_2) groups to produce efficient, self-collected monolayers. Despite the fact that Au NPs give an extensive surface territory to associate with section surface and analyte, next to no examination has been committed to comprehension their effect on separation science. Despite the fact that the use of Au NPs is still in its start, past reviews have shown their potential as multifunctional parts to enhance chemical stability, explanatory selectivity, and partition proficiency [118].

12.5.3 Magnetic Nanoparticles

The chemical composition of NPs, type and the degree of defectiveness of the crystal lattice, the particle size and shape, the morphology, the interaction of the particle with the surrounding matrix, and the neighboring particles are the key to determine the magnetic properties of NPs.

By changing the nanoparticle measure, shape, arrangement, and structure, one can control to a degree the attractive attributes of the material in light of them. Nonetheless, these elements can't generally be controlled amid the combination of NPs that are about equivalent in size and substance synthesis; in this way, the properties of nanomaterials of a similar sort can be extremely astonishing [119]. In recent times, in a variety of fields, the iron oxide MNPs uses in various extensive applications [120–122]. The Fe_3O_4 (magnetite) and Fe_2O_3 form of magnetic iron oxide nanoparticles have superparamagnetic properties [123].

Lee *et al.* [124] affirmed that the titration method was used to determine the value of point of zero charge (PZC) of MNP, magnetite (Fe_3O_4), was pH 7. Superparamagnetic NPs have vast attractive minutes that make them act as a huge paramagnetic particle with a quick reaction to the outside attractive field. The collection of nanoparticles in large volume of aqueous samples is quite easy and suitable in the ecological applications [125]. Because of their great scattering in arrangement, their high particular surface territory, and their capacity to be controlled and isolated with an outside attractive field MNPs are reasonable sorbents in SPE. Compared with other customary extraction strategies, which frequently utilize extensive volumes of arrangement, attractive strong stage extraction (MSPE) has a few favorable circumstances: high productivity and recuperation as consequence of high particular surface territory, simplicity of dealing with, and fast speed and minimal cost [126]. However, it should be pointed out

that pure inorganic nanoparticles (such as Fe_3O_4 and Fe_2O_3) can easily form large aggregates, which may alter their magnetic properties. [127]. Therefore, a helpful covering is fundamental to beat such impediments. Additionally, these nanometer-sized metal oxides are not target-specific and are inadmissible for analysis with complicated frameworks. In this way, the adjustment of these attractive nanoparticles with an appropriate covering has been ended up being a standout amongst the most productive ways [128].

12.5.4 Carbonaceous Nanomaterials

Carbonaceous materials are isolated by a valance gap or band gap and have valence and conduction groups. To make CNMs exceptionally alluring, they have an arrangement of extraordinary properties for application in small-scale and nanoelectronics and subatomic gadgets, hydrogen control building, catalysis, medication, and so forth. Due to the physicochemical properties of CNMs and their sorption capacity, these are utilized as a good adsorbent. Regarding this, for the morphology, virtue, particular territory, and sorption movement relying upon their treatment after amalgamation of CNMs, these are critical to describe.

12.5.4.1 Carbon Nanotubes

The hollow graphitic nanomaterials or layers of graphene sheets such as single-walled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes (MWNTs) are known as carbon nanotubes. The lengths of SWNT and coaxial MWNT is from 0.2 to 2 nm and from 2 to 100 nm, respectively [129]. In spite of other features, the high surface zones and great electrical, mechanical, compound, and leading properties are the characterization tool for the nanotubes.

The both classes of carbonaceous materials which are SWNTs and MWNTs show fabulous determination for both gas and fluid stage separation. The synthetic dormancy and solid van der Waals connections between nanotubes confound their manufacture. In this manner, it is critical to separate individual nanotubes from the groups to boost the impacts of the inherent mechanical properties of carbon nanotubes; along these lines, nanotube solubilization is a key issue. From a diagnostic perspective, numerous uses of nanotubes, when utilized as either a scientific target or an explanatory device, are constrained as a result of their low solvency, which is a region that is at present being examined widely. Haddon and collaborators [130] thought about systematic

methods for assessing the immaculateness of single-walled carbon nanotubes, including electron microscopy (both filtering and transmission), spectroscopic procedures, for example, Raman and close infrared (NIR), and thermogravimetric investigation [131]. The pore shape, surface territory, pore volume, and surface functionality are the varied parameters. In CNTs, the external surface and the empty spaces are the sorption sites of the open tubes. In this manner, their discharge by both warm procedures and solvents is generally less complex and not constrained by dispersion. In this way, an extensive variety of mixes from little atoms to vast semivolatiles can be effortlessly focused on, and desorbed from, CNTs [132]. The adsorption data well fitted to the Langmuir, BET, or Freundlich isotherms [133]. The point of zero charge is a valuable estimation for the observation of the surface acidity of multiwalled carbon nanotubes and to portray utilitarian groups on the multiwalled carbon nanotube surface. Due to various functionalization strategies such as refluxing in $\text{H}_2\text{SO}_4/\text{HNO}_3$ or nitrosylation, the carbon nanotube surfaces may have an extensive variety of PZC values reported by McPhail *et al.* [134].

12.5.5 Silicon Nanomaterials

12.5.5.1 Silica Dioxide Nanoparticles

Grafted materials such as SiO_2 are the easiest and most open type of nanomaterials, which are obtained by simple association of a nanoobject a natural polymer grid or an oxide lattice, for reasons of cost, availability, and utilizes. Silica does not have great communication with nonpolar natural mixes and this is an inorganic polymer. Therefore, for the extraction of natural toxins by the utilization of nanosilica is fairly irrelevant. So, to enhance the removal capacity of nanosilica particles, these are grafted with natural modifier [135]. The PZC of SiO_2 is around 2–3. At high or nutrient pH, silica nanoparticles are negatively charged. Silica nanoporous materials have been generally utilized in view of their special properties, among them its high surface region. Changed silica nanoparticles have been utilized for preconcentration of natural contaminations and many metal particles, and promising outcomes have been accomplished when utilized for follow examination of various samples [136].

12.5.5.2 Silica Nanotubes

Due to various properties of silica nanotubes like easy to make, highly convenient to form the delicate recognition site, and have cross-connected

structure, these are perfect vehicles for confirmation of idea experiments [137]. Because of the nearness of more electrons in its external shells, silicon is more polarizable than carbon. The adsorption of hydrogen is described on the SiNT clusters by Lan *et al.* [138], and they also found that the limit of hydrogen adsorption on SiNT exhibits is impressively higher than that on CNTs.

12.5.6 Nanofibers (NFs)

In past few years, many reports about NP applications has been published which concludes that nanoparticles and nanofibers have been in the focal point of center, and, including as adsorbents for SPE. Having adequately high subatomic weight, numerous polymers can be electrospun as indicated by the attributes of the object samples, for example, nylon 6. The structure of nylon comprises amide groups, which were isolated by methylenic sequences. The amide groups have planar structure because of the double bond character of the C–N bond. The fundamental factor deciding the fruitful extraction is the aqueous stage used to bring the hydrophobic analyte through the nylon nanofibers. Nonpolar cooperations are normal for hydrophobic analytes, between these mixes and the methylenic chains of nylon. To upgrade the water development into the sorbent, enhancing mass exchange and making it more effective, the hydrophilic amide groups are relied upon [139]. Over recent years, a few analysts have researched distinctive parameters affecting nylon 6 nanofibers [140], and it turns out to be extremely intriguing to investigate the utilization of nylon 6 nanofibers as sorbents for SPE. Nylon 6 nanofibers as adsorbent accomplish bigger particular surface and more dynamic destinations for adsorption due to having high surface-to-volume proportion and length-to-diameter proportion. Xu *et al.* [141] found that a bigger segment zone of nanofibers, contrasted and SPE cartridges, made the weight drop permitting test handling at higher stream rates. In this way, it is much simpler to manage vast volume tests to acquire a superior improvement coefficient and meet lower LOD.

12.6 Applications in Aqueous Media

In spite of the fact that nanomaterials have an extensive variety of uses in various logical and innovative fields, this chapter summarizes the nanomaterials that have been utilized for the removal of pollutants as adsorbent from water samples.

