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Lead Remediation Using Smart Materials. A Review

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Abstract: The nanoparticles have been prepared and employed as excellent adsorbents for the sequestration of heavy metal ions and hazardous impurities from the aqueous media. The surface morphological, textural and structural properties of nanoparticles have been modified, which are capable and potentially useful for the remediation of metal ions. Several metals (oxides, doped, nanocomposites of Fe, Ti, Zn, SiO₂, SiC, Mo, Co, Ni, Zr, Mn, Si, S, Al, Cu, Ce, graphene, CNTs) were reported an efficient adsorbents for the removal of lead (Pb) ions from aqueous media and polluted water. The present review focuses on different kinds of nanoparticles such as metal oxides, carbon based and host supported employed for removal of Pb ions under varying experimental conditions such as pH, temperature, contact time and concentrations. The preparation strategies, physicochemical properties and adsorption are also discussed. Based on studies, it was found that the smart materials are affective adsorbents for the purification of wastewater containing Pb ions and could possibly extended for the remediation of other heavy metal ions.

Keywords: adsorption; lead removal; metal oxides; nanocomposites; waste water treatment.

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1 Introduction

Due to rapid industrialization, the environment faces a serious problem of pollution with diverse types of pollutants. Among different types of pollutants, the pollution due to heavy metal ions is more serious since heavy metals are non-biodegradable and accumulates in the body of living organisms and are responsible for health hazards to animals and human beings [1–5]. Among heavy metals, Pb(II) is one of the highly toxic metals [2, 6–13]. Lead and its compounds are widely used in printing, storage batteries, fuel, plumbing, mining, automobile batteries, printing and various other industries which resultantly, released into water at elevated concentration in to the environment [14]. Exposure to lead Pb to various health issue i.e. nervous system, mental retardation, renal kidney disease, anemia and cancer [15]. Due to highly toxic nature of Pb, maximum contaminant level (MCL) for Pb is 0.015 mg/L in drinking water [16]. Therefore, the effective removal of lead is important from water system to clean up the environment. In this regard, adsorption is regarded as efficient technique for the adsorption of pollutants form polluted water. The industrial and agricultural wastes have been efficiently used for the removal of diverse types of pollutants form synthetic aqueous solution and industrial wastewater [6–8, 17–22] i.e. crab shell, activated carbon, zeolite, fly ash, coconut shell, rice husk and others have been successfully used as an efficient adsorbents [23]. However, the application of nanomaterials (smart materials) attracted the attention of scientific community as adsorbents. There are various techniques employed for the synthesis of advanced materials, which have been employed as an adsorbents and photocatalysts [24–37]. The adsorption is simple process, low cost and efficiency is high and is preferred for the remediation of pollutants.

The nanotechnology attained much attention in recent years and various types of adsorbents have been developed for the fabrication of smart material with variable structural and morphologies diversity i.e. nano (spheres, sheets, tubes, rods, belts, wires, flower, stars, cubes, combs, needles, rings) and others [38–41]. At nanoscale materials exhibit magical properties because of their large surface area to volume ratio which enhance the activity versus bulk materials [42]. Thus at nanoscale, nanoparticles exhibit different electrical, optical and magnetic properties than their normal size equivalents [43]. However, due to very small size, nanoparticles exhibit high surface energy which inevitably leads to the poor stability as particles agglomerated due to Van der Waals or other interactions, which consequently reduces the selectivity and efficiency. Hence, for the improvement of applicability of nanostructures, the surfaces were modified with different materials such as natural materials, activated carbon and synthetic polymer and resultantly, the nanocomposites showed better performance.

Tab. 1: Average surface area, particle size and pore of nanoadsorbents used for Pb(II) ions adsorption.

Surface area (m ² /g)	Particle size (nm)	X-ray measured particle size (nm)	BET surface area (m ² /g)	External surface area (m ² /g)	Average pore volume (cm ³ /g)
40	20–30	22 ± 1.5	43	39	0.38

Appropriate modifications onto surface of nanoparticles enhance the selectivity and consequently, enhances the efficiency of nanomaterial’s [44, 45]. The average surface area, particle size, surface area and pore volume of smart material employed for adsorption purposes are shown in Table 1.

Different types of nanoparticles and nanocomposites (Fe, Ti, Zn, SiO₂, SiC, Mo, Co, Ni, Zr, Mn, Si, S, Al, Cu, Ce, graphene, CNTs) have been reported for the removal of Pb ions from aqueous media. Thus, this review was undertaken to discuss nanomaterial’s utilized for the removal of Pb ions from aqueous media under varying experimental conditions such as pH, temperature, contact time and concentration. Moreover, synthesis, sorption capacity, sorption mechanism and recycling ability for reusability of nanoparticles and nanocomposites are also discussed.

2 Metal oxide nanoparticles

Adsorbents based on metal oxide nanoparticles (MONPs) such as ferric oxides, aluminum oxide, zinc oxides, titanium oxide, cerium oxide, and manganese oxide have been studied widely as adsorbents for Pb adsorption and MONPs exhibit high sorption capacities and selectivity towards Pb. Hence, the application of MONPs for the remediation of Pb was suggested [46–51]. The MONPs are prepared in different forms such as particles, wires, rods, tubes and others in stable, shape-controlled, uniform size and monodisperse forms. However, the shape and size of MONPs was limiting factor, which affect the adsorption performance. Synthesis methods used for the synthesis of MONPs are categorized into two classes; physical approaches including arc discharge, inert gas condensation, ultrasound shot peening, ion sputtering, spray pyrolysis, laser ablation and high-energy ball milling. Chemical approaches include co-precipitation, reduction, solvothermal, chemical vapor condensation, liquid flame spray, reverse micelle (or microemulsion), sonochemical, pulse electrode position, etc. [52]. Among these synthesis techniques, thermal decomposition and/or reduction [53], co-precipitation [54] and hydrothermal [55] are widely used for the synthesis of MONPs due to their high yield and low cost. Recently, environmental friendly green synthesis approach

also gained much importance for the synthesis of MONPs. This technique uses naturally occurring reagents such as plant extracts, sugars, vitamins, microorganisms and biodegradable polymers as capping and reducing agents. This technique employed nontoxic solvents, closed reactors and low temperature [56].

2.1 Iron oxide nanoparticles

The iron oxide (magnetic) nanoparticles have been widely employed as adsorbent for removal of Pb ions from waste water due to low cost and ease in synthesis i.e. hematite ($\alpha\text{-Fe}_2\text{O}_3$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), goethite ($\alpha\text{-FeOOH}$), magnetite (Fe_3O_4), amorphous hydrous Fe oxides and iron/iron oxide ($\text{Fe@Fe}_x\text{O}_y$) [57, 58] (Table 2). Idris et al. [59] fabricated magnetic alginate beads consisting of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles embedded in alginate for the removal of Pb ions from wastewater. The maghemite nanoparticles were synthesized by co-precipitation method and then, mixed with sodium-alginate solution to form magnetic alginate beads having a diameter of 8.9464 nm and spherical morphology with an iron content of 0.119 mmol/g. Results showed removal of 95.2% of Pb ions at pH 7 within 2 h contact time. The amount of Pb ions adsorbed onto the magnetic bead was found to be 50 mg/g. Similarly, Li et al. [60] reported magnetic sodium alginate gel beads ($\text{Fe}_3\text{O}_4\text{@SA-Zr}$) by using zirconium(IV) as a crosslinking ions as adsorbent for the removal of Pb ions. The Fe_3O_4 nanoparticles were synthesized by co-precipitation method and then, mixed with sodium-alginate solution. Adsorption followed Langmuir isotherm model with a maximum Pb ions adsorption capacity of 333.33 mg/g. Roy et al. [61] evaluated adsorption mechanism of Cu, Zn and Pb ions on magnetic maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanotubes prepared via microwave irradiation method. Nanotubes with lengths in the range of 150–250 nm, diameters 10–15 nm, wall thickness of 6–8 nm and specific surface area of 321.638 m^2/g . Adsorption data well represented by pseudo-second-order kinetics and Langmuir isotherm model with the maximum adsorption capacities of 71.42 mg/g for Pb ions. Optimum contact time was found to be 240 min and pH 6.0 for maximum Pb adsorption.

Wang et al. [62] studied adsorption of Pb and Cr ions onto magnetite nanoparticles synthesized through co-precipitation method with NCM and

Tab. 2: Magnetic nanoparticle properties.

MNPs	Morphology	Diameter (nm)	Length (nm)
$\alpha\text{-FeOOH}$	Spheres	10–60	
$\gamma\text{-FeOOH}$	Needle	10–30	100–300

without CM. Procedure involves the mixing of ferric chloride hexahydrate and ferrous chloride tetrahydrate solutions followed by addition of ammonia solution under stirring conditions. In NCM, the magnetite was obtained under a continuous nitrogen flux, whereas CM without nitrogen gas. NCM and CM showed an average diameter of 15 nm. The SEM images of synthesized magnetite nanoparticles are shown in Figure 1. The BET surface area was reported to be 125.77 and 107.55 m²/g for NCM and CM, respectively. In the case of Pb ions, the NCM showed 80.56% removal after 3 h, CM showed the Pb adsorption capacity of 48.06% and adsorption data followed Freundlich model and pseudo second order kinetics. Kumari et al. [16] employed mesoporous magnetite (Fe₃O₄) nanospheres for Cr and Pb ions adsorption. Magnetite (Fe₃O₄) nanospheres was prepared by solvothermal method with BET 11.3 m²/g, average pore size diameter of 24.1 nm and the single point adsorption total volume of 0.031 cm³/g at P/P₀ = 0.97. The maximum Pb ions adsorption capacities at different temperatures were 6.64 mg/g (at 25 °C), 7.31 mg/g (at 35 °C) and 8.90 mg/g (at 45 °C). Madrakian et al. [63] modified surface of magnetite nanoparticles by incorporating reactive blue-19 dye and used for the adsorption of Pb ions. The diameter of the magnetite nanoparticles was in the range of 52–54 nm with crystallite size of 25 nm. The specific surface area of magnetite nanoparticles was 95.63 m²/g, total pore volume of 0.2758 cm³/g and the mean pore diameter was 11.53 nm. Langmuir model gives a better fit to the experimental data with maximum Pb ions adsorption capacity of 79.3 mg/g. Ahmed et al. [64] prepared mixed magnetite–hematite nanoparticles of size 4–52 nm and used for Pb, Cd and Cr ions removal. Co-precipitation in air and N₂ atmosphere, citrate–nitrate, glycine–nitrate and microwave-assisted citrate methods were adopted for synthesis. The co-precipitation in N₂ gives single phase magnetite, by co-precipitation in air, most of the magnetite is transformed into hematite. HRTEM micrographs of magnetite–hematite mixtures prepared by

Fig. 1: SEM images of synthesized magnetite nanoparticles, (a) NCM, (b) CM (Wang et al. [62]).

different synthesis methods are shown in Figure 2. However, among the combustion methods, the highest percentage composition of magnetite was obtained by the microwave-assisted method (80%), 70% in case of glycine–nitrate method and in case of citrate–nitrate method, 60% magnetite was obtained. In combustion methods, the particle size was in the range of 37–52 nm and in case of coprecipitation, the particle size was in the range of 4–12 nm. The maximum Pb ions sorption was observed 617.3 mg/g for Pb at pH 7.

