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A Review: Analytical methods for heavy metals determination in environment and human samples

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ABSTRACT

Heavy metals are vital and necessary in our daily lives. Moreover, if the amounts of heavy metals are more than the acceptable amounts (mentioned by WHO) in soil, water, and air, indeed, they cause a lot of diseases in human bodies. Therefore, monitoring and measuring the amounts of heavy metals which are arduous and difficult are so important. In this review paper, a lot of studies which have been carried out on the determination and quantification of heavy metals in human bodies, soil, and water are considered. Moreover, the effect of toxicity of each heavy metal on human health is assessed. According to WHO, EPA, NIOSH, ACGIH, and clinical chemistry, determination of heavy metals such as Cd, Pb, Zn, Hg, Cu, Mn is very important in human body and Environmental matrixes. For example, the range concentration of heavy metals in human body such as, cadmium is about 0.3 to 0.98, and for cooper, it is about 0.01 – 1.107 ppm. In addition, most obtained results demonstrate that the lowest and highest range concentration of heavy metals in blood of human body has been equal to 0.56–8.78 ppm and 0.08 – 4.67 ppm respectively. Finally, in this review paper, the approaches of quantification of heavy metals using atomic absorption spectrometry, gas chromatography, inductively coupled plasma mass spectrometry etc. in human bodies, water, and soil are assessed.

1. Introduction

Many different techniques have been applied for determination of heavy metal in different samples. Atomic absorption spectrometry (AAS) is a quantitative method of metals analysis which was suitable for the determination of 70 elements by three option accessory (flame, furnace, Hydride generation). AAS measures the concentration of the metals by passing light (wave length emitted) by a radiation source of a particular element such as Hg, As, Pb and etc. Many metals determined by electrothermal atomic absorption spectrometry (ET-AAS) [1-9], flame atomic absorption spectrometry (F-AAS and FS-AAS) [10-18], atom trapping flame atomic absorption spectrometry (AT-FAAS), Hydride generation atomic absorption spectrometry, Cold vapor-atomic absorption spectrometry (HG-AAS, CV-AAS)[19, 20] and fluorescence spectrometry (XRF) [21-24]. Also, direct current polarography (DCP) [25, 26], differential pulse polarography (DPP), neutron activation analysis (NAA), inductively coupled plasma-optical emission spectrometry (ICP OES) [27, 28], inductively

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coupled plasma- mass spectrometry (ICP-MS) [29, 30], UV-VIS [31], HPLC-inductively coupled plasma-mass spectrometry (HPLC - ICP - MS) [32], electrophoresis(EP) [33], Anodic striping voltammetry (AVS) and inductively coupled plasma-mass spectrometry (ICP-MS) was used for heavy metal determination in different matrix [34, 35]. Arida et al showed that the assessment of heavy and toxic metals in the blood and hair by modern analytical techniques in review paper. Heavy metals and toxic metal effect in blood and hair of some smokers was determined by modern analytical techniques. The levels of Hg, Pb, Cd, As, Se, Mn, Zn, Ni, and Cr were determined using inductively coupled plasma-atomic emission spectrometer (ICP-AES) [36]. A review procedure based on heavy metal analyzing in soil was developed with sequential extraction by Zimmerman et al in 2010. They showed that the quantification extraction and determination of heavy contamination in soil cannot give reliable results. They showed, the procedures of community bureau of reference (BCR) and geological society of Canada (GCS) procedures were examined to clarify benefits and limitations of each [37]. Also, determination of heavy metal in blood evaluated with AAS by Batool and Ahmad at 2018. The blood samples were divided into two parts .First for analysis of total blood and other for serum. By centrifuging the blood and serum sample separated. Serum after adding de ionized water analyzed by instrument after digestion. For whole blood samples wet digestion apply before analysis. Before analysis, blood samples were kept in freezer at 4 ^{o}C. In this study, wet digestion includes decomposition by acids carried out on hotplate and continued by AAS model Varian AA 240 [38]. Yuan Fu et al used Titanate/TiO_2 as adsorption sorbent for heavy metals determination and adsorption by nanotechnology. The titanate/TiO2 Nanomaterials were synthesized by Biomolecules (lignin). The titanate/TiO_2 characterized by XRD, FESEM, TEM, FTIR and BET, and their adsorption for heavy metals were studied. The found the maximum adsorption capacity of heavy metal ions (Pb^{2+}, Cu^{2+}, Cd^{2+}) based on procedure [39]. Zhang et al showed, the nanomaterials can be treatment in water and wastewater samples. They introduce a novel nanotehecnology which was used by researcher included, the synthesis and physiochemical properties of nanomaterials, carbon based nanomaterial, metal and metal oxides nanoparticles were focused on removal of various heavy metals in water and wastewater [40]. Chromium speciation in natural water samples was developed by solid phase extraction procedure. Cr(VI) can be extracted with ammonium pyrrolidine dithiocarbamate (APDC) pasted on multi walled carbon nanotubes (MWNTs). The total chromium was determined by oxidation of Cr(III) to Cr(VI). The Cr(III) concentration is calculated by subtracting of total chromium and Cr(VI) [41]. Cr (VI) compounds, once inside the bloodstream, are actively transported into red blood cells (RBC) via nonspecific anionic channels and then rapidly reduced to Cr (III) which becomes bound to hemoglobin. As cancerogenic effect of Cr (VI) determination of Cr (VI) very important. Also, in Figure 1, metabolism and formation of DNA damage by CrVI at pH 7.4 are shown.