12.6.1 Nanoparticles

12.6.1.1 Al_2O_3 Nanoparticles

12.6.1.1.1 Metal Ions

Fine Al_2O_3 nanopowders have been generally utilized as sorbents. Manzoori *et al.* [142] described strong stage removal of copper on modified Al_2O_3 NPs. Effect of pH, measure of ligand, flow rate, sort of eluting agent, and volume of eluent are the optimized parameters. Afkhami *et al.* [143] explored adsorption conditions for lead and chromium on Al_2O_3 NPs. The 2,4-dinitrophenylhydrazine were used to set up the sorbent by immobilization on sodium dodecyl sulfate modified Al_2O_3 NPs. For the determination of cadmium particles and its adsorption limit, nanoscale alumina was used on single-walled carbon nanotubes [144]. The adsorption limit of the incorporated material to cadmium particle was higher than that of SWCNT.

12.6.1.1.2 Organic Compounds

For the separation of formaldehyde (FA), Afkhami and Bagheri [145] exhibited a sensitive technique in light of the utilization of adjusted alumina nanoparticles for its preconcentration. For the modification of alumina nanoparticles, the 2,4-dinitrophenylhydrazine (DNPH) through sodium dodecyl sulfate as a surfactant were used. Effect of pH, measure of sorbent, shaking time, stream rate, nature of the eluent, eluent volume, and test volume were the optimized parameters. High sorption capacity has been shown by these functionalized nanoparticles for FA. Renuka *et al.* [146] reported that the nano-sized mesoporous γ -alumina for the removal of Congo red dye. Congo red is a human cancer-causing agent and an optional diazo color, which metabolize to benzidine. For the removal of Congo red, meso alumina NPs was used as the most productive adsorbent.

12.6.1.2 ZnO Nanoparticles

12.6.1.2.1 Gaseous Species

Zinc oxide (ZnO) is a phenomenal adsorbent for the removal of gasses from aqueous system. A nanosized ZnO was combined by a matrix-assisted method. A review on the arranged ZnO was done to decide another conceivable application to the hot gas desulfurization (HGD) prepare in the coordinated gasification joined cycle (IGCC) control plants [147]. Zinc oxide sorbents were described for the removal of sulfur mixes (H_2S) at a low fixation in a gasified fuel gas [148]. A dynamic carbon was utilized as a matrix, and zinc acetate ($Zn-(C_2H_3O_2)_2 \cdot 2H_2O$) was chosen as a precursor.

The removal of H_2S using ZnO nanostructures were performed in a settled bed reactor. The outlet gasses from the reactor were consequently dissected by gas chromatography (GC). Most arranged nano-sized zinc oxides demonstrated an incredible execution for the evacuation of H_2S at a low fixation.

12.6.1.3 *TiO₂ Nanoparticles*

Anatase-TiO₂ was observed to be a prevalent photocatalytic material for sanitization, remediation of dangerous waste and purification of water and air because of its solid photoinduced redox power [149]. TiO₂ NPs have been broadly utilized for preconcentration and partition of trace and ultra-trace metal particles and natural poisons.

12.6.1.3.1 Metal Ions

Due to progressively lower limits forced on the trace metal substance, the separation of elluents, including cadmium, in ecological and sustenance tests has turned out to be more genuine. Anatase-TiO₂ nanoparticles [150] were used for the Fe-solid phase extraction from coastal salt water. For the extraction of iron from salt water, the TiO₂ (anatase) was optimally used at pH 7, and it is more efficient with salt water than with clean water. The Fourier transformed infrared (FTIR) spectroscopy was used for the TiO₂ surface sites undervarying conditions of salinity and pH interacting with Fe.

12.6.1.3.2 Organic Compounds

The mesoporous TiO₂ NPs have been used for the degradation of 4 chlorophenol. The TiO₂ has high surface area and small particle size, and less pore volume, attributed to less reactivity. The potential application of TiO₂ nanoparticles were utilized for the removal of phenol and phenolic derivatives from petroleum refinery wastewater [151]. Various parameters have been studied for the removal of phenol such as pH, temperature, and concentration of catalyst.

12.6.1.4 *Metallic Nanoparticles*

12.6.1.4.1 Au Nanoparticles

12.6.1.4.1.1 Metal Ions

Gold nanoparticles are bound to polymer functional groups through covalent bonds, for example, CN, NH₂, or SH, and a gold nanoparticles monolayer can be set up without anyone else's input get together on the polymer-coated substrate. Besides, organic macromolecules hold their movement when adsorbed on AuNPs. Gold nanoparticles containing

N,N-didecylaminomethylbenzene (DAMAB) as a neutral carrier were first assembled on the surface of PVC-NH₂ membrane. The assembled gold nanoparticles and inactive enzyme layers denatured by Hg²⁺ can be rinsed out via a saline solution with acid and alkali successively is an advantage of the self-assembled immobilization. For the determination of inhibitor, this sensor is usually of great consequence in contrast with expensive base transducers. The removal of As and Sb metals in salt solutions were described on gold nanoparticles (Au NPs) [152]. For the synthesis of the Au NPs, chloroauric acid was reduced with sodium citrate. The Au NPs were effectively used for the determination of the two metals in spiked salt water samples and certified reference materials. Different mercury species have been adsorbed on the silica surface by resulting Au nanoparticles efficiently.

12.6.1.4.1.2 Organic Compounds

For the determination of cysteine, Li *et al.* [153] discussed self-assembly of gold nanoparticles. Various parameters have been studied for the removal of cysteine such as pH of solution, buffer concentration, and concentration of gold nanoparticles. The cysteine contains both the NH₃⁺ and the SH groups, thus it shows high selectivity for the determination of cysteine. Various organic compounds have been removed from aqueous solution using Au NPs as adsorbent such as polycyclic aromatic hydrocarbons (PAHs), and neutral steroid analytes [154].

12.6.2 Nanostructured Mixed Oxides

12.6.2.1 Fe–Ti Mixed Oxide Nanoparticles

12.6.2.1.1 Metal Ions

In groundwater environment of West Bengal (India) and Bangladesh, arsenic contamination is a serious issue. The Fe–Ti binary mixed oxide used for the removal of arsenic [155]. Arsenic(V) have more affinity than arsenic(III) for this adsorbent [156]. The hydrous titanium(IV) oxide have higher efficiency than the hydrous iron(III) oxide [157].

12.6.2.2 Magnetic Nanoparticles

The magnetic nanoparticles have higher adsorption capacity due to the high surface area. By the help of an external magnetic field, the separation of metal-loaded sorbent can be easily occurring due to superparamagnetic nature. Some proteins, organic compounds, and metal ions were easily removed using MNPs [158].

12.6.2.2.1 Metal Ions

The Cr(VI) metal ion removal Fe_2O_3 nanoparticles have been utilized by Hu *et al.* [159] as a sorbent with a very high adsorption capacity. For adsorption of nickel, magnetic alginate doped microcapsules were prepared [160]. Poly(1-vinylimidazole)-grafted magnetic nanosorbent were used to remove copper ions from groundwater [161]. The effect of pH, volume of sample, concentration, and volume of eluent, and coexisting ions are the different parameters, which were studied for the separation process.

12.6.2.2.2 Organic Compounds

The nanocomposite of carbon ferromagnetic was utilized for the removal of PAHs in ecological samples using a magnetic solid phase extraction method by Bai *et al.* [162]. Various parameters have been studied for the removal productivity such as, volume of nanoparticles, shaking speed, extraction time, solvent desorption, desorption time, and salt expansion. Magnetic nanoparticles covered with cetyltrimethyl ammonium bromide were utilized by Zhao *et al.* [163] for the removal of phenolic mixes from natural water. Their study examined the adsorption onto magnetic nanoparticles of cation surfactants, cetyltrimethylammonium bromide (CTAB), and cetylpyridinium chloride (CPC). The utilization of this blended hemimicelles strong stage extraction strategy for the separation of several typical phenolic compounds from ecological water samples. The charged surfactants CTAB and CPC form mixed hemimicelles on Fe_3O_4 NPs causes retention of analytes in SPE method, which by strong hydrophobic and electrostatic interactions. This novel SPE method joins the upsides of blended hemimicelles and attractive nanoparticles. The fundamental parameters which influence the adsorption of analytes are the measure of Fe_3O_4 NPs and surfactants, surfactants types, pH, sample volume, and the desorption conditions were explored and enhanced.