Flame spray pyrolysis (FSP) technique was successfully employed to synthesize super paramagnetic maghemite (γ - Fe_2O_3) nanoparticles (NPs) with controllable morphology. The physico-chemical properties were determined using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), selected area electron diffraction patterns (SAED), SEM-EDX and scanning electron microscopy (SEM). Elemental contents before

Fig. 2: (a–f) HRTEM micrographs of magnetite–hematite mixtures prepared by different synthesis methods. (f) Selected area electron diffraction pattern of the sample prepared by coprecipitation in air (Ahmed et al. [64]).

and after adsorption were identified using energy dispersive X-ray fluorescence (ED-XRF), energy dispersive X-ray analysis (EDX) and elemental mapping. The adsorption study using γ -Fe₂O₃ NPs synthesized by FSP to successfully remediate Pb ions from water is reported. An optimum pH of 5.0 was studied for Pb ions removal. The removal methodology for Pb ions by these maghemite NPs were presented and it was highly pH-dependent. The electrostatic attractions were mainly responsible for the phenomenon of metal ion uptake and sorption kinetic was of pseudo-second-order. The maximum Langmuir adsorption capacities of these NPs were 68.9 mg/g at 45 °C for Pb ions. Therefore, these maghemite NPs were readily prepared, characterized and showed promise for heavy metal ions remediation from aqueous solution [65].

Another adsorbent, iron oxide nanoparticles along with *A. fabrum* strains compressed in calcium alginate, was employed for lead removal. The petroleum degrading strain was secluded from core samples from Assam Oilfield, India. Chemically synthesized Fe₃O₄ MNPs (10–20 nm) by co-precipitation method were characterized. Vibrating Sample Magnetometer (VSM) showed saturation magnetization of 46.6 emu g⁻¹, indicating super paramagnetic nature of synthesized MNPs, which will help in separation of bio-sorbent after adsorption. Lead removal was studied using the bio-sorbent synthesized by immobilizing biomass and MNPs in calcium alginate beads at 200 rpm and 37 °C, and the adsorption capacity was found to be maximum at pH 5.5. Adsorption kinetics was examined using pseudo first order, pseudo second order and intra-particle diffusion (IPD) models. The maximum adsorption capacity of the synthesized bio-sorbent was found to be 197.02 mg/g [66]. Zincon-immobilized silica-coated magnetic Fe₃O₄ nanoparticles (Zincon-Si-MNPs) as SPE medium was developed for the separation and preconcentration of trace lead in aqueous medium. Numerous parameters such as pH, extraction time, concentration and volume of eluent, sample volume, and influence of co-existing ions have been investigated in order to establish the optimum conditions for the determination of lead in combination with graphite furnace atomic absorption spectrometry (GFAAS). This method has been positively applied to the analysis of trace lead in natural and drinking water samples and the recoveries for the spiked samples were in the range of 84–104% [67].

2.1.1 Fe₃O₄ and α , γ FeOOH

Nassar [68] studied the adsorption mechanistic, equilibrium, kinetics and thermodynamic of Pb(II) ions present in waste water onto the Fe₃O₄ nanoadsorbent, properties are shown in Tables 1 and 2. Adsorption achieved equilibrium within 30 min because Fe₃O₄ nanoadsorbent was a nonporous as

Fig. 3: Schematic representations of possible mechanism for adsorption of metal ions by $\text{Fe}_3\text{O}_4@\text{APS}@\text{AA-co-CA}$ (Ge et al. [69]).

confirmed by porosity and surface area measurements, here only external adsorption occurs and this type of adsorption requires less time to reach equilibrium. Maximum removal of 36 mg/g was observed at pH 5.5 and Freundlich model was the best-fitting model for the experimental data. Fe_3O_4 magnetic nanoparticles (MNPs) modified with 3-aminopropyltriethoxysilane (APS), acrylic acid (AA) and crotonic acid (CA) have been employed for removal of heavy metals [69]. MNPs have cubic spine structures with diameter of 15–20 nm and remove metal ions efficiently at pH 5.5 (mechanism shown in Figure 3). Adsorption is dependent on pH as by changing pH, surface of adsorbent changed. At low pH, surface is covered by carboxyl groups and hence adsorption was low and when pH was increased, carboxyl groups changed into carboxylate anions and adsorption becomes maximum. Adsorption well represented by Langmuir model with monolayer capacity of 32.0, 39.4, 76.8, and 62.1 (mg/g) for Cd(II), Zn(II), Pb(II), and Cu(II), respectively. Venkateswarlu [70] reported recently, green synthesis of Fe_3O_4 magnetic nanorods by using *Punica Granatum* rind ((fruit waste) extract as the reducing agent. Experimental procedure consists of mixing of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and sodium acetate with freshly prepared *P. Granatum* rind extract solution under stirring conditions. Batch adsorption experiments were done and the maximum adsorption capacity was found to be 46.18 mg/g at pH 5, temperature 301 K and dose 0.1 g/L best fitted to pseudo-second-order kinetic model rather than the pseudo-first-order kinetic model. Rahimi et al. [71] fabricated lepidocrocite ($\gamma\text{-FeOOH}$) and goethite ($\alpha\text{-FeOOH}$) to investigate lead adsorption. Goethite was found to be more efficient adsorbent for lead removal having adsorption capacity (820.165 mg/g) 1.64 times higher than lepidocrocite (527.944 Lmg/g) at optimum conditions of, pH = 5.2 and $C^0 = 5$ mg/L.

2.1.2 Zero valent iron nanoparticles

In recent years, nanoscale zero-valent iron has attracted much attention to remediate contaminated groundwater. The physicochemical properties of nZVI and its

reductive capacity allow rapid decontamination of many pollutants in aqueous system. However, studies show that nZVI is often aggregated by Vander Waals forces which lead to decrease in their reactivity with contaminants. Hence, to improve nZVI dispersivity, various immobilization technologies are being developed such as guar gum stabilized nZVI, starch-stabilized nZVI, sodium carboxymethyl cellulose (CMC) immobilized nZVI, bentonite/iron nanoparticles [72].

Polyacrylic acid [73], kaolin [72] and graphene sheets [74] modified nZVI composites have been reported for Lead removal from waste water. Zerovalent iron nanoparticles graphene composite (G-nZVI) synthesized by sodium borohydride reduction of iron chloride and graphene oxide and Nanoscale zerovalent iron coated with kaolin (K-nZVI) prepared by Fe(III) reduction method. It was found that K-nZVI has a larger specific surface area of $26.11 \text{ m}^2/\text{g}$ as compared to kaolin having surface area of $3.67 \text{ m}^2/\text{g}$. At 50 mg/L of initial concentration of Pb ions, removal percentages for K-nZVI, nZVI and kaolin were found to be 97%, 51.2% and 6.7%, respectively. When initial concentration of Lead increased to 500 mg/L, the removal percentages for K-nZVI, nZVI and kaolin were 96.7%, 15.8% and 8.6%. Hence results showed that 5 g/L of K-nZVI could remove Pb(II) efficiently and optimum pH value ranges from 4 to 6 at contact time of 60 min. PAA-nZVI is prepared by reduction of iron sulfate via borohydride reductor. Adsorption data bet fitted with pseudo first-order kinetic model.

2.1.3 Amine and thiol functionalized magnetic nanoparticles

Porous solids due to large surface area possess a lot of commercial applications as an absorbent, catalyst and catalyst base. According to IUPAC definition, porous solids are classified according to their pore diameter as macro-porous, meso-porous and micro-porous [75]. To prevent agglomeration and enhance activity, surface of porous particles is usually modified by traditional functional groups, such as amino [76], imidazole [77], carboxylic [78] and thiol [79]. The introduction of amino group on the surface of MNPs as chelating layer usually done by two ways: direct synthesis or co-condensation [80] and post-modification or grafting [76].

Amine-functionalized mesoporous Fe_3O_4 nanoparticles (AF- Fe_3O_4) prepared by hydrothermal method have been reported for heavy metal ions removal [81]. The maximum adsorption capacities for Pb(II), Cd(II), and Cu(II) were found to be from 369.0 to 523.6 (mg/g) with removal of 98% of Cu(II), Cd(II) and Pb(II) in 50 mL of solution containing 5 mg/L metal ions at optimized conditions. Recently silica gel functionalized with thiol ($-\text{SH}$) group magnetic sorbents imprinted by Pb(II) ions ($\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-IIP}$) of size 140 nm has been prepared by ion imprinted

technique followed by sol gel process using 3-mercaptopropyl trimethoxysilane (MPTS) as a functional monomer [82]. The ion imprinting technique has shown great potential towards synthesis of materials for removal of heavy metals ions pollutants selectively from waste water. Ion-imprinted polymers (IIP) show good chemical and thermal stability and prevent agglomeration. Adsorption of Lead is maximum at pH 7 and followed Langmuir adsorption isotherm with maximum adsorption capacity of 32.58 mg/g. Kinetic data obey pseudo-second order kinetic model. Sorbent shows high selectivity towards Lead could be regenerated by washing with HCl solution (aqueous) and hence is reusable and stable. Superparamagnetic iron oxide (Fe_3O_4) nanoparticles with a surface functionalized by dimercaptosuccinic acid (DMSA) act as sorbent for toxic metals such as Hg, Ag, Pb, Cd, and Tl. These metals bind effectively to the DMSA ligands. And results shows that these nanoparticles removed 99 wt% of 1 mg/L Pb within a minute [83].

El-Toni et al. [84], fabricated amino group functionalized Mesoporous core shell silica spheres through soft templating method by using ultrasonic waves. (NH_2 -HCMSSs) shows high efficiency towards removal of Cd(II), Pb(II), and Zn(II) metal cations at pH 6 after time interval of 150 min. Adsorption of Cd, Pb and Zn followed second order kinetics model. Adsorption capacity depend on the the initial concentration of Cd, Pb and Zn, if concentration increases from 10 to 200 ppm then adsorption of Cd, Pb and Zn increases from 6.5 to 190.3, 6.8 to 194.3, and 7.8 to 193 (mg/g), respectively.