Zendehdel et al studied on a HAp/NaP nanocomposite by adding a synthesized nano-hydroxyapatite to zeolite NaP gel. They used HAp/NaP for the removal of lead(II) and cadmium(II) ions from aqueous solution. This nanocomposite was characterized by FTIR, X-ray, SEM, energy-dispersive X-ray analysis and thermal analyses [42]. Microwave-assisted method was used for synthesizing of graphene nanosheet/δ-MnO_2 (GNS/MnO_2) composite. TheGNS/MnO_2 as sorbent was used for removal of NI(II) from waters. SEM, TEM and FTIR show that nanoscale δ-MnO_2 deposit well on GNS. The adsorption process was achieved in optimized pH [43]. Ojea-Jiménez et al showed that the removal of mercury from the Ebro River by Colloidal gold nanoparticles (Au NPs). Au NPs have been used for sequestration removal of Hg(II) from multicomponent waters. Under optimized conditions, sodium citrate was reduced Au NPs as the catalyst in the reduction of Hg(II), which is efficiently trapped in the presence of Cu(II) and

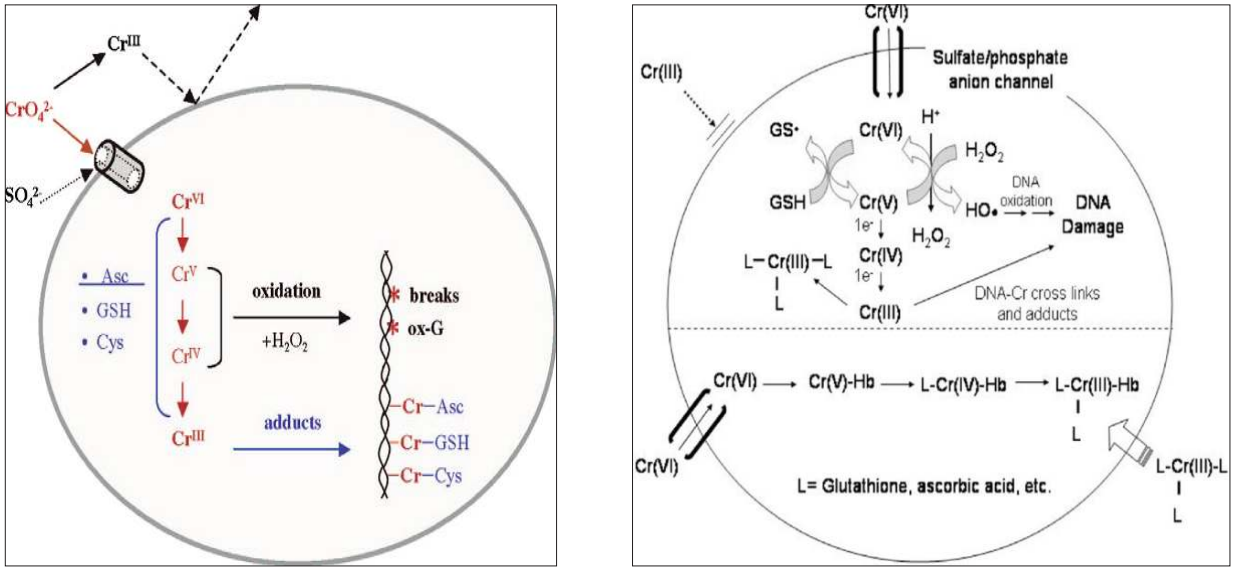


Fig. 1. Metabolism, and formation of DNA damage by Cr (VI) at pH 7.4.

Fe(III) [44]. Many references existed for separation and preconcentration and determination based on LLME, SPE, MSPE, IL/MSPE, USA-MSPE etc. in water, human biological and food samples by nanotechnology [45-56]. Also many developed methods was reported by researchers by green solvents such as ionic liquid for extraction of heavy metals in different matrixes [57-88]. In addition, an advanced approach for separating As(III) and As(V) ions in environmental matrixes was presented by Soylak et al in 2009 [89]. In their research, when dilute $KMnO_4$ was used to oxidize As(III), then the developed coprecipitation was used to determine total arsenic [89]. The difference between the total arsenic content and As(V) content was calculated as Arsenic(III) [89]. Moreover, in their study, hydride generation atomic absorption spectrometry (HG-AAS) was used to determine arsenic levels. Also, after calculating the factor of preconcentration, it was found out that the factor was equal to 25. In addition, the detection limits (LOD) for As(V) was 0.012 µg.L^{-1} [89]. A new approach for solid phase extraction (SPE) of gold(III) by using Dowex M 4195 chelating