12.6.3 Carbonaceous Nanomaterials

12.6.3.1 Carbon Nanotubes

Carbon nanotubes, particularly SWNTs, hold extraordinary guarantee for cutting edge applications in aviation, gadgets, and pharmaceutical. Carbon nanotubes are most broadly utilized as a part in electrochemical sensors. These are used in test cleanup strategies or analyte preconcentration by means of either channels/layers or a sorbent packed material. Lately, numerous utilizations of MWCNTs for the preconcentration of

overwhelming metal particles, uncommon earth components, and organo-metallic mixes were reported [164]. CNTs were additionally abused in investigative science and the preconcentration of follow measures of natural materials [165].

12.6.3.1.1 Metal Ions

The systematic capability of C_{60} fullerene and a carbon nanotube-related structure as a strong stage adsorbent were described for removal of chelates or particle sets of metal particles from aqueous solution [166]. The multiwalled carbon nanotubes were studied by Shamspur and Mostafavi [167] as a sorbent for the removal of trace measures of gold and manganese. The technique was successfully applied for partition and determination of gold and manganese particles in water. The determination of trace rare earth elements (REEs) studied by inductively coupled plasma atomic emission spectrometry (ICP-AES) by Liang *et al.* [168] after preconcentration with multiwalled carbon nanotubes. Various parameters have studied for the removal of REEs, such as sample pH, sample flow rate and volume, elution solution, and interfering ions.

12.6.3.1.2 Organic Compounds

The carbon nanotubes strongly interact with organic molecules due to their characteristic structures and electronic properties. In 2001, it was observed that dioxins were strongly adsorbed on MWNTs reported by Long and Yang. The volatile organic compounds can also remove and separate using carbon nanotubes. The acidic herbicides adsorbed on carbon nanotubes [169]. Carbon nanotubes and graphitized carbon were examined as adsorbents for strong stage extraction of dicamba and 2,4,5-T, two phenoxyalkanoic corrosive herbicides. The process of adsorption was optimized at different pH values. The absorption increases at lower pH of sample solution. Therefore, at the strong acidic media, the adsorption properties were the highest. The use of soluble carboxylic-SWNTs proposed by Wang *et al.* [170] and observed distinct changes in the electrophoretic parameters of homologous molecules such as caffeine and theobromine. The changes for structural isomers of catechol and hydroquinone were also observed.

12.6.4 Silicon Nanomaterials

12.6.4.1 SiO_2 Nanoparticles

SiO_2 nanoparticles are supporting substrates for different types of adsorbents. In various sorts of strong phase extractors, silica gel introduces the

upsides of no swelling, quick energy, and great mechanical and also warm and chemical dependability [171].

12.6.4.1.1 Metal Ions

For the removal of heavy metal ions, the surface of silica NPs was modified [172]. The sensing of trace metals examined on modified silica gel and on modified silica nanoparticles by Zhang *et al.* [173]. The 4-(2-aminoethylamino)-*N*-(2-(2-aminoethylamino)ethyl) butanamide (SG-AAEB and nanometer SiO₂-AAEB) immobilized silica gel and SiO₂ NPs were used as sorbents for the solid-phase extraction of Cu(II), Fe(III), and Pb(II). Batch and column methods were used to determine adsorption capacities of the two adsorbents toward metal ions. Various parameters have studied for both adsorbents, for example, effects of pH, shaking time, sample flow rate, and adsorption capacity.

12.6.4.1.2 Organic Compounds

For the removal of organic materials and pollutants, silica nanoparticles have been utilized. Dye-doped silica nanoparticles were used to remove tetracarboxy aluminum phthalocyanine as an organic dye for fluorescent labeling of biological materials [174]. Therefore, due to its cost and accessibility, SiO₂ was selected as a solid surface. Additionally, the hydrolysis condition of SiO₂ is able to easily manage. Alternatively, because of double bond carbonyl group of octadecenoic acid (OA) along with alkyl chain, grafted on nanosilica was chosen as a good alternative. For the quantitative investigation of PAHs by GC-MS, the authors performed approval systems of the created strategy under streamlined conditions in a spiked distilled water test.

12.6.4.2 Silicon Nanotubes

In analytical separations, a number of efforts accomplished to utilize SiNTs as solid phase. However, adsorption of hydrogen on SiNTs was successfully executed in a few studies [175]. The hydrogen and methane adsorption on silicon nanotubes studied by Balilehvand *et al.* [176]. It was studied that CNTs have less adsorption capacity than that of hydrogen on SiNTs.

12.6.4.2.1 Metal Ions

For the removal of copper metal ions, an ion imprinted sol-gel silicon nanotubes membrane was synthesized [177]. The prepared imprinted nanotube film demonstrated a few one of a kind quality, for example, evident quick adsorption and desorption energy, moderate accessible form, inexpensive, and legitimate selectivity for copper.

12.6.5 Nanofibers (NFs)

12.6.5.1 Metal Ions

The Ni(II) ions were removed on Ni(II)-dimethylglyoxime ion-imprinted polymer (Ni(II)-DMG IIP) by ICPOES polysulphone and electrospun into nanofibers [178]. For the removal of Mn, Co, and Ni metal ions, carbon nanofibers (CNFs) as a strong stage extraction adsorbent was synthesized by Chen *et al.* [179]. Various parameters have been studied for the removal process, for example, pH, sample flow rate and volume, elution arrangement, and meddling particles.

12.6.5.2 Organic Compounds

Kang *et al.* [180] synthesized packed polystyrene nanofibers. The edaravone, cinchonine, quinine, voriconazole, chlordiazepoxide, verapamil, and rutonding are the seven representative drugs for optimization of the experiment techniques. The three kinds of nanofibers, for example, poly(styrene-comethacrylicacid), poly(styrene-co-p-styrene sulfonate), and polystyrene have been synthesized for the removal of aromatic hydrocarbon compounds such as nitrobenzene, 2-naphthol, benzene, n-butyl, phydroxybenzoate, naphthalene, and p dichlorobenzene in environmental water. A nylon 6 nanofiber [181] examined for the determination of phthalate esters based on solid-phase extraction technique in water samples. Various parameters have been studied which affects the electrospun nylon 6 nanofibers [182–184].

12.7 Conclusions

The present chapter aims on the current progress associated with the desalination and heavy metal ion detoxification of water and wastewater using nanomaterials as nanoadsorbents. These nanoadsorbents were utilized for the removal of metal ions, organic compounds, and dyes from water samples. The adsorption capacities demonstrated in the various publications present effectiveness of the sorbent for the specific type of metal species which in turn depends on various experimental parameters. The utilization of nanomaterials, nanotubes, naowires, and naofilters for water and wastewater desalination and heavy metal detoxification presents excellent adsorption capacity toward metal ions, economic viability, nonhazardous nature, and biocompatibility. We imagine that nanomaterials will get to be distinctly basic parts of open water treatment and modern frameworks.

12.8 Future Scenario

Although extensive studies in literature on the utilization of nanomaterials sorbents for preconcentration, desalination and heavy metal ion detoxification of water and wastewater have been done, still there are a number of research gaps that require to be filled. Some of the vital characteristics that need to be addressed are summed up as:

1. The main issue is to select a suitable variety of nanomaterials to attain the highest adsorption of a particular contaminant according to the adsorbent–adsorbate interactions.
2. To improve the separation effectiveness toward a variety of contaminants, the optimization of different parameters leading to these nanomaterials with high functional groups on its surface is required.
3. The adsorbents based on nanomaterials with low manufacture price and high adsorption capability should be encouraged.
4. For the enhanced fiscal viability of the method, detailed regeneration studies should be carried out with the used nanomaterials in order to recover the metals with adsorbent.
5. Multicomponent contaminants treatment potential of nanomaterials is required for the large-scale utilization of the adsorbents.
6. In addition to the effect of various co-contaminants, more experiments should be performed on the effect of the presence of phenols, dyes on adsorption of metal ions is needed.
7. In addition to lab based batch studies, large-scale pilot–plant studies are needed to test chitosan derivative's applications at industrial level.
8. The process efficiency depends not only on the adsorbent and adsorbate characteristics but also on different experimental conditions. Therefore, these variables need to be considered for studying the efficiency of nanomaterials-based adsorbents.

Therefore, development of the nanoadsorbents having all the above-stated properties may present noteworthy benefits than presently developed commercially costly activated sorbents.