2.1.4 Ceramic ferrites

In recent years, ceramic ferrites with structure MFe_2O_4 (M: Co, Ca, Mn, Ni, Cu, Zn) have been investigated for their high magnetic permeability, corrosive and chemical stability [85, 86]. Andal and Buvaneswari [87] fabricated NiFe_2O_4 nanoparticles for Lead ions removal. The experimental procedure involves mixing of ferric chloride and nickel chloride solution followed by addition of alginate acid solution. Finally gel was formed which calcined 100–1000 °C to get NiFe_2O_4 . Various parameters such as the pH, contact time and temperature were studied and maximum uptake was found to be at basic pH at a contact time of 1 h. Zhou et al. [88] manufactured a novel adsorbent for Pb(II) and tetrabromobisphenol A (TBBPA) removal from waste water composed of multiwalled carbon nanotubes (MWCNTs) coated with amino modified magnetic nanoparticles (MNP) ($\text{CoFe}_2\text{O}_4\text{-NH}_2$) prepared by polyol method. These nanocomposites further react with terephthalaldehyde followed by grafting of chitosan on MNPs (MNP-CTS) via Schiff base reaction. MNP-CTS have diameter of 72.8 nm. Adsorption of TBBPA followed Freundlich isotherm while Langmuir model describes Pb(II) adsorption well with maximum adsorption capacities of 140.1 and 42.48 for Pb ions and TBBPA, respectively.

Kinetics obeys pseudo second order model and optimum pHs were found to be as pH 6.0 for Pb ions and pH 6.3 for TBBPA. Magnetic nanocomposites could be magnetically separable and regenerated by using 0.2 M NaOH solution.

2.2 Nickel oxide nanoparticles

Among transition metal oxides, bulk and nano size nickel oxide (NiO) have received great attention due to their wide range of applications in various fields, such as: fuel cell electrodes, battery cathodes, catalysis, gas sensor, electrochromic films, photovoltaic devices and magnetic materials. NiO nanoparticles, due to their quantum size and surface effects exhibit catalytic, electronic, optical, and magnetic properties that are significantly different than those of bulk-sized NiO particles [89] and hence also employed as adsorbent for removal of heavy metal pollutants. Khoshhesab et al. [90], reported NiO nanoparticles of size 25 nm prepared by reactions of NH_4HCO_3 solution with microsize NiO powder. Then urea was added to the reaction mixture under stirring and finally mixture was calcined at 400 °C for 1 h to obtain NiO nanoparticles. The maximum adsorption capacity of the NiO nanoparticles obtained by Langmuir model is 62.5 mg/g which is about six times greater than for microsize NiO having adsorption capacity of 10.9 mg/g.

NiO nanoparticles of size 28 nm prepared by co-precipitation methods have been reported for cadmium and lead ions removal from water [91]. Adsorption data well represented by pseudo second order kinetics and the maximum adsorption capacity based on Langmuir isotherms was 909 and 625 mg/g for Cd(II) and Pb(II) ions, respectively. While Positive values of ΔH° and ΔS° showed adsorption is endothermic in nature, and spontaneous. While Ossman [92] reported NiO nanopowders of diameter 38–130 nm and surface area of 191 m²/g prepared by reaction of nickel sulphate and oxalic acid to give nickel oxalate which further mixed with polyethylene glycol for Pb and Zn ions removal. Adsorbent showed high affinity toward Pb with the maximum adsorption capacity calculated from Langmuir isotherm is 50.505 and 63.694 (mg/g).

2.3 Copper oxide nanoparticles

CuO NPs are widely used in various applications such as in batteries, catalysis, heat transfer fluids, gas sensors, and solar energy (Table 3). CuO crystal structures due to narrowband gap, giving useful photovoltaic and photocatalytic properties [93] and can also be employed as adsorbent to remove heavy metal ions. CuO nanostructures of various morphologies such as cluster, small rod, oval,

Tab. 3: CuO nanostructures properties.

CuO nanostructures	Size (nm)	Width (nm)	Length (nm)	Diameter (nm)	Surface area (m ² /g)	Sorption capacity (mg/g)
Oval	20	150–200	350–400		5.62	125
Cluster	13		110–250	5–8	2.95	116
Leaves		100–200	250–450		14.35	117
Rod			50–70	6–12	3.598	120
Porous nanosheets		70–100	145–230	0.8–2	4.774	115

Fig. 4: TEM images of nano-sized copper oxide powder (a) oval shape, (b) cluster shape, (c) leaves shape, (d) rod shape, (e, f) porous nano sheet (Farghali et al. [94]).

leaves, porus have been prepared by using microwave radiation for adsorption of Pb(II) ions from water [94] and adsorption data followed pseudo-second-order kinetics and Langmuir isotherm model (Figure 4). Similarly, CuO nanoparticles

with hierarchical morphologies were used for Pb ions adsorption and CuO exhibited excellent performance for the removal of Pb(II) from aqueous solution. The Pb ions equilibrium adsorption data were best fitted by the Langmuir isothermal model, with the maximum adsorption capacity of 1428.5 mg/g and kinetics followed the pseudo-second-order kinetic and intra-particle diffusion models. Results revealed that heavy metal ions can be effectively removed for wastewater cleanup [95]. Raul et al. [96] also reported CuO NPs for the adsorption of Pb(II) ions. The of rhombohedral CuO, with average diameter ~ 5 nm, length extending up to 50 nm and BET surface area ~ 52.57 m²/g removed the Pb ions >70% within the first 10 min contact time and attained >92% after 60 min contact time. The maximum sorption capacity of Pb(II) was recorded to be 3.31 mg/g at 298 K. The CuO was regenerated up to 82.2% using dilute acid, which can be reutilized for removal of Pb ions from aqueous medium.

2.4 Zinc oxide nanoparticles

ZnO is a semiconductor material having various applications in gas sensors, catalyst industry, solar cells, electrode materials, and electrochromic films [97–99]. ZnO particles have many hydroxyl groups which readily exchanged their protons with heavy metal ions in aqueous system [91, 100] and hence employed as promising adsorbent for pollutant removal and environmental remediation. Mesoporous ZnO with specific surface area of 15.75 m²/g and pore volume of 0.038 cm³/g have been synthesized by hydrothermal method as an adsorbents for the removal of Pb ions [101]. TEM analysis demonstrated the formation of nanorods having hexagonal crystal structure and porosity of structures were determined by nitrogen sorption. Maximum adsorption capacities of Cd(II) and Pb(II) were found to be 147.25 and 160.7 (mg/g), respectively. Similarly, ZnO nanoparticles of 40 nm size and specific surface area of 80.425 m²/g prepared by gel combustion method by using zinc nitrate hexahydrate was prepared and used for Pb ions adsorption [102]. Adsorption of Pb was maximum at lower concentration of Pb ions, which enhanced when adsorbent dosage was increased. The maximum adsorption capacity was found to be 26.109 mg/g at optimum pH of 4.0 was achieved. Kinetics of adsorption followed both Langmuir and Freundlich adsorption isotherm models.

2.5 Aluminium oxide nanoparticles

Alumina is a well-known classical adsorbent exists in various forms such as α -alumina and γ -alumina [103, 104] (Table 4). However, γ -Al₂O₃ nanoparticles

Tab. 4: Properties of aluminium oxide nanoparticles.

Nanoparticles	Diameter (nm)	Surface area (m ² /g)
Uncoated alumina	53	42.62
Coated alumina	68–87	30.38

exhibit promising material as a solid-phase adsorbent due to their high mechanical properties, high surface area, and good resistivity to thermal degradation [105–107]. Alumina has been used for the removal of heavy metals like lead, nickel, and cadmium. But some heavy metal ions are poorly adsorbed on alumina. To deal with this problem, the surface of γ -Al₂O₃ nanoparticles have been chemically or physically modified with certain functional groups having donor atoms such as nitrogen, phosphorus, oxygen, and sulfur. By immobilization of donor atoms at the surface of alumina, metal ion removal mechanism was totally changed. Now metal ions removed not only by the surface of alumina but also by the surface attraction or chemical bonding phenomenon of newly added chemicals [107–112].

Gupta et al. [113] reported alumina-coated carbon nanotubes for Pb ions removal from industrial waste water. Adsorption study were done in batch mode and fixed bed mode. From XRD, SEM and FTIR analysis it was deduced that aluminum atoms aligned closer to the oxygen atom of the carbonyl group of MWCNTs and oxygen atoms of alumina aligned closer to the hydrogen atom of hydroxyl group of MWCNTs due the formation of hydrogen bonding. Nanotubes show an effective removal of lead at pH 3 and 7 and amount of removal of Pb ions increased by increasing contact time, agitation speed, and adsorbent dosage. Fixed-bed column experiments showed that adsorption of lead ions increases by increasing the thickness of the layer on column. By increasing thickness, surface area of

Fig. 5: Effect of layer thickness and flow rate on adsorption of Pb(II) ions in fixed-bed system (Gupta et al. [113]).

adsorbent increases which provided more binding sites for adsorption of lead and hence efficiency is increased. But adsorption of Pb ions decreases by increasing flow rate due to decrease in retention time (Figure 5a, b). Silica/alumina nanoparticles of size 50 nm prepared via sol–gel method by mixing of aluminum tri-sec-butoxide (ASB) with isopropyl alcohol and tetraethyl orthosilicate (TEOS) with ethanol [114] was prepared. The sol gel method produced highly porous nanoparticles with large internal and external surface areas which in result increased metal ion adsorption. The surface of nanoparticles has silanol (Si–OH) and aluminol (Al–OH) groups which could be deprotonated under basic conditions, to give negative charge to the particles. Hence adsorption took place by cation exchange between the H^+ and Pb^{2+} as shown in Eqs. 1 and 2.

Sodium dodecyl sulfate coated nano-alumina modified by 2,4-Dinitrophenylhydrazine (DNPH) have been fabricated for removal of heavy metal ions such as Cd(II), Pb(II), Cr(III), Ni(II), Co(II), and Mn(II) from water. Nano-adsorbent showed significantly higher adsorption capacities for Cd(II), Pb(II), and Cr(III), with maximum adsorption capacity of 83.33, 100.0, and 100.0 (mg/g), respectively [115].

2.6 Titanium dioxide nanoparticles

Titanium dioxide is a transition metal oxide having many applications as, photoelectric conversion in solar cells, photocatalysis, gas sensor and antimicrobial coating. There are four known forms of TiO_2 exists in nature such as: brookite (orthorhombic), rutile (tetragonal), anatase (tetragonal), and TiO_2 (B) (monoclinic) [116]. Among all these, anatase crystalline form is well known because of its high photocatalytic activity which is attributed to its favorable band gap energy and strong oxidizing power. When surface of anatase is illuminated, several electrons and holes pairs are generated which further initiated chemical redox reactions at the surface of anatase due to the migration of electron hole pairs [117]. The electrons promote formation of hydroxyl functional groups at the interface between anatase surface and water and then these hydroxyl groups react with metal ions and hence increased adsorption rate. Due to these properties titanium dioxide nanoparticles could be applied as adsorbents for removal of heavy metal ions from water as at nanoscale titanium dioxide exhibit high surface area, high surface reactivity, more surface atoms, high suspension stability, and unique catalytic activity as compared to bulk titanium dioxide [118, 119].