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References

1. Sánchez, A., Recillas, S., Font, X., Casals, E., González, E., Puentes, V., Ecotoxicity of, and remediation with, engineered inorganic nanoparticles in the environment. *Trends in Anal. Chem.*, 30, 507, 2011.
2. Diallo, M.S., Savage, N., Nanoparticles and water quality. *J. Nano. Res.*, 7, 325, 2005.
3. Qi, L., Xu, Z., Jiang, X., Hu, C., Zou, X., Preparation and antibacterial activity of chitosan nanoparticles. *Carbohydr. Res.*, 339, 2693, 2004.
4. Morones, J.R., Elechiguerra, J.L., Camacho, A., Holt, K., Kouri, J.B., Ramírez, J.T., Yacaman, M.J., The bactericidal effect of silver nanoparticles. *Nanotechnology*, 16, 2346, 2005.
5. Cho, M., Chung, H., Choi, W., Yoon, J., Different inactivation behaviors of MS-2 phage and Escherichia coli in TiO₂ photocatalytic disinfection. *Appl. Environ. Microbiol.*, 71, 270, 2005.
6. Wei, C., Lin, W.Y., Zainal, Z., Williams, N.E., Zhu, K., Krusic, A.P., Smith, R.L., Rajeshwar, K., Bactericidal activity of TiO₂ photocatalyst in aqueous media toward a solar-assisted water disinfection system. *Environ. Sci. Technol.*, 28, 934, 1994.
7. Kang, S., Pinault, M., Pfefferle, L.D., Elimelech, M., Single-walled carbon nanotubes exhibit strong antimicrobial activity. *Langmuir*, 23, 8670, 2007.
8. Nair, A.S., Pradeep, T., Extraction of chlorpyrifos and malathion from water by metal nanoparticles. *J. Nanosci. Nanotechnol.*, 7(6), 1871-1877, 2007.
9. Zhang, L., Fang, M., Nanomaterials in pollution trace detection and environmental improvement. *Nano Today*, 5, 128, 2010.
10. T. C. Zhang, and R. Y. Surampalli, *Nanotechnologies for water environment applications*, 2009, ASCE Publisher, Virginia.
11. B. Karn, T. Masciangioli, W-X.Zhang, V. Colvin, and P. Alivisatos, *Nanotechnology and the environment-applications and implications*, American Chemical Society (ACS) symposium series 890, 2005, ACS, Washington DC.
12. Kim, Y.K., Park, H.B., Lee, Y.M., Carbon molecular sieve membranes derived from metal-substituted sulfonated polyimide and their gas separation properties. *J. of Membrane Sci.*, 226, 145, 2003.

13. Taurozzi, J.S., Arul, H., Bosak, V.Z., Burban, A.F., Voice, T.C., Bruening, M.L., Tarabara, V.V., Effect of filler incorporation route on the properties of polysulfone–silver nanocomposite membranes of different porosities. *J. of Membrane Sci.*, 325, 58, 2008.
14. Bottino, A., Capannelli, G., Comite, A., Di Felice, R., Polymeric and ceramic membranes in three-phase catalytic membrane reactors for the hydrogenation of methylenecyclohexane. *Desalination*, 144, 411, 2002.
15. Fu, F., Wang, Q., Removal of heavy metal ions from wastewaters: a review. *J. Environ. Manage.*, 92, 407, 2011.
16. Naser, H.A., Assessment and management of heavy metal pollution in the marine environment of the Arabian Gulf: a review. *Mar. Pollut. Bull.*, 72, 6, 2013.
17. Mendoza, O.T., Hernández, M.A.A., Abundis, J.G., Mundo, N.F., Geochemistry of leachates from the El Fraile sulfide tailings piles in Taxco, Guerrero, Southern Mexico, *Environ. Geochem. Health*, 28, 243, 2006.
18. Erdem, E., Karapinar, N., Donat, R., The removal of heavy metal cations by natural zeolites. *J. Colloid Interface Sci.*, 280(2), 309–314, 2004.
19. Wang, S., Mulligan, C.N., Effect of natural organic matter on arsenic release from soils and sediments into groundwater. *Environ. Geochem. Health*, 28, 197, 2006.
20. Brown, G.E., Foster, A.L., Ostergren, J.D., Mineral surfaces and bioavailability of heavy metals: a molecular scale perspective. *Proc. Natl. Acad. Sci. U. S. A.*, 96, 3388, 1999.
21. Lim, S.R., Schoenung, J.M., Human health and ecological toxicity potentials due to heavy metal content in waste electronic devices with flat panel displays. *J. Hazard. Mater.*, 177, 251, 2010.
22. Karlsson, K., Viklander, M., Scholes, L., Revitt, M., Heavy metal concentrations and toxicity in water and sediment from storm water ponds and sedimentation tanks. *J. Hazard. Mater.*, 178, 612, 2010.
23. Madoni, P., Romeo, M.G., Acute toxicity of heavy metals towards freshwater ciliated protists. *Environ. Pollut.*, 141, 1, 2006.
24. Agency, U. S. E. P. Water: Drinking Water Contaminants, <http://water.epa.gov/drink/contaminants/index.cfm#Inorganic>, 01/07/2015.
25. Akieh, M.N., Lahtinen, M., Väisänen, A., Sillanpää, M., Preparation and characterization of sodium iron titanate ion exchange and its application in heavy metal removal from waste waters. *J. Hazard. Mater.*, 152, 640, 2008.
26. Ismail, A.A., Mohamed, R.M., Ibrahim, I.A., Kini, G., Koopman, B., Synthesis, optimization and characterization of zeolite A and its ion-exchange properties. *Colloids Surf., A*, 366, 80, 2010.
27. Qiu, W., Zheng, Y., Removal of lead, copper, nickel, cobalt, and zinc from water by a cancrinite-type zeolite synthesized from fly ash. *Chem. Eng. J.*, 145, 483, 2009.
28. Dyalnas, E., Diamadopoulos, E., Integration of a membrane bioreactor coupled with reverse osmosis for advanced treatment of municipal wastewater. *Desalination*, 238, 302, 2009.

29. Mohsen-Nia, M., Montazeri, P., Modarress, H., Removal of Cu^{2+} and Ni^{2+} from wastewater with a chelating agent and reverse osmosis processes. *Desalination*, 217, 276, 2007.
30. Meunier, N., Drogui, P., Montané, C., Hausler, R., Mercier, G., Blais, J.F., Comparison between electrocoagulation and chemical precipitation for metals removal from acidic soil leachate. *J. Hazard. Mater.*, 137, 581, 2006.
31. Hunsom, M., Pruksathorn, K., Damronglerd, S., Vergnes, H., Duverneuil, P., Electrochemical treatment of heavy metals (Cu^{2+} , Cr^{6+} , Ni^{2+}) from industrial effluent and modeling of copper reduction. *Water Res.*, 39, 610, 2005.
32. Deng, Y., Englehardt, J.D., Electrochemical oxidation for landfill leachate treatment. *Waste Manage.*, 27, 380, 2007.
33. Rana, P., Mohan, N., Rajagopal, C., Electrochemical removal of chromium from wastewater by using carbon aerogel electrodes. *Water Res.*, 38, 2811, 2004.
34. Qdais, H.A., Moussa, H., Removal of heavy metals from wastewater by membrane processes: a comparative study. *Desalination*, 164, 105, 2004.
35. Yuan, X.Z., Meng, Y.T., Zeng, G.M., Fang, Y.Y., Shi, J.G., Evaluation of tea-derived biosurfactant on removing heavy metal ions from dilute wastewater by ion flotation. *Colloids Surf., A*, 317, 256, 2008.
36. Kumar, V., Talreja, N., Deva, D., Sankararamkrishnan, N., Sharma, A., Verma, N., Development of bi-metal doped micro- and nano multi-functional polymeric adsorbents for the removal of fluoride and arsenic(V) from wastewater. *Desalination*, 282, 27, 2011.
37. Dada, A.O., Olalekan, A.P., Olatunya, A.M., Dada, O., Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn^{2+} unto phosphoric acid modified rice husk, *IOSR. J. Appl. Chem.*, 3, 38, 2012.
38. Karami, H., Heavy metal removal from water by magnetite nanorods. *Chem. Eng. J.*, 219, 209, 2013.
39. Garg, U.K., Kaur, M.P., Garg, V.K., Sud, D., Removal of hexavalent chromium from aqueous solution by agricultural waste biomass. *J. Hazard. Mater.*, 140, 60, 2007.
40. Mohan, D., Singh, K.P., Singh, V.K., Removal of hexavalent chromium from aqueous solution using low cost activated carbons derived from agricultural waste materials and activated carbon fabric cloth. *Ind. Eng. Chem. Res.*, 44, 1027, 2005.
41. Kurniawan, T.A., Sillanpaa, M.E.T., Sillanpaa, M., Nanoadsorbents for remediation of aquatic environment: local and practical solutions for global water pollution problems. *Crit. Rev. Environ. Sci. Technol.*, 42, 1233, 2012.
42. Petrovic, M., Diaz, A., Ventura, F., Barcelo, D., Occurrence and removal of estrogenic short-chain ethoxy nonylphenolic compounds and their halogenated derivatives during drinking water production. *Environ. Sci. Technol.*, 37, 4442, 2003.