To enhance adsorption capacity and photocatalytic efficiency, surface of TiO_2 is modified by the addition of electron donors, noble-metal loading, incorporation of carbonate salts, anion doping, metal ion doping, dye sensitization, and polymers such as polystyrene, cellulose microspheres, and polyethylene oxide, etc. [120–126]. Sreekantan et al. [127], synthesized copper incorporated titanium dioxide (TiO_2) nanotubes (SEM image, Figure 6) for Pb ions removal from water via wet impregnation technique, whereas Sharma and Lee [128] reported acrylamide (AM) doped TiO_2 nanocomposites (Ti-AM) prepared by sol gel method for Pb ions adsorption. Polymer doped nanocomposites showed higher adsorption capacity of 476.19 mg/g as compared to copper doped nanoparticles and anatase nanoadsorbent [129]. Rashidi et al. [130] studied the kinetics and thermodynamics of Pb ions removal from aqueous medium by using nanocrystalline TiO_2 which was prepared by hydrolysis of titanium tetrachloride. Adsorption followed pseudo-second order kinetic model and Freundlich model with maximum adsorption capacity of 132.458 mg/g.

2.7 Manganese oxide nanoparticles

Nanosized manganese oxides (NMnOs) has been widely used in advance materials batteries and waste water treatment as they exhibit adsorptive performance superior to its bulk counterpart because of its polymorphic structures and higher specific surface area [131]. Shihabudheen et al. [132], synthesized

Fig. 6: Cu doped titania (SEM image) (Sreekantan et al. [127]).

cellulose-manganese oxide composite of size 5–10 nm (C-NMOC) for Pb ions removal from aqueous medium via impregnation of KMnO_4 solution into cellulose fiber which were reduced further by adding ethanol drop wise under stirring conditions. Then stirring was stopped after 15 min and mixture was kept at rest for 2 h. By increasing manganese loading from 0.39 to 4.64%, cellulose fibers changed their colour from golden brown to brownish black. This colour change indicated formation of C-NMOC. SEM analysis (Figure 7) showed that at lower Mn loading well dispersed manganese oxide particles are formed on the surface of cellulose but at higher Mn loading, the entire surface is modified with uniform coating. The effect of initial concentration of Lead ion and contact time showed rapid adsorption at start which gradually slowed down after achieving equilibrium at 60 min of contact time which is due to the presence of large active sites. Maximum uptake capacity for Lead was found to be as 80.1 mg/g. Hydrous manganese dioxide (HMO) nanoparticles impregnated into microporous membrane

Fig. 7: Manganese oxide loaded cellulose fibers (C-NMOC) showing various loadings of Mn on cellulose fibers (a) 0.39% Mn, (b) 0.66% Mn, (c) 3.7% Mn and (d) 4.64% Mn (Maliyekkal et al. [132]).

Fig. 8: FTIR spectra of HMO nanoparticles (a) before and (b) after Pb(II) adsorption (Gohari et al. [133]).

made of polyethersulfone (PES) have been reported [133]. Batch adsorption experiments were conducted to study the behavior of PES/HMO membranes for Pb ions adsorption. As shown by FTIR spectra (Figure 8), peaks at 1650 and 3370 cm^{-1} represent $-\text{OH}$ functional group which are responsible for metal ion adsorption. By increasing HMO nanoparticle in the PES membrane matrix, membrane pore size tended to decrease but membrane porosity increased. The highest uptake capacity was found to be 204.1 mg/g at pH 6–8.

2.8 Cerium oxide nanoparticles

Ceria is the most common rare earth metal oxide having many industrial applications such as UV blocking and shielding materials, catalysts, polishing materials, luminescence, gas sensors, fuel cells, and adsorbents [134–136]. A suspension of CeO_2 , Fe_3O_4 and TiO_2 Nanoparticles (NPs) have been synthesized and used for ions removal [137]. Ceria nanoparticles were synthesized by oxidation of Ce^{3+} from $\text{Ce}(\text{NO}_3)_3$ salt to Ce^{4+} at basic pH using hexamethylenetetramine (HMT). Synthesized CeO_2 nanocrystals were further stabilized in aqueous solution with HMT reagent which forms double electrical layer to prevent agglomeration of nanoparticles. TEM image and XRD pattern revealed cubic fluorite structure of CeO_2 with average diameter of 12.4 nm. Batch adsorption experiments were done to evaluate adsorption mechanism and adsorption data followed pseudo-second-order kinetics (Table 5).

Tab. 5: A suspension of CeO_2 , Fe_3O_4 and TiO_2 nanoparticles.

Nanoparticles	Concentrations (mg/L)	Adsorption capacity (mg/g)
CeO_2	320	188.70
TiO_2	320	158.73
Fe_3O_4	320	82.64

3 Silica nanoparticles

Silicate materials have been studied tremendously due to their special features such as high porosity, large surface area, low-cost and environmental friendliness. Mesoporous silica nanoparticles are unique versatile materials due to their low toxicity, tunable porosity, thermal and chemical stabilities, and compatibilities with other nanoparticles and thus considered as appropriate adsorbent for removal of environmental pollutants [138]. Silicon carbide (SiC) NPs were applied as a new solid phase adsorbent for pre-concentration of Pb ions. Pb(II) ions are adsorbed on SiC NPs, eluted with nitric acid and determined by flame atomic absorption spectrometry. The solid phase extraction (SPE) conditions were optimized. The calibration graph was linear in the range of 2–150 ng/mL ($r = 0.9995$) with a detection limit of 0.4 ng/mL. The relative standard deviation (RSD) for eight measurements of 20 ng/mL of Pb ions was 1.3%. The adsorption capacity was 156.2 mg/g of Pb ions. The method was applied to determination of Pb(II) in different samples [139]. Adsorbent containing silica nanopowder entrapped in calcium alginate have been reported for Pb ions removal [140]. Alginate is a natural polymer obtained from brown algae and has been used widely in immobilization studies because of their hydrophilicity, simple preparation, and high adsorption potential for removing target contaminants. EDX analysis revealed weight percent of Si, Ca, Na and Ca compounds within entrapped silica nanopowders as 38.67, 55.14, 3.33 and 2.86 (%), respectively and data indicates that major portion of the composite is composed of Si compounds which entrapped efficiently metal cations from aqueous solution. Adsorption obeyed pseudo-second order kinetic and Langmuir model with maximum sorption capacity of 83.33 mg/g. Nanocomposites of silica modified with XG-g-PAM (xanthan gum grafted with polyacrylamide) of size 10–20 nm was also synthesized by sol gel method and used for Pb removal [141]. Xanthan gum (XG) is a linear natural polymer consists of β -(1-4)-D-glucopyranose unit having a charged trisaccharide side chain on every alternate D-glucose residue. The polyacrylamide based water insoluble copolymers have been employed widely as adsorbents for removal of heavy metals. (XG-g-PAM/SiO₂) nanocomposites shows maximum sorption capacity of 537.634 mg/g.

Different parameters were studied and it was found that maximum removal of Lead ions took place at 30 °C, pH 5.5 and contact time of 120 min with agitation speed of 80 rpm from a solution of Pb ions having concentration 400 ppm. Similarly, Peng et al. [142] reported Fe₃O₄/silica-xanthan gum (XG) nanocomposite for effective removal and recovery of Pb²⁺ from industrial wastewater. First magnetite (Fe₃O₄) nanoparticles were prepared by co-precipitation method and then XG combined with silica immobilized on the surface of Fe₃O₄ particles via sol-gel reaction process. Adsorption was studied in a batch mode and it followed pseudo second order kinetics. According to Langmuir isotherm, the maximum adsorption capacity at pH = 6 and 293 K was found to be 21.32 mg g⁻¹. Recovery of Pb ions was done by using 0.05 mol/L HCl. A tetrasulfide-functionalized silica sorbent manufactured by functionalization of silanol (SiOH) groups on the surface of silica with bis[3-(triethoxysilyl)propyl]tetrasulfide via a hydrothermal-assisted surface grafting method was adopted for the removal Pb ions from aqueous medium [143]. Adsorption studies were done at pH range 2.7–9.5 at 25 °C, time (5–60 min), concentrations (50–1000 mg/L), and temperature (25, 35 and 45 °C). Optimum pH was found to be in the range of 3.7–8.5. The Cd and Pb ions adsorbed by tetrasulfide-silica sorbent rapidly increased during the first 20 min very fast and then gradually reached to equilibrium from 30 to 50 min. Kinetics data obeyed pseudo second-order kinetic model and Langmuir isotherm model with adsorption capacities of 22.3 and 46.3 mg/g for Cd²⁺ and Pb²⁺ ions, respectively. The thermodynamic study showed that adsorption process was spontaneous and endothermic in nature. Awual et al. [144] synthesized a novel adsorbent prepared by indirect immobilization of 4-ter-octyl-4-((phenyl)diazenyl)phenol on mesoporous silica for Pb ions sensing and removal from wastewater. The adsorbent was active at neutral pH with maximum adsorption capacity 200.80 mg/g and detection limit of 0.12 g/L.

4 Carbon based nanoparticles

Activated carbon has been used widely as an adsorbent for the removal of organic and inorganic contaminants present in the water system. It has a high surface area that ranges from 500 to 1500 m²/g. The effectiveness of Activated carbon in cleaning up polluted water is due to the presence of a wide spectrum of surface functional groups and well developed porosity structure [145]. Due to development of nanotechnology Carbon based nanoparticles are employed as sorbent for pollutant removal due to their high sorption capacities and nontoxicity. Carbon based nanoparticles consists of carbon and are generally in the form of hollow spheres, or tubes. They includes: carbon nanotubes, graphene and fullerenes [146].

4.1 Carbon nanotubes

Carbon nanotubes (CNTs) are the elongated fullerenes where the walls of the tubes are hexagonal carbons which are often capped at each end. There are two types of CNTs such as multi-walled carbon nanotubes (MWCNTs) and single walled carbon nanotubes (SWCNTs). Single walled carbon nanotubes (SWCNTs) consists of a single graphene cylinder while Multi-walled carbon nanotubes (MWCNTs) consists of two or more concentric cylindrical shells of graphene sheets arranged around a central hollow core with interlayer separations as in graphite [147]. Carbon nanotubes (CNTs) due to their physical, chemical, mechanical, optoelectronic, electronic, semiconductor, and unique structural properties, have been applied widely to remove heavy metal ion pollutants in wastewater treatment. Further, to enhance the adsorption capacities, CNTs are modified by oxidation [148, 149], combining with other metal ions or metal oxides such as Al_2O_3 [150], and coupling with organic compounds [151].

Oxidized multiwalled carbon nanotubes for the removal of Pb ions from aqueous solution have been fabricated [152]. Oxidized MWCNTs have cylindrical shapes with an external diameter of 20–30 nm. Fourier transform infrared spectrum (Figure 9) of oxidized MWCNTs revealed presence of several oxygen containing functional groups on the external and internal surfaces of oxidized MWCNTs pores, which enhance the sorption capacity of oxidized MWCNTs. The experimental data of adsorption Pb(II) on oxidized MWCNTs follows the Langmuir, Freundlich and D–R sorption isotherms. MWCNT/ Al_2O_3 composites and

Fig. 9: Fourier transformed infrared spectra of oxidized MWCNTs (Xu et al. [152]).

MWCNTs/MnO₂ composites [113, 153] have been fabricated for Pb ions removal from industrial waste water. Maximum removal of Pb ions was found to be at a pH 7–9 for MWCNTs/MnO₂, while alumina-coated carbon nanotubes show an effective removal of Pb ions at pH 3–7. As SWCNTs show the most adsorption capability for Pb ions, so single-walled carbon nanotubes-doped walnut shell composite (SWCNTs/WSH) have been synthesized by immobilization of SWCNT particles on the surface of walnut shell. Walnut shell due to its porous structures, nontoxic nature, low cost, excellent mechanical and physical properties, and its widespread availability, can serve as an ideal immobilizing nanomaterial for heavy metal adsorption in environmental protection. Parameters such as solution pH, contact time, metal concentration, adsorbent dose, and temperature, were studied to optimize conditions and maximum Lead uptake was found to be 185.2 mg/g [154]. Ordered mesoporous carbons (OMCs) due to large surface area, large pore volume, unique pore size, and thermal and physicochemical stability are promising agents for pollutant removal. To enhance their functionality, acid-base stability, catalytic and hydrophilic properties, transition metal nanoparticles such as Co, Fe and Pt or nonmetal atoms of N and P are incorporated onto amorphous OMCs. The introduction of nonmetal heteroatom of N elements boosts their chelation with heavy metals or organic pollutants. Yang et al. [155] reported nitrogen-functionalized magnetic ordered mesoporous carbon (N-Fe/OMC) to investigate the removal behaviors of Pb ions and phenol from wastewater. It was assumed that, Pb ions was removed by direct adsorption onto the ordered mesoporous carbon pores on N-Fe/OMC.

4.2 Graphene

Graphene is a single or several atomic layered graphites having hexagonally bonded and sp² hybridized carbons. Graphene has tremendous applications in many technological fields, such as electronics, supercapacitors, energy storage materials, quantum dots, resonators, solar cells, and sensors. While large specific surface area of 2630 m²/g makes graphene nanosheets excellent candidates for adsorption technologies. Further, graphene nanosheets could also be used as substrates for decorating the surfaces of nanoparticles, to enhance their adsorption capacities. Various methods have been developed to prepare graphene nanosheets such as chemical vapor deposition (CVD), pressurized oxidation and multiplex reduction, epitaxial growth, micromechanical cleavage, ionic-liquid-assisted electrochemical synthesis [156–159]. Guo et al. [160] synthesized a high performance sorbent via compositing ferroferric oxide with graphene sheets (Fe₃O₄-GS) and employed for the removal of Pb ions from water system. According to the N₂ sorption analysis the BJH desorption cumulative volume of pores is

0.3546 cm³/g and BET surface area of Fe₃O₄-GS was found to be 62.43 m²/g, while isotherm is of type IV and display the H3 hysteresis loop. Kinetic data followed pseudo second order equation and Freundlich model with maximum adsorption capacities of 27.95 mg/g of Pb ions. The sorbent was magnetically separable and sorption mechanism took place by ion exchange or chelation method. An oligomer-linked graphene oxide sorbents has been prepared by simple cross linking reaction of poly 3-aminopropyltriethoxysilane (PAS) oligomers with graphene oxide (GO) sheets [161]. The adsorbent removes Pb(II) selectively at 303 K with maximum adsorption capacity of 312.5 mg/g within a wide range of pH 4.0–7.0. Poly(o-phenylenediamine)/reduced graphene oxide (PoPD/RGO) composite nanosheets have been prepared [162], and employed as an adsorbent for effective removal of lead ions showing maximum adsorption capacity of 228 mg/g.

5 Host supported nanoparticles

5.1 Polymer supported ion exchangers

In recent years, porous polymeric cation/anion exchangers were employed as host materials for metal oxides loading. Commonly, D-001 (a polystyrenesulfone cation exchanger) was selected as a support material because of the Donnan membrane effect caused by negatively charged sulfonic acid groups bound on the exchanger matrix which facilitates and enhance preconcentration and permeation of the trace target metal ion [163]. By impregnating cation-exchange resin D-001 with hydrated Fe(III) oxide (HFO) nanoparticles, titanium phosphate (TiP) nanoparticles, and hydrous manganese dioxide (HMO) nanoparticles, new sorbents HFO-001 [164] (Figure 10), TiP-001 [119] and HMO-001 [163] have been developed. Adsorption mechanism was pH dependent and optimum pH for all three sorbent was found to be within 4–5. HMO-001 exhibited more favorable lead adsorption with maximum adsorption capacity of 395 mg/g.

5.2 Natural polymer based nanoparticles

Chitosan a biopolymer is a de-acetylated product of chitin obtained from the exoskeleton of shellfish. It is a linear polymer of β -(1, 4)-linked glucosamine units, having reactive amino and hydroxyl groups as chelation sites. These sites help in chelation of heavy metal ions with chitosan and thus chitosan is a suitable material to be used in heavy metal removal [165]. Chitosan nanoparticles synthesized by ionic gelation of chitosan and tripolyphosphate (CS-TPP) with size ranges from 40 to 100 nm for Lead removal from polluted water have been reported

Fig. 10: HFO-001 (a) TEM micrograph (b) Schematic illustration of HFO-001 spherical beads (Pan et al. [164]).

[166]. Adsorption data well represented by Langmuir isotherm model and maximum adsorption capacity was about 398 mg/g. By polymerizing methacrylic acid (MAA) with chitosan solution, Chitosan–MAA nanoparticles (CS–MAA) of size 10–70 nm have been reported as an adsorbent for Pb ions from aqueous solution [167]. The maximum adsorption capacity obtained by the Langmuir isotherm was found to be as 11.30 mg/g for Pb ions. Calcium phosphates, such as hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), have been employed as a sorbent for Pb ions removal now a days due to their high thermodynamic stability which did not allow release of Pb ions into the environment. Hence hydroxyapatite (HAP) based sorbents have been prepared by alkaline residue obtained from Soda Ash plants containing calcium sulfate, calcium carbonate and other substances [168]. HAP shows 8.9 times higher adsorption capacity for Pb ions than activated carbon. Maximum adsorption capacity obtained by Langmuir isotherm was found to be 1429 mg/g, and kinetics of adsorption obeyed pseudo second order kinetic model. Similarly, by incorporating hydroxyapatite into chitosan solution, chitosan/Fe-substituted

hydroxyapatite nanocomposite beads have been prepared for the removal of Pb ions from aqueous medium [169]. Maximum adsorption capacity for Pb ions was recorded to be 1385 mg/g, respectively and adsorption agreed with Langmuir adsorption model. In another study, nanodiamond/MoS₂ nanorod composite was prepared by hydrothermal method and its application as adsorbent Pb ions was checked. The sorption capacity of synthesized adsorbent for Pb ions was 19.87 mg/g [170].

5.3 Natural diatomaceous earth based nanoparticles

Natural diatomaceous earth (diatomite, DE), is a fossilized skeletal remains of aquatic diatoms, a unicellular planktonic algae, and mainly composed of amorphous hydrated silica (SiO₂·nH₂O). It has a porous structure and finds many applications in adsorption of pollutants, catalyst support, drug delivery carrier or template to fabricate porous materials [171, 172]. Li et al. [171] synthesized a new adsorbent via modifying surface of diatomaceous earth by amorphous MnO₂. The experimental procedure involves carbonization of surface of DE by reaction with glucose and then MnO₂ are grown in the pores of DE surface by Eq. 3.

Adsorption of Pb ions on modified DE increased 6 times than unmodified DE which is due to the incorporation of nanocrystals of MnO₂ having large surface area to volume ratio. Adsorption data followed both Langmuir and Freundlich model well. Similarly, Alijani et al. [172] reported magnetic multiwalled carbon nanotubes/diatomite earth nanocomposites. First, diatomite support was prepared by using aluminum nitrate and diatomite via impregnation method and then CNTs were synthesized on the surface of diatomite as a substrate by chemical vapor deposition (CVD) of methane. The prepared composite was activated with HNO₃ solution and used as a sorbent for the removal of lead ions from aqueous solution. SEM image showed spherical-shaped particles having a pore size of 40–60 nm. Diatomite-CNTs composites have specific surface area of 15.26 m²/g and the pore volume of 0.055 cm³/g as observed by N₂-BET method and showed the maximum adsorption capacity for pB ions of 60 mg/g within 10 min of contact time. The overview of literature revealed that smart materials (metal oxides, doped material and composites) are efficient materials for the adsorption of Pb from aqueous medium (Table 6). Under the current scenario of environmental pollution due to anthropogenic contamination of toxic material to the environment [7, 17–19, 21, 40, 174–201], there is need to adopt the smart materials for the efficient remediation of heavy metal ions.

Tab. 6: The adsorption capacities and types of nanomaterial used for Pb ions adsorption.

S. No.	Nanoparticles	Adsorption capacity (mg/g)	References
1	$\gamma\text{-Fe}_2\text{O}_3$	50	[59]
2	$\text{Fe}_3\text{O}_4\text{@SA-Zr}$	333.33	[173]
3	$\gamma\text{-Fe}_2\text{O}_3$	71.42	[61]
4	Fe_3O_4	79.3	[63]
5	Mixed magnetite–hematite	617.3	[64]
6	Fe_3O_4	36	[68]
7	Fe_3O_4	76.8	[69]
8	Fe_3O_4	46.18	[70]
9	$\gamma\text{-FeOOH}$	527.944	[71]
10	$\alpha\text{-FeOOH}$	820.165	[71]
11	G-nZVI	97	[74]
12	AF- Fe_3O_4	369	[81]
13	$\text{Fe}_3\text{O}_4\text{-DMSA}$	(99) ^a	[83]
14	$\text{NH}_2\text{-HCMSSs}$	194.3	[84]
15	$\text{CoFe}_2\text{O}_4\text{-NH}_2$	140.1	[88]
16	NiO (25 nm)	62.5	[90]
17	NiO (28 nm)	625	[91]
18	NiO (38-130 nm)	50.505	[92]
19	CuO	160.7	[95]
20	ZnO	26.109	[102]
21	Si–OH & Al–OH	100	[63]
22	TiO ₂	132.458	[130]
23	Ti-AM	476.19	[129]
24	MnOs	80.1	[132]
25	Hydrated MnOs	204.1	[133]
26	Si	83.3	[140]
27	XG-g-PAM/SiO ₂	537.634	[141]
28	$\text{Fe}_3\text{O}_4\text{/silica-XG}$	21.32	[142]
29	SiOH	46.3	[143]
30	Si	200.80	[144]
31	SWCNTs/WSH	185.2	[154]
32	$\text{Fe}_3\text{O}_4\text{-GS}$	27.95	[160]
33	PAS-GO	312.5	[161]
34	PoPD/RGO	228	[162]
35	HFO-001, TiP-001, HMO-001	395	[119, 163, 164]
36	CS-TPP	398	[166]
37	CS-MAA	11.30	[167]
38	HAP	1429	[168]
39	CS/Fe-HAP	1385	[169]
40	SiO ₂ -nH ₂ O	60	[171]
41	$\gamma\text{-Fe}_2\text{O}_3$	68.9	[65]
42	SiC	156.2	[139]
43	Fe_3O_4	197.02	[66]
44	Zincon–Si–MNPs	84–104 ^a	[67]
45	MoS ₂	19.87	[170]

^a%,.