43. Westerhoff, P., Yoon, Y., Snyder, S., Wert, E., Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes. *Environ. Sci. Technol.*, 39, 6649, 2005.
44. Vieno, N., Tuhkanen, T., Kronberg, L., Removal of pharmaceuticals in drinking water treatment: Effect of chemical coagulation. *Environ. Technol.*, 27, 183, 2006.
45. Adams, C., Wang, Y., Loftin, K., Meyer, M., Removal of antibiotics from surface and distilled water in conventional water treatment processes. *J. Environ. Eng.*, 128, 253, 2002.
46. Strathmann, H., Membrane separation processes: current relevance and future opportunities. *AIChE Journal*, 47, 1077, 2001.
47. Van der Bruggen, B., Vandecasteele, C., Distillation vs. membrane filtration: overview of process evolutions in seawater desalination. *Desalination*, 143, 207, 2002.
48. Ahmad, A.L., Ooi, B.S., Mohammad, A.W., Choudhury, J.P., Development of a highly hydrophilic nanofiltration membrane for desalination and water treatment. *Desalination*, 168, 215, 2004.
49. Qin, J.J., Oo, M.H., Kekre, K.A., Nanofiltration for recovering wastewater from a specific dyeing facility. *Sep. Purif. Technol.*, 56, 199, 2007.
50. Walha, K., Amar, R.B., Firdaous, L., Quemeneur, F., and Jaouen, P., Brackish groundwater treatment by nanofiltration, reverse osmosis and electrodialysis in Tunisia: performance and cost comparison. *Desalination*, 207, 95, 2007.
51. M. Mulder, The use of membrane processes in environmental problems. An introduction, in *Membrane Processes in Separation and Purification*, J. G. Crespo and K.W.B. Oddeker, Eds., pp.229–262, Springer, 1994.
52. Kiso, Y., Kon, T., Kitao, T., Nishimura, K., Rejection properties of alkyl phthalates with nanofiltration membranes. *J. Membr. Sci.*, 182, 205, 2001.
53. Bodzek, M., Dudziak, M., Luks-Betlej, K., Application of membrane techniques to water purification. Removal of phthalates. *Desalination*, 162, 121, 2004.
54. Yoon, Y., Westerhoff, P., Yoon, J., Snyder, S.A., Removal of 17 β estradiol and fluoranthene by nanofiltration and ultrafiltration. *J. Environ. Eng.*, 130, 1460, 2004.
55. Yoon, Y., Westerhoff, P., Snyder, S.A., Wert, E.C., Nanofiltration and ultrafiltration of endocrine disrupting compounds, pharmaceuticals and personal care products. *J. Membr. Sci.*, 270, 88, 2006.
56. Braeken, L., Bettens, B., Boussu, K., Van Der Meeren, P., Cocquyt, J., Vermant, J., Van der Bruggen, B., Transport mechanisms of dissolved organic compounds in aqueous solution during nanofiltration. *J. Membr. Sci.*, 279, 311, 2006.
57. Bolong, N., Ismail, A.F., Salim, M.R., Matsuura, T., A review of the effects of emerging contaminants in wastewater and options for their removal. *Desalination*, 238, 229, 2009.

58. Bottero, J.Y., Rose, J., Wiesner, M.R., Nanotechnologies: tools for sustainability in a new wave of water treatment processes. *Int. Environ. Assess. Manag.*, 2, 391, 2006.
59. Obare, S.O., Meyer, G.J., Nanostructured materials for environmental remediation of organic contaminants in water. *J. Environ. Sci. and Health—Part A*, 39, 2549, 2004.
60. Schmid, G., Bäuml, M., Geerkens, M., Heim, I., Osemann, C., Sawitowski, T., Current and future applications of nanoclusters. *Chem. Soc. Rev.*, 28, 179, 1999.
61. Shipway, A.N., Katz, E., Willner, I., Nanoparticle arrays on surfaces for electronic, optical, and sensor applications. *Chem. Phys. Chem.*, 1, 18, 2000.
62. Willard, D.M., Nanoparticles in bioanalytics. *Anal. Bioanal. Chem.*, 376, 284, 2003.
63. Katz, E., Willner, I., Integrated nanoparticle–biomolecule hybrid systems: synthesis, properties, and applications. *Angew. Chem., Int. Ed.*, 43, 6042, 2004.
64. Eustis, S., El-Sayed, M.A., Why gold nanoparticles are more precious than pretty gold: noble metal surface plasmon resonance and its enhancement of the radiative and nonradiative properties of nanocrystals of different shapes. *Chem. Soc. Rev.*, 35, 209, 2006.
65. Welch, C.M., Compton, R.G., The use of nanoparticles in electroanalysis: a review. *Anal. Bioanal. Chem.*, 384,601, 2006.
66. Wu, C.S., Wu, C.T., Yang, Y.S., Ko, F.H., An enzymatic kinetics investigation into the significantly enhanced activity of functionalized gold nanoparticles. *Chem. Commun.*, 5327, 2008.
67. Chang, T.H., Liu, F.K., Chang, Y.C., Chu, T.C., Rapidly characterizing the growth of Au nanoparticles by CE. *Chromatogr.*, 67, 723, 2008.
68. Liu, F.K., Analysis and applications of nanoparticles in the separation sciences: a case of gold nanoparticles. *J. Chromatogr. A*, 1216, 9034, 2009.
69. Boisselier, E., Astruc, D., Gold nanoparticles in nanomedicine: preparations, imaging, diagnostics, therapies and toxicity. *Chem. Soc. Rev.*, 38, 1759, 2009.
70. Zhong, W., Nanomaterials in fluorescence-based biosensing. *Anal. Bioanal. Chem.*, 394, 47, 2009.
71. Wu, C.S., Liu, F.K., Ko, F.H., Potential role of gold nanoparticles for improved analytical methods: an introduction to characterizations and applications. *Anal. Bioanal. Chem.*, 399,103, 2011.
72. Delay, M., Frimmel, F.H., Nanoparticles in aquatic systems. *Anal. Bioanal. Chem.*, 402, 583, 2012.
73. Türker, A.R., New sorbents for solid-phase extraction for metal enrichment. *Clean: Soil, Air, Water*, 35, 548, 2007.
74. Zhang, L., Huang, T., Zhang, M., Guo, X., Yuan, Z., Studies on the capability and behavior of adsorption of thallium on nano- Al_2O_3 . *J. Hazard. Mater.*, 157, 352, 2008.