6 Conclusion

Recent advances in nanoscale science and engineering providing new opportunities to develop more cost-effective and environmental friendly technologies for the treatment of wastewater. To date, a number of smart materials have been explored as highly efficient adsorbents for removal of Pb(II) ions from aqueous medium. The oxides, doped, nanocomposites of Fe, Ti, Zn, SiO₂, SiC, Mo, Co, Ni, Zr, Mn, Si, S, Al, Cu, Ce, graphene, CNTs have been successfully employed for Pb(II) ions and this efficiency was due to enhanced physicochemical properties, affinity, unique structure and surface characteristics smart materials, which emerged as attractive for wastewater purification contain Pb(II) ions.

References

1. M. Saeed, A. Mansha, M. Hamayun, A. Ahmad, A. Ulhaq, M. Ashfaq, *Z. Phys. Chem.* **232** (2018) 359.
2. A. Shanmugalingam, A. Murugesan, *Z. Phys. Chem.* **232** (2018) 489.
3. P. Indhumathi, S. Sathiyaraj, J. P. Koelmel, S. U. Shoba, C. Jayabalakrishnan, M. Saravanabhavan, *Z. Phys. Chem.* **232** (2018) 527.
4. M. Saeed, M. Siddique, M. Usman, A. ul Haq, S. G. Khan, H. A. Raoof, *Z. Phys. Chem.* **231** (2017) 1559.
5. A. H. Abubakar Siddique, S. R. Khan, A. Inayat, A. Nazir, M. Iqbal, *Chem. Int.* **4** (2018) 1.
6. A. Babarinde, K. Ogundipe, K. T. Sangosanya, B. D. Akintola, A.-O. Elizabeth Hassan, *Chem. Int.* **2** (2016) 89.
7. A. Babarinde, G. O. Onyiaocha, *Chem. Int.* **2** (2016) 37.
8. N. K. Benabdallah, D. Harrache, A. Mir, M. de la Guardia, F.-Z. Benhachem, *Chem. Int.* **3** (2017) 220.
9. A. M. Engida, B. S. Chandravanshi, *Chem. Int.* **3** (2017) 213.
10. M. Iqbal, R. A. Khera, *Chem. Int.* **1** (2015) 157b.
11. K. Ramesh, A. Rajappa, V. Nandhakumar, *Z. Phys. Chem.* **231** (2017) 1057.
12. K. Inouye, I. Nagumo, K. Kaneko, T. Ishikawa, *Z. Phys. Chem.* **131** (1982) 199.
13. P. Behr, A. Terziyski, R. Zellner, *Z. Phys. Chem.* **218** (2004) 1307.
14. Q. Manzoor, R. Nadeem, M. Iqbal, R. Saeed, T. M. Ansari, *Bioresourc. Technol.* **132** (2013) 446.
15. R. Nadeem, Q. Manzoor, M. Iqbal, J. Nisar, *J. Ind. Eng. Chem.* **35** (2016) 185.
16. M. Kumari, C. U. Pittman, D. Mohan, *J. Colloid Interface Sci.* **442** (2015) 120.
17. M. Fazal-ur-Rehman, *Chem. Int.* **4** (2018) 109.
18. S. Ghezali, A. Mahdad-Benzerdjeb, M. Ameri, A. Z. Bouyakoub, *Chem. Int.* **4** (2018) 24.
19. N. E. Ibisi, C. A. Asoluka, *Chem. Int.* **4** (2018) 52.
20. K. Legrouri, E. Khouya, H. Hannache, M. El Hartti, M. Ezzine, R. Naslain, *Chem. Int.* **3** (2017) 301.
21. K. K. Mehta, R. S. Chandra, D. R. Mehta, M. M. Maisuria, *Chem. Int.* **4** (2018) 33.
22. K. D. Ogundipe, A. Babarinde, *Chem. Int.* **3** (2017) 135.

23. J. Ruparelia, S. Duttagupta, A. Chatterjee, S. Mukherji, *Desalination* **232** (2008) 145.
24. X. Du, Y. Duan, J. Zhang, G. Mi, *Z. Phys. Chem.* **232** (2018) 431.
25. M. Kumar, H. Chauhan, B. Satpati, S. Deka, *Z. Phys. Chem.* **233** (2018) 85.
26. T. Cao, F. Zhao, Z. Da, F. Qiu, D. Yang, Y. Guan, G. Cao, Z. Zhao, J. Li, X. Guo, *Z. Phys. Chem.* **231** (2017) 1797.
27. L. Wu, J. Lan, S. Wang, J. Zhu, *Z. Phys. Chem.* **231** (2017) 1525.
28. N. Xiang, J. Huang, H. Zhao, C. Liu, X. Liu, *Z. Phys. Chem.* **230** (2016) 1711.
29. D. C. Tranca, G. Seifert, *Z. Phys. Chem.* **230** (2016) 791.
30. C. Chakravarty, P. Ghosh, B. Mandal, P. Sarkar, *Z. Phys. Chem.* **230** (2016) 777.
31. N. Promthong, N. Nunthaboot, W. Banchob, *Z. Phys. Chem.* **230** (2016) 267.
32. L. Huang, K. E. Gubbins, *Z. Phys. Chem.* **229** (2015) 1211.
33. R. Whitesides, M. Frenklach, *Z. Phys. Chem.* **229** (2015) 597.
34. M. Höltig, C. Ruhmlied, C. Strelow, T. Kipp, A. Mews, *Z. Phys. Chem.* **229** (2015) 301.
35. H. Vieker, A. Beyer, H. Blank, D. H. Weber, D. Gerthsen, A. Götzhäuser, *Z. Phys. Chem.* **225** (2011) 1433.
36. A. Goriachko, H. Over, *Z. Phys. Chem.* **223** (2009) 157.
37. D. Guerard, N.-E. Elalem, L. Elansari, J.-F. Mareche, E. Mcrae, H. Estrade-Szwarcckopf, B. Rousseau, P. Lauginie, J. Conard, *Z. Phys. Chem.* **164** (1989) 1579.
38. T. Kawano, H. Imai, *Colloid. Surf. A: Physicochem. Eng. Aspect.* **319** (2008) 130.
39. O. U. Igwe, F. Nwamezie, *Chem. Int.* **4** (2018) 60.
40. M. Arshad, A. Qayyum, G. Abbas, R. Haider, M. Iqbal, A. Nazir, *J. Mol. Liq.* **260** (2018) 272.
41. A. Ashar, M. Iqbal, I. A. Bhatti, M. Z. Ahmad, K. Qureshi, J. Nisar, I. H. Bukhari, *J. Alloy. Comp.* **678** (2016) 126.
42. Y. Liu, M. Tourbin, S. Lachaize, P. Guiraud, *Powder Technol.* **255** (2014) 149.
43. S. Thatai, P. Khurana, J. Boken, S. Prasad, D. Kumar, *Microchem. J.* **116** (2014) 62.
44. T. Pradeep, *Thin Solid Film* **517** (2009) 6441.
45. B. Pan, B. Pan, W. Zhang, L. Lv, Q. Zhang, S. Zheng, *Chem. Eng. J.* **151** (2009) 19.
46. J. E. Van Benschoten, B. E. Reed, M. R. Matsumoto, P. McGarvey, *Water Environ. Res.* **66** (1994) 168.
47. J. A. Coston, C. C. Fuller, J. A. Davis, *Geochim. Cosmochim. Acta.* **59** (1995) 3535.
48. A. Agrawal, K. Sahu, *J. Hazard. Mater.* **137** (2006) 915.
49. A. Henglein, *Chem. Rev.* **89** (1989) 1861.
50. M. A. El-Sayed, *Account. Chem. Res.* **34** (2001) 257.
51. E. Deliyanni, E. Peleka, K. Matis, *J. Hazard. Mater.* **172** (2009) 550.
52. L. Li, M. Fan, R. C. Brown, J. Van Leeuwen, J. Wang, W. Wang, Y. Song, P. Zhang, *Crit. Rev. Environ. Sci. Technol.* **36** (2006) 405.
53. J. Park, K. An, Y. Hwang, J.-G. Park, H.-J. Noh, J.-Y. Kim, J.-H. Park, N.-M. Hwang, T. Hyeon, *Nat. Mater.* **3** (2004) 891.
54. A. L. Willis, N. J. Turro, S. O'Brien, *Chem. Mater.* **17** (2005) 5970.
55. X. Wang, J. Zhuang, Q. Peng, Y. Li, *Nature* **437** (2005) 121.
56. O. V. Kharissova, H. R. Dias, B. I. Kharisov, B. O. Pérez, V. M. J. Pérez, *Trend. Biotechnol.* **31** (2013) 240.
57. M. Hua, S. Zhang, B. Pan, W. Zhang, L. Lv, Q. Zhang, *J. Hazard. Mater.* **211** (2012) 317.
58. S. Laurent, D. Forge, M. Port, A. Roch, C. Robic, L. Vander Elst, R. N. Muller, *Chem. Rev.* **108** (2008) 2064.
59. A. Idris, N. S. M. Ismail, N. Hassan, E. Misran, A.-F. Ngomsik, *J. Ind. Eng. Chem.* **18** (2012) 1582.

60. X. Li, Y. Qi, Y. Li, Y. Zhang, X. He, Y. Wang, *Bioresour. Technol.* **142** (2013) 611.
61. A. Roy, J. Bhattacharya, *Chem. Eng. J.* **211** (2012) 493.
62. T. Wang, X. Jin, Z. Chen, M. Megharaj, R. Naidu, *J. Ind. Eng. Chem.* **20** (2014) 3543.
63. T. Madrakian, A. Afkhami, M. Ahmadi, *Chemosphere* **90** (2013) 542.
64. M. Ahmed, S. Ali, S. El-Dek, A. Galal, *Mater. Sci. Eng. B.* **178** (2013) 744.
65. S. Rajput, L. P. Singh, C. U. Pittman Jr, D. Mohan, *J. Colloid Interface Sci.* **492** (2017) 176.
66. S. Tiwari, A. Hasan, L. M. Pandey, *J. Environ. Chem. Eng.* **5** (2017) 442.
67. H.-M. Jiang, Z.-P. Yan, Y. Zhao, X. Hu, H.-Z. Lian, *Talanta* **94** (2012) 251.
68. N. N. Nassar, *J. Hazard. Mater.* **184** (2010) 538.
69. F. Ge, M.-M. Li, H. Ye, B.-X. Zhao, *J. Hazard. Mater.* **211** (2012) 366.
70. S. Venkateswarlu, B. N. Kumar, B. Prathima, Y. SubbaRao, N. V. V. Jyothi, *Arab. J. Chem.* (2014). <https://doi.org/10.1016/j.arabjc.2014.09.006>.
71. S. Rahimi, R. M. Moattari, L. Rajabi, A. A. Derakhshan, M. Keyhani, *J. Ind. Eng. Chem.* **23** (2015) 33.
72. X. Zhang, S. Lin, X.-Q. Lu, Z.-L. Chen, *Chem. Eng. J.* **163** (2010) 243.
73. A. R. Esfahani, A. F. Firouzi, G. Sayyad, A. Kiasat, *Res. J. Environ. Earth Sci.* **5** (2013) 548.
74. H. Jabeen, K. C. Kemp, V. Chandra, *J. Environ. Manage.* **130** (2013) 429.
75. H. W. Edwards, R. P. Petersen, *Phys. Rev.* **50** (1936) 871.
76. J. Wang, S. Zheng, Y. Shao, J. Liu, Z. Xu, D. Zhu, *J. Colloid Interface Sci.* **349** (2010) 293.
77. T. Madrakian, A. Afkhami, M. A. Zolfigol, M. Ahmadi, N. Koukabi, *Nano-Micro Lett.* **4** (2012) 57.
78. X. Fu, X. Chen, J. Wang, J. Liu, *Micropor. Mesopor. Mater.* **139** (2011) 8.
79. O. Hakami, Y. Zhang, C. J. Banks, *Water Res.* **46** (2012) 3913.
80. H. Qu, D. Caruntu, H. Liu, C. J. O'Connor, *Langmuir* **27** (2011) 2271.
81. X. Xin, Q. Wei, J. Yang, L. Yan, R. Feng, G. Chen, B. Du, H. Li, *Chem. Eng. J.* **184** (2012) 132.
82. B. Guo, F. Deng, Y. Zhao, X. Luo, S. Luo, C. Au, *Appl. Surf. Sci.* **292** (2014) 438.
83. W. Yantasee, C. L. Warner, T. Sangvanich, R. S. Addleman, T. G. Carter, R. J. Wiacek, G. E. Fryxell, C. Timchalk, M. G. Warner, *Environ. Sci. Technol.* **41** (2007) 5114.
84. A. M. El-Toni, M. A. Habila, M. A. Ibrahim, J. P. Labis, Z. A. AlOthman, *Chem. Eng. J.* **251** (2014) 441.
85. J. Hu, I. M. Lo, G. Chen, *Separat. Purificat. Technol.* **56** (2007) 249.
86. Y. Ren, N. Li, J. Feng, T. Luan, Q. Wen, Z. Li, M. Zhang, *J. Colloid Interface Sci.* **367** (2012) 415.
87. V. Andal, G. Buvaeswari, *Int. J. Res. Eng. Technol.* **3** (2014) 475.
88. L. Zhou, L. Ji, P.-C. Ma, Y. Shao, H. Zhang, W. Gao, Y. Li, *J. Hazard. Mater.* **265** (2014) 104.
89. A. Barakat, M. Al-Noaimi, M. Suleiman, A. S. Aldwayyan, B. Hammouti, T. B. Hadda, S. F. Haddad, A. Boshuala, I. Warad, *Int. J. Mol. Sci.* **14** (2013) 23941.
90. Z. M. Khoshhesab, Z. Hooshyar, M. Sarfaraz, *Synth. React. Inorg. Metal-Org. Nano-Metal Chem.* **41** (2011) 1046.
91. T. Sheela, Y. A. Nayaka, *Chem. Eng. J.* **191** (2012) 123.
92. M. Ossman, *Int. J. Environ. Res.* **8** (2014) 741.
93. M. Ahamed, H. A. Alhadlaq, M. Khan, P. Karuppiyah, N. A. Al-Dhabi, *J. Nanomater.* **2014** (2014) 17.
94. A. Farghali, M. Bahgat, A. E. Allah, M. Khedr, Beni-Suef Uni. *J. Basic Appl. Sci.* **2** (2013) 61.
95. K. Y. Kumar, H. Muralidhara, Y. Nayaka, H. Hanumanthappa, M. Veena, S. K. Kumar, *Separat. Sci. Technol.* **49** (2014) 2389.

96. P. K. Raul, S. Senapati, A. K. Sahoo, I. M. Umlong, R. R. Devi, A. J. Thakur, V. Veer, *RSC Adv.* **4** (2014) 40580.
97. X. Wang, C. J. Summers, Z. L. Wang, *Nano Lett.* **4** (2004) 423.
98. Z. L. Wang, J. Song, *Sci.* **312** (2006) 242.
99. R. Yakimova, G. Steinhoff, R. Petoral, C. Vahlberg, V. Khranovskyy, G. Yazdi, K. Uvdal, A. L. Spetz, *Biosen. Bioelectron.* **22** (2007) 2780.
100. X. Wang, W. Cai, Y. Lin, G. Wang, C. Liang, *J. Mater. Chem.* **20** (2010) 8582.
101. K. Y. Kumar, H. Muralidhara, Y. A. Nayaka, J. Balasubramanyam, H. Hanumanthappa, *Powder Technol.* **239** (2013) 208.
102. V. Venkatesham, G. Madhu, S. Satyanarayana, H. Preetham, *Proc. Eng.* **51** (2013) 308.
103. J. Li, Y. Shi, Y. Cai, S. Mou, G. Jiang, *Chem. Eng. J.* **140** (2008) 214.
104. M. Hiraide, J. Iwaswa, S. Hirmatsu, H. Kawaguchi, *Anal. Sci.* **11** (1995) 611.
105. L. Zhang, T. Huang, M. Zhang, X. Guo, Z. Yuan, *J. Hazard. Mater.* **157** (2008) 352.
106. Y. Sharma, V. Srivastava, S. Upadhyay, C. Weng, *Ind. Eng. Chem. Res.* **47** (2008) 8095.
107. A. R. Türker, *Clean-Soil, Air, Water.* **35** (2007) 548.
108. M. Hiraide, M.-H. Sorouradin, H. Kawaguchi, *Anal. Sci.* **10** (1994) 125.
109. J. Manzoori, M. Sorouraddin, A. á. H. Shabani, *J. Anal. Atom. Spectromet.* **13** (1998) 305.
110. M. Ghaedi, M. Reza khani, S. Khodadoust, K. Niknam, M. Soylak, *Sci. World J.* **2012** (2012) 1.
111. S. Dadfarnia, A. H. Shabani, H. D. Shirie, *Bulletin-Korean Chem. Soc.* **23** (2002) 545.
112. S. Dadfarnia, A. M. H. Shabani, E. Kamranzadeh, *Talanta* **79** (2009) 1061.
113. V. K. Gupta, S. Agarwal, T. A. Saleh, *J. Hazar. Mater.* **185** (2011) 17.
114. M. Medina, J. Tapia, S. Pacheco, M. Espinosa, R. Rodriguez, *J. Non-Cryst. Solid.* **356** (2010) 383.
115. A. Afkhami, M. Saber-Tehrani, H. Bagheri, *J. Hazard. Mater.* **181** (2010) 836.
116. O. Carp, C. L. Huisman, A. Reller, *Prog. Solid State Chem.* **32** (2004) 33.
117. J.-C. Lee, M.-S. Kim, B.-W. Kim, *Water Res.* **36** (2002) 1776.
118. M.-S. Kim, K.-M. Hong, J. G. Chung, *Water Res.* **37** (2003) 3524.
119. K. Jia, B. Pan, L. Lv, Q. Zhang, X. Wang, B. Pan, W. Zhang, *J. Colloid Interface Sci.* **331** (2009) 453.
120. Y. C. Nah, I. Paramasivam, P. Schmuki, *ChemPhysChem.* **11** (2010) 2698.
121. Z. Su, W. Zhou, *J. Mater. Chem.* **21** (2011) 8955.
122. P. Roy, S. Berger, P. Schmuki, *Angewandte Chem. Int. Edit.* **50** (2011) 2904.
123. H.-i. Kim, J. Kim, W. Kim, W. Choi, *J. Phys. Chem. C.* **115** (2011) 9797.
124. M. Kitano, M. Matsuoka, M. Ueshima, M. Anpo, *Appl. Catal. A: Gen.* **325** (2007) 1.
125. A. E. R. Mohamed, S. Rohani, *Energy Environ. Sci.* **4** (2011) 1065.
126. X. Chen, S. S. Mao, *Chem. Rev.* **107** (2007) 2891.
127. S. Sreekantan, S. M. Zaki, C. W. Lai, T. W. Tzu, *Mater. Sci. Semiconduct. Proces.* **26** (2014) 620.
128. A. K. Sharma, B.-K. Lee, *J. Environ. Manage.* **128** (2013) 787.
129. Z. Ö. Kocabaş-Ataklı, Y. Yürüm, *Chem. Eng. J.* **225** (2013) 625.
130. F. Rashidi, R. S. Sarabi, Z. Ghasemi, A. Seif, *Superlattice. Microstruct.* **48** (2010) 577.
131. H.-Q. Wang, G.-f. Yang, Q.-Y. Li, X.-X. Zhong, F.-P. Wang, Z.-S. Li, Y.-h. Li, *New J. Chem.* **35** (2011) 469.
132. S. M. Maliyekkal, K. P. Lisha, T. Pradeep, *J. Hazard. Mater.* **181** (2010) 986.
133. R. J. Gohari, W. J. Lau, T. Matsuura, E. Halakoo, A. F. Ismail, *Separat. Purificat. Technol.* **120** (2013) 59.