75. Khajeh, M., Sanchooli, E., Synthesis and evaluation of silver nanoparticles material for solid phase extraction of cobalt from water samples. *Appl. Nanosci.*, 1, 205, 2011.
76. Khajeh, M., Silver nanoparticles for the adsorption of manganese from biological samples. *Biol. Trace Elem. Res.*, 138, 337, 2010.
77. Khajeh, M., Sanchooli, E., Silver nanoparticles as a new solid-phase adsorbent and its application to preconcentration and determination of lead from biological samples. *Biol. Trace Elem. Res.*, 143, 1856, 2011.
78. He, Q., Chang, X., Huang, X., Hu, Z., Determination of trace elements in food samples by ICP-AES after preconcentration with p-toluenesulfonyl-amide immobilized on silica gel and nanometer SiO_2 . *Microchim. Acta*, 160, 147, 2008.
79. Hadjiivanov, K., Klissurski, D., Kantcheva, M., Davydov, A., State and localization of cobalt, nickel and copper ions adsorbed on titania (anatase). *J. Chem. Soc., Faraday. Trans.*, 87, 907, 1991.
80. Lian, N., Chang, X., Zheng, H., Wang, S., Cui, Y., Zhai, Y., Application of dithizone-modified TiO_2 nanoparticles in the preconcentration of trace chromium and lead from sample solution and determination by inductively coupled plasma atomic emission spectrometry. *Microchim. Acta*, 151, 81, 2005.
81. Bolis, V., Fubini, B., Giamello, E., Effect of form on the surface chemistry of finely divided solids. *Mater. Chem. Phys.* 1991, 29,153.
82. Cui, Y., Chang, X., Zhai, Y., Zhu, X., Zheng, H., Lian, N., ICP-AES determination of trace elements after preconcentrated with p-dimethylaminobenzaldehyde-modified nanometer SiO_2 from sample solution. *Microchem. J.*, 83, 35, 2006.
83. Afkhami, A., Moosavi, R., Madrakian, T., Preconcentration and spectrophotometric determination of low concentrations of malachite green and leucomalachite green in water samples by high performance solid phase extraction using maghemite nanoparticles. *Talanta*, 82, 785, 2010.
84. Afkhami, A., Saber-Tehrani, M., Bagheri, H., Simultaneous removal of heavy-metal ions in wastewater samples using nano-alumina modified with 2, 4-dinitrophenylhydrazine. *J. Hazard. Mater.*, 181, 836, 2010.
85. Afkhami, A., Moosavi, R., Adsorptive removal of Congo red, a carcinogenic textile dye, from aqueous solutions by maghemite nanoparticles. *J. Hazard. Mater.*, 174, 398, 2010.
86. Afkhami, A., Norooz-Asl, R., Removal, preconcentration and determination of Mo (VI) from water and wastewater samples using maghemite nanoparticles. *Colloids. Surf., A*, 346, 52, 2009.
87. Suleiman, J.S., Hu, B., Pu, X., Huang, C., Jiang, Z., Nanometer-sized zirconium dioxide microcolumn separation/preconcentration of trace metals and their determination by ICP-OES in environmental and biological samples. *Microchim. Acta*, 159, 379, 2007.

88. Hang, C., Hu, B., Jiang, Z., Zhang, N., Simultaneous on-line preconcentration and determination of trace metals in environmental samples using a modified nanometer-sized alumina packed micro-column by flow injection combined with ICP-OES. *Talanta*, 71, 1239, 2007.
89. Zhai, Y., He, Q., Yang, X., Han, Q., Solid phase extraction and preconcentration of trace mercury (II) from aqueous solution using magnetic nanoparticles doped with 1,5-diphenylcarbazide. *Microchim. Acta*, 169, 353, 2010.
90. Vassileva, E., Proinova, I., Hadjiivanov, K., Solid-phase extraction of heavy metal ions on a high surface area titanium dioxide (anatase). *Analyst*, 121, 607, 1996.
91. Brunelle, J. P. Proceedings of the Second International Symposium on the Preparation of Catalysts, Louvain-la-Neuve; Delmon, B., Grange, P., Jacobs, P., Poncelet, G., Eds.; Elsevier: Amsterdam, 1979; p 211.
92. Baliza, P.X., Teixeira, L.S.G., Lemos, V.A., A procedure for determination of cobalt in water samples after dispersive liquid-liquid microextraction. *Microchem. J.*, 93, 220, 2009.
93. Lead, J.R., Wilkinson, K.J., Aquatic colloids and nanoparticles: current knowledge and future trends. *Environ. Chem.*, 3, 159, 2006.
94. Wang, J., Hansen, E.H., On-line sample-pre-treatment schemes for trace-level determinations of metals by coupling flow injection or sequential injection with ICP-MS. *TrAC Trends. Anal. Chem.*, 22, 836, 2003.
95. Komjarova, I., Blust, R., Comparison of liquid-liquid extraction, solid-phase extraction and co-precipitation preconcentration methods for the determination of cadmium, copper, nickel, lead and zinc in seawater. *Anal. Chim. Acta*, 576, 221, 2006.
96. Parham, H., Pourreza, N., Rahbar, N., Solid phase extraction of lead and cadmium using solid sulfur as a new metal extractor prior to determination by flame atomic absorption spectrometry. *J. Hazard. Mater.*, 163, 588, 2009.
97. Engates, K.E., Shipley, H.J., Adsorption of Pb, Cd, Cu, Zn, and Ni to titanium dioxide nanoparticles: effect of particle size, solid concentration, and exhaustion. *J. Environ. Sci. Pollut. Res.*, 18, 386, 2011.
98. Baer, D.R., Gaspar, D.J., Nachimuthu, P., Techane, S.D., Castner, D.G., Application of surface chemical analysis tools for characterization of nanoparticles. *Anal. Bioanal. Chem.*, 396, 983, 2010.
99. Jiménez-Soto, J. M., Lucena, R., Cárdenas, S., Valcárcel, M. *Solid Phase (Micro) extraction Tools Based on Carbon Nanotubes and Related Nanostructures, Carbon Nanotubes; Carbon Nanotubes*; Marulanda, J. M., Ed.; InTech: New York, 2010.
100. Vuković, G.D., Marinković, A.D., Čolić, M., Ristić, M.Đ., Aleksić, R., Perić-Grujić, A.A., Uskoković, P.S., Removal of cadmium from aqueous solutions by oxidized and ethylenediamine-functionalized multi-walled carbon nanotubes. *Chem. Eng. J.*, 157, 238, 2010.

101. Datsyuk, V., Kalyva, M., Papagelis, K., Parthenios, J., Tasis, D., Siokou, A., Kallitsis, I., Galiotis, C., Chemical oxidation of multiwalled carbon nanotubes. *Carbon*, 46, 833, 2008.
102. Thompson, T.L., Panayotov, D.A., Yates, J.T., Martyanov, I., Klabunde, K., Photodecomposition of adsorbed 2-chloroethyl ethyl sulfide on TiO₂: involvement of lattice oxygen. *J. Phys. Chem. B*, 108, 17857, 2004.
103. Ghosh, S., Mashayekhi, H., Pan, B., Bhowmik, P., Xing, B., Colloidal behavior of aluminum oxide nanoparticles as affected by pH and natural organic matter. *Langmuir*, 24, 12385, 2008.
104. Bund, A., Thiemig, D., Influence of bath composition and pH on the electrode position of alumina nanoparticles and copper. *J. Appl. Electrochem.*, 37, 345, 2007.
105. Rupasinghe, R.; A-Thilini, P. *Dissolution and Aggregation of ZincOxide Nanoparticles at Circumneutral pH; a Study of Size Effects in the Presence and Absence of Citric Acid*. Master of Science, Thesis, University of Iowa, 2011.
106. Sayyadnejad, M.A., Ghaffarian, H.R., Saeidi, M., Removal of hydrogen sulfide by zinc oxide nanoparticles in drilling fluid. *Int. J. Environ. Sci. Technol.*, 5, 565, 2008.
107. Li, J.G., Kamiyama, H., Wang, X.H., Moriyoshi, Y., Ishigaki, T., TiO₂ nanopowders via radio-frequency thermal plasma oxidation of organic liquid precursors: synthesis and characterization. *J. Eur. Ceram. Soc.*, 26, 423, 2006.
108. Xu, Z., Liu, X.W., Ma, Y.S., Gao, H.W., Interaction of nano-TiO₂ with lysozyme: insights into the enzyme toxicity of nanosized particles. *Environ. Sci. Pollut. Res.*, 17, 798, 2010.
109. Glazier, R., Venkatakrisnan, R., Gheorghiu, F., Walata, L., Nash, R., Zhang, W.X., Nanotechnology takes root. *Civ. Eng.*, 73, 64, 2003.
110. Yantasee, W., Warner, C.L., Sangvanich, T., Addleman, R.S., Carter, T.G., Wiacek, R.J., Fryxell, G.E., Timchalk, C., Warner, M.G., Removal of heavy metals from aqueous systems with thiol functionalized superparamagnetic nanoparticles. *Environ. Sci. Technol.*, 41, 5114, 2007.
111. Hadjiivanov, K.I., Klissurski, D.G., Surface chemistry of titania (anatase) and titania-supported catalysts. *Chem. Soc. Rev.*, 25, 61, 1996.
112. Qian, S., Zhang, S., Huang, Z., Xiao, M., Huang, F., Preconcentration of ultra-trace copper in water samples with nanometer-size TiO₂ colloid and determination by GFAAS with slurry sampling. *Microchim. Acta*, 166, 251, 2009.
113. Niemeyer, C.M., Nanoparticles, proteins, and nucleic acids: Biotechnology meets materials science. *Angew. Chem., Int. Ed.*, 40, 4128, 2001.
114. Shenhar, R., Norsten, T.B., Rotello, V.M., Polymer-mediated nanoparticle assembly: Structural control and applications. *Adv. Mater.*, 17, 657, 2005.
115. De, M., Ghosh, P.S., Rotello, V.M., Applications of nanoparticles in biology. *Adv. Mater.*, 20, 4225, 2008.
116. Wilson, R., The use of gold nanoparticles in diagnostics and detection. *Chem. Soc. Rev.*, 37, 2028, 2008.