134. S. Yabe, T. Sato, J. Solid Stat. Chem. **171** (2003) 7.
135. L. Wang, K. Zhang, Z. Song, S. Feng, Appl. Surf. Sci. **253** (2007) 4951.
136. E. L. Brosha, R. Mukundan, D. R. Brown, F. H. Garzon, J. Visser, Solid Stat. Ionic. **148** (2002) 61.
137. S. Recillas, A. Garcia, E. Gonzalez, E. Casals, V. Puentes, A. Sanchez, X. Font, Desalination **277** (2011) 213.
138. A. Stein, B. J. Melde, R. C. Schroden, Adv. Mater. **12** (2000) 1403.
139. N. Pourreza, T. Naghdi, J. Ind. Eng. Chem. **20** (2014) 3502.
140. R. D. C. Soltani, G. S. Khorramabadi, A. Khataee, S. Jorfi, J. Taiwan Instit. Chem. Eng. **45** (2014) 973.
141. S. Ghorai, A. Sinhamahapatra, A. Sarkar, A. B. Panda, S. Pal, Bioresourc. Technol. **119** (2012) 181.
142. X. Peng, F. Xu, W. Zhang, J. Wang, C. Zeng, M. Niu, E. Chmielewská, Colloid. Surf. A: Physicochem. Eng. Aspect. **443** (2014) 27.
143. H.-T. Fan, J.-B. Wu, X.-L. Fan, D.-S. Zhang, Z.-J. Su, F. Yan, T. Sun, Chem. Eng. J. **198** (2012) 355.
144. M. R. Awual, M. M. Hasan, A. Shahat, Sensor. Actuator. B: Chem. **203** (2014) 854.
145. Q.-S. Liu, T. Zheng, P. Wang, J.-P. Jiang, N. Li, Chem. Eng. J. **157** (2010) 348.
146. X. Wang, Y. Guo, L. Yang, M. Han, J. Zhao, X. Cheng, J. Environ. Anal. Toxicol. **2** (2012) 1000154.
147. X.-L. Xie, Y.-W. Mai, X.-P. Zhou, Mater. Sci. Eng. R: Report. **49** (2005) 89.
148. G. P. Rao, C. Lu, F. Su, Separat. Purificat. Technol. **58** (2007) 224.
149. D. Afzali, R. Jamshidi, S. Ghaseminezhad, Z. Afzali, Arab. J. Chem. **5** (2012) 461.
150. X. Zhao, Q. Jia, N. Song, W. Zhou, Y. Li, J. Chem. Eng. Data. **55** (2010) 4428.
151. S. A. Kosa, G. Al-Zhrani, M. A. Salam, Chem. Eng. J. **181** (2012) 159.
152. D. Xu, X. Tan, C. Chen, X. Wang, J. Hazard. Mater. **154** (2008) 407.
153. M. A. Salam, Colloid. Surf. A: Physicochem. Eng. Aspect. **419** (2013) 69.
154. S. Saadat, A. Karimi-Jashni, M. M. Doroodmand, J. Environ. Chem. Eng. **2** (2014) 2059.
155. G. Yang, L. Tang, G. Zeng, Y. Cai, J. Tang, Y. Pang, Y. Zhou, Y. Liu, J. Wang, S. Zhang, Chem. Eng. J. **259** (2015) 854.
156. J. Chang, M. Jin, F. Yao, T. H. Kim, V. T. Le, H. Yue, F. Gunes, B. Li, A. Ghosh, S. Xie, Adv. Funct. Mater. **23** (2013) 5074.
157. J.-G. Yu, L.-Y. Yu, H. Yang, Q. Liu, X.-H. Chen, X.-Y. Jiang, X.-Q. Chen, F.-P. Jiao, Sci. Total Environ. **502** (2015) 70.
158. G. Wang, J. Yang, J. Park, X. Gou, B. Wang, H. Liu, J. Yao, J. Phys. Chem. C. **112** (2008) 8192.
159. H.-L. Guo, X.-F. Wang, Q.-Y. Qian, F.-B. Wang, X.-H. Xia, ACS Nano. **3** (2009) 2653.
160. X. Guo, B. Du, Q. Wei, J. Yang, L. Hu, L. Yan, W. Xu, J. Hazard. Mater. **278** (2014) 211.
161. S. Luo, X. Xu, G. Zhou, C. Liu, Y. Tang, Y. Liu, J. Hazard. Mater. **274** (2014) 145.
162. L. Yang, Z. Li, G. Nie, Z. Zhang, X. Lu, C. Wang, Appl. Surf. Sci. **307** (2014) 601.
163. Q. Su, B. Pan, B. Pan, Q. Zhang, W. Zhang, L. Lv, X. Wang, J. Wu, Q. Zhang, Sci. Total Environ. **407** (2009) 5471.
164. B. Pan, H. Qiu, B. Pan, G. Nie, L. Xiao, L. Lv, W. Zhang, Q. Zhang, S. Zheng, Water Res. **44** (2010) 815.
165. B. Krajewska, Separat. Purificat. Technol. **41** (2005) 305.
166. L. Qi, Z. Xu, Colloid. Surf. A: Physicochem. Eng. Aspect. **251** (2004) 183.
167. A. Heidari, H. Younesi, Z. Mehraban, H. Heikkinen, Int. J. Biol. Macromol. **61** (2013) 251.

168. Y. Yan, Y. Wang, X. Sun, J. Li, J. Shen, W. Han, X. Liu, L. Wang, *Appl. Surf. Sci.* **317** (2014) 946.
169. S. Saber-Samandari, S. Saber-Samandari, N. Nezafati, K. Yahya, *J. Environ. Manage.* **146** (2014) 481.
170. N. Baghban, E. Yilmaz, M. Soylak, *J. Mol. Liq.* **234** (2017) 260.
171. S. Li, D. Li, F. Su, Y. Ren, G. Qin, *Appl. Surf. Sci.* **317** (2014) 724.
172. H. Alijani, M. H. Beyki, Z. Shariatinia, M. Bayat, F. Shemirani, *Chem. Eng. J.* **253** (2014) 456.
173. T.-T. Li, Y.-G. Liu, Q.-Q. Peng, X.-J. Hu, T. Liao, H. Wang, M. Lu, *Chem. Eng. J.* **214** (2013) 189.
174. M. Abbas, M. Adil, S. Ehtisham-ul-Haque, B. Munir, M. Yameen, A. Ghaffar, G. A. Shar, M. A. Tahir, M. Iqbal, *Sci. Total Environ.* **626** (2018) 1295.
175. K. Aftab, K. Akhtar, A. Kausar, S. Khaliq, N. Nisar, H. Umbreen, M. Iqbal, *J. Photochem. Photobiol. B.* **175** (2017) 182.
176. M. Z. Ahamd, S. Ehtisham-ul-Haque, N. Nisar, K. Qureshi, A. Ghaffar, M. Abbas, J. Nisar, M. Iqbal, *Water Sci. Technol.* **76** (2017) 323.
177. M. Z. Ahmad, K. Qureshi, I. A. Bhatti, M. Zahid, J. Nisar, M. Iqbal, M. Abbas, *Mater. Res. Bull.* **100** (2018) 120.
178. M. Akram, H. N. Bhatti, M. Iqbal, S. Noreen, S. Sadaf, *J. Environ. Chem. Eng.* **5** (2017) 400.
179. M. Arshad, A. Qayyum, G. A. Shar, G. A. Soomro, A. Nazir, B. Munir, M. Iqbal, *J. Photochem. Photobiol. B.* **185** (2018) 176.
180. A. Aslam, S. R. Thomas-Hall, M. Manzoor, F. Jabeen, M. Iqbal, Q. uz Zaman, P. M. Schenk, M. A. Tahir, *J. Photochem. Photobiol. B.* **179** (2018) 126.
181. I. Bibi, N. Nazar, M. Iqbal, S. Kamal, H. Nawaz, S. Nouren, Y. Safa, K. Jilani, M. Sultan, S. Ata, F. Rehman, M. Abbas, *Adv. Powder Technol.* **28** (2017) 2035.
182. M. Bilal, M. Asgher, M. Iqbal, H. Hu, X. Zhang, *Int. J. Biol. Macromol.* **89** (2016) 181.
183. M. Bilal, M. Iqbal, H. Hu, X. Zhang, *Biochem. Eng. J.* **109** (2016) 153.
184. M. Iqbal, *Chemosphere* **144** (2016) 785.
185. M. Iqbal, M. Abbas, M. Arshad, T. Hussain, A. U. Khan, N. Masood, M. A. Tahir, S. M. Hussain, T. H. Bokhari, R. A. Khera, *Pol. J. Environ. Stud.* **24** (2015) 2745.
186. M. Iqbal, Z. Ali, M. A. Qamar, A. Ali, F. Hussain, M. Abbas, J. Nisar, *Water Sci. Technol.* **76** (2017) 219.
187. M. Iqbal, I. A. Bhatti, *J. Hazard. Mater.* **299** (2015) 351.
188. M. Iqbal, N. Iqbal, I. A. Bhatti, N. Ahmad, M. Zahid, *Ecol. Eng.* **88** (2016) 265.
189. M. Iqbal, J. Nisar, *J. Environ. Chem. Eng.* **3** (2015) 1912.
190. M. Sasmaz, A. Sasmaz, *J. Geochem. Explorat.* **181** (2017) 236.
191. M. Sasmaz, E. I. A. Topal, E. Obek, A. Sasmaz, *J. Environ. Manage.* **163** (2015) 246.
192. D. Yildirim, A. Sasmaz, *J. Geochem. Explorat.* **182** (2017) 228.
193. S. Mansouri, N. Elhammoudi, S. Aboul-hrouz, M. Mouiya, L. Makouki, A. Chham, A. Abourriche, H. Hannache, M. Oumam, *Chem. Int.* **4** (2018) 7.
194. C. P. Ukpaka, *Chem. Int.* **4** (2018) 146.
195. W. Yohannes, B. S. Chandravanshi, G. Moges, *Chem. Int.* **4** (2018) 91.
196. M. Palutoglu, B. Akgul, V. Suyarko, M. Yakovenko, N. Kryuchenko, A. Sasmaz, *Bull. Environ. Contam. Toxicol.* **100** (2018) 293.
197. M. Saeed, S. Adeel, M. Ilyas, M. A. Shahzad, M. Usman, E.-u. Haq, M. Hamayun, *Desalin. Water Treat.* **57** (2016) 12804.
198. A. Sasmaz, I. M. Dogan, M. Sasmaz, *Water Environ. J.* **30** (2016) 235.

199. A. Sasmaz, S. Ozkan, M. F. Gursu, M. Sasmaz, *Appl. Radiat. Isotop.* **129** (2017) 185.
200. M. Sasmaz, B. Akgül, A. Sasmaz, *Bull. Environ. Contam. Toxicol.* **94** (2015) 598.
201. A. Chham, E. Khouya, M. Oumam, A. K. Abourriche, S. Gmouh, M. Iarzek, S. Mansouri, N. Elhammoudi, N. Hanafi, H. Hannache, *Chem. Int.* **4** (2018) 67.