117. Katz, E., Willner, I., Integrated nanoparticle–biomolecule hybrid systems: Synthesis, properties, and applications. *Angew. Chem., Int. Ed.*, 43, 6042, 2004.
118. Wu, C.S., Liu, F.K., Ko, F.H., Potential role of gold nanoparticles for improved analytical methods: An introduction to characterizations and applications. *Anal. Bioanal. Chem.*, 399, 103, 2011.
119. Gubin, S.P., Koksharov, Y.A., Khomutov, G.B., Yurkov, G.Y.E., Magnetic nanoparticles: Preparation, structure and properties. *Russ. Chem. Rev.*, 74, 489, 2005.
120. Song, Y., Zhao, S., Tchounwou, P., Liu, Y.M., A nanoparticle-based solid-phase extraction method for liquid chromatography–electrospray ionization–tandem mass spectrometric analysis. *J. Chromatogr., A*, 1166, 79, 2007.
121. Ito, A., Shinkai, M., Honda, H., Kobayashi, T.J., Medical application of functionalized magnetic nanoparticles. *Biosci. Bioeng.*, 100, 1, 2005.
122. Berry, C.C., Possible exploitation of magnetic nanoparticle–cell interaction for biomedical applications. *J. Mater. Chem.*, 15, 543, 2005.
123. Elliott, D.W., Zhang, W.X., Field assessment of nanoscale bimetallic particles for groundwater treatment. *Environ. Sci. Technol.*, 35, 4922, 2001.
124. Lee, H. K., Do, S. H., Kong, S. H., Proceedings of the World Congress on Engineering and Computer Science 2010 Vol II WCECS; October 20–22, 2010, San Francisco.
125. Suleiman, J.S., Hu, B., Peng, H., Huang, C., Separation/preconcentration of trace amounts of Cr, Cu and Pb in environmental samples by magnetic solid-phase extraction with Bismuthiol-II-immobilized magnetic nanoparticles and their determination by ICP-OES. *Talanta*, 77, 1579, 2009.
126. Čampelj, S., Makovec, D., Drofenik, M., Functionalization of magnetic nanoparticles with 3-aminopropyl silane. *J. Magn. Mater.*, 321, 1346, 2009.
127. Shishehbore, M.R., Afkhami, A., Bagheri, H., Salicylic acid functionalized silica-coated magnetite nanoparticles for solid phase extraction and preconcentration of some heavy metal ions from various real samples. *Chem. Cent. J.*, 5, 41, 2011.
128. Huang, C., Hu, B., Speciation of inorganic tellurium from seawater by ICP-MS following magnetic SPE separation and preconcentration. *J. Sep. Sci.*, 31, 760, 2008.
129. Harris, P.J.F., *Carbon Nanotubes and Related Structures*, Cambridge University Press: Cambridge, 1999.
130. Itkis, M.E., Perea, D.E., Jung, R., Niyogi, S., Haddon, R.C., Comparison of analytical techniques for purity evaluation of single-walled carbon nanotubes. *J. Am. Chem. Soc.*, 127, 3439, 2005.
131. Matisová, E., Škrabáková, S., Carbon sorbents and their utilization for the preconcentration of organic pollutants in environmental samples. *J. Chromatogr., A*, 707, 145, 1995.
132. Mauter, M.S., Elimelech, M., Environmental applications of carbon-based nanomaterials. *Environ. Sci. Technol.*, 42, 5843, 2008.

133. Agnihotri, S., Rood, M.J., Rostam-Abadi, M., Adsorption equilibrium of organic vapors on single-walled carbon nanotubes. *Carbon*, 43, 2379, 2005.
134. McPhail, M.R., Sells, J.A., He, Z., Chusuei, C.C., Charging nanowalls: Adjusting the carbon nanotube isoelectric point via surface functionalization. *J. Phys. Chem., C*, 113, 14102, 2009.
135. Bagheri, H., Roostaie, A., Babanezhad, E., New grafted nanosilica-based sorbent for needle trap extraction of polycyclic aromatic hydrocarbons from water samples followed by GC/MS. *Chromatogr.*, 74, 429, 2011.
136. Syed, S., Alhazzaa, M.I., Asif, M.J., Treatment of oily water using hydrophobic nano-silica. *Chem. Eng.*, 167, 99, 2011.
137. Katz, A. and Davis, M.E., Molecular imprinting of bulk, microporous silica. *Nature*, 403, 286, 2000.
138. Lan, J., Cheng, D., Cao, D., Wang, W., Silicon nanotube as a promising candidate for hydrogen storage: from the first principle calculations to grand canonical Monte Carlo simulations. *J. Phys. Chem. C*, 112, 5598, 2008.
139. Dombrowski, T.R., Wilson, G.S., Thurman, E.M., Investigation of anion-exchange and immunoaffinity particle-loaded membranes for the isolation of charged organic analytes from water. *Anal. Chem.*, 70, 1969, 1998.
140. Zhang, S., Shim, W.S., Kim, J. Design of ultra-fine nonwovens via electrospinning of Nylon 6: Spinning parameters and filtration efficiency. *Mater. Des.*, 30, 3659, 2009.
141. Xu, Q., Yin, X., Wu, S., Wang, M., Wen, Z., Gu, Z., Determination of phthalate esters in water samples using Nylon-6 nanofibers mat-based solid-phase extraction coupled to liquid chromatography. *Microchim. Acta*, 168, 267, 2010.
142. Manzoori, J.L., Amjadi, M., Darvishnejad, M., Separation and preconcentration of trace quantities of copper ion using modified alumina nanoparticles, and its determination by flame atomic absorption spectrometry. *Microchim. Acta*, 176(3-4), 437-443, 2012.
143. Afkhami, A., Saber-Tehrani, M., Bagheri, H., Madrakian, T., Flame atomic absorption spectrometric determination of trace amounts of Pb (II) and Cr (III) in biological, food and environmental samples after preconcentration by modified nano-alumina. *Microchim. Acta*, 172, 125, 2011.
144. Kalfa, O.M., Yalçinkaya, Ö., Türker, A.R., Synthesis and characterization of nano-scale alumina on single walled carbon nanotube. *Inorg. Mater.*, 45, 988, 2009.
145. Afkhami, A., Bagheri, H., Preconcentration of trace amounts of formaldehyde from water, biological and food samples using an efficient nanosized solid phase, and its determination by a novel kinetic method. *Microchim. Acta*, 176, 217, 2012.
146. Renuka, N.K., Shijina, A.V., Praveen, A.K., Mesoporous γ -alumina nanoparticles: Synthesis, characterization and dye removal efficiency. *Mater. Lett.*, 82, 42, 2012.

147. Ryu, S.O., Park, N.K., Chang, C.H., Kim, J.C., Lee, T.J., Multicyclic study on improved Zn/Ti-based desulfurization sorbents in mid-temperature conditions. *Ind. Eng. Chem. Res.*, 43, 1446, 2004.
148. Park, N.K., Han, G.B., Yoon, S.H., Ryu, S.O., Lee, T.J., *Int. J. Precis. Eng. Manuf.*, 11, 321, 2010.
149. Yu, H.F., Zhang, Z.W., Hu, F.C.J. Phase stabilities and photocatalytic activities of P/Zn-TiO₂ nanoparticles able to operate under UV-vis light irradiation. *Alloys. Compd.*, 465, 484, 2008.
150. Quétel, C.R., Vassileva, E., Petrov, I., Chakarova, K., Hadjiivanov, K.I., First results on Fe solid-phase extraction from coastal seawater using anatase TiO₂ nano-particles. *Anal. Bioanal. Chem.*, 396, 2349, 2010.
151. Shahrezaei, F., Akhbari, A., Rostami, A., Photodegradation and removal of phenol and phenolic derivatives from petroleum refinery wastewater using nanoparticles of TiO₂. *Int. J. Energy Environ.*, 3, 267, 2012.
152. Gunduz, S., Akman, S., Baysal, A., Culha, M., The use of gold nanoparticles as an effective modifier for the determination of arsenic and antimony by electrothermal atomic absorption spectrometry. *Microchim. Acta*, 172, 403, 2011.
153. Li, Z.P., Duan, X.R., Liu, C.H., Du, B.A., Selective determination of cysteine by resonance light scattering technique based on self-assembly of gold nanoparticles. *Anal. Biochem.*, 351, 18, 2006.
154. Liu, F.K., Preconcentration and separation of neutral steroid analytes using a combination of sweeping micellar electrokinetic chromatography and a Au nanoparticle-coated solid phase extraction sorbent. *J. Chromatogr. A*, 1215, 194, 2008.
155. Gupta, K., Saha, S., Ghosh, U.C., Synthesis and characterization of nano-structure hydrous iron-titanium binary mixed oxide for arsenic sorption. *J. Nanopart. Res.*, 10, 1361, 2008.
156. Mohan, D., Pittman, C.U., Arsenic removal from water/wastewater using adsorbents—A critical review. *J. Hazard. Mater.*, 142, 1, 2007.
157. Manna, B.R., Dey, S., Debnath, S., Ghosh, U.C., Removal of arsenic from groundwater using crystalline hydrous ferric oxide(CHFO). *Water Qual. Res. J. Can.*, 38, 193, 2003.
158. Tsai, H.Y., Hsu, C.F., Chiu, I.W., Fuh, C.B., Detection of C-reactive protein based on immunoassay using antibody-conjugated magnetic nanoparticles. *Anal. Chem.*, 79, 8416, 2007.
159. Hu, J., Chen, G., Lo, I.M., Removal and recovery of Cr (VI) from wastewater by maghemite nanoparticles. *Water Res.*, 39, 4528, 2005.
160. Bautista, L.F., Morales, G., Sanz, R., Immobilization strategies for laccase from *trametes versicolor* on mesostructured silica materials and the application to the degradation of naphthalene. *Bioresour. Technol.*, 101, 8541, 2010.
161. Takafuji, M., Ide, S., Ihara, H., Xu, Z., Preparation of poly (1-vinylimidazole)-grafted magnetic nanoparticles and their application for removal of metal ions. *Chem. Mater.*, 16, 1977, 2004.

162. Bai, L., Mei, B., Guo, Q.Z., Shi, Z.G., Feng, Y.Q., Magnetic solid-phase extraction of hydrophobic analytes in environmental samples by a surface hydrophilic carbon-ferromagnetic nanocomposite. *J. Chromatogr., A*, 1217, 7331, 2010.
163. Zhao, X., Shi, Y., Cai, Y., Mou, S., Cetyltrimethylammonium bromide-coated magnetic nanoparticles for the preconcentration of phenolic compounds from environmental water samples. *Environ. Sci. Technol.*, 42, 1201, 2008.
164. Afzali, D., Mostafavi, A., Potential of modified multiwalled carbon nanotubes with 1-(2-pyridylazo)-2-naphthol as a new solid sorbent for the preconcentration of trace amounts of cobalt (II) ion. *Anal. Sci.*, 24, 1135, 2008.
165. Zhou, Q., Xiao, J., Wang, W., Using multi-walled carbon nanotubes as solid phase extraction adsorbents to determine dichlorodiphenyltrichloroethane and its metabolites at trace level in water samples by high performance liquid chromatography with UV detection. *J. Chromatogr., A*, 1125, 152, 2006.
166. Baena, J.R., Gallego, M., Valcarcel, M., Fullerenes in the analytical sciences. *TrAC Trends Anal. Chem.*, 21, 187, 2002.
167. Shamspur, T., Mostafavi, A., Application of modified multiwalled carbon nanotubes as a sorbent for simultaneous separation and preconcentration trace amounts of Au (III) and Mn (II). *J. Hazard. Mater.*, 168, 1548, 2009.
168. Liang, P., Liu, Y., Guo, L. *Spectrochim. Acta B*, 60, 125, 2005.
169. Pyrzynska, K., Stafiej, A., Biesaga, M., Sorption behavior of acidic herbicides on carbon nanotubes. *Microchim. Acta*, 159, 293, 2007.
170. Wang, Z., Luo, G., Chen, J., Xiao, S., Wang, Y., Carbon nanotubes as separation carrier in capillary electrophoresis. *Electrophoresis*, 24, 4181, 2003.
171. Ngeontae, W., Aeungmaitrepirom, W., Tuntulani, T., Chemically modified silica gel with aminothioamidoanthraquinone for solid phase extraction and preconcentration of Pb (II), Cu (II), Ni (II), Co (II) and Cd (II). *Talanta*, 71, 1075, 2007.
172. Sadeghi, S., Sheikhzadeh, E., Solid phase extraction using silica gel functionalized with Sulfasalazine for preconcentration of uranium (VI) ions from water samples. *Microchim. Acta*, 163, 313, 2008.
173. Zhang, L., Zhai, Y., Chang, X., He, Q., Huang, X., Hu, Z., Determination of trace metals in natural samples by ICP-OES after preconcentration on modified silica gel and on modified silica nanoparticles. *Microchim. Acta*, 165, 319, 2009.
174. Chen, X.L., Zou, J.L., Zhao, T.T., Li, Z.B., Preparation and fluoroimmunoassay application of new red-region fluorescent silica nanoparticles. *J. Fluoresc.*, 17, 235, 2007.
175. Razavi, S., Hashemianzadeh, S.M., Razavi, S., Balilehvand, S., Yari, F., Sigarchi, F., A Combined Ab-Initio and Monte-Carlo investigation of an equimolar H₂/He mixture adsorption in silicon nanotubes: temperature, pressure, and pore size effects. *J. Comput. Theor. Nanosci.*, 9, 737, 2012.
176. Balilehvand, S., Hashemianzadeh, S.M., Razavi, S., Karimi, H., Investigation of hydrogen and methane adsorption/separation on silicon nanotubes: a

- hierarchical multiscale method from quantum mechanics to molecular simulation. *Adsorption*, 18, 13, 2012.
177. Zhuqing, W., Min, W., Genhua, W., Yuyong, S., Chiyang, H., Ion imprinted sol-gel nanotubes membrane for selective separation of copper ion from aqueous solution. *Microchim. Acta*, 169, 195, 2010.
 178. Rammika, M., Darko, G., Torto, N., Incorporation of Ni(II)-dimethylglyoxime ion-imprinted polymer into electrospun polysulphone nanofibre for the determination of Ni(II) ions from aqueous samples. *Water SA*, 37, 539, 2011.
 179. Chen, S., Xiao, M., Lu, D., Wang, Z., The use of carbon nanofibers micro-column preconcentration for inductively coupled plasma mass spectrometry determination of Mn, Co and Ni. *Spectrochim. Acta B*, 62, 1216, 2007.
 180. Kang, X., Pan, C., Xu, Q., Yao, Y., Wang, Y., Qi, D., Gu, Z., The investigation of electrospun polymer nanofibers as a solid-phase extraction sorbent for the determination of trazodone in human plasma. *Anal. Chim. Acta*, 587, 75, 2007.
 181. Xu, Q., Yin, X., Wu, S., Wang, M., Wen, Z., Gu, Z., Determination of phthalate esters in water samples using Nylon6 nanofibers mat-based solid-phase extraction coupled to liquid chromatography. *Microchim. Acta*, 168, 267, 2010.
 182. Zhang, S., Shim, W.S., Kim, J., Design of ultra-fine nonwovens via electrospinning of nylon-6: Spinning parameters and filtration efficiency. *Mater. Des.*, 30, 3659, 2009.
 183. Ojha, S.S., Afshari, M., Kotek, R., Gorga, R.E., Morphology of electrospun nylon-6 nanofibers as a function of molecular weight and processing parameters. *J. Appl. Polym. Sci.*, 108, 308, 2008.
 184. Bazbouz, M.B., Stylios, G.K., Alignment and optimization of nylon-6 nanofibers by electrospinning. *J. Appl. Polym. Sci.*, 107, 3023, 2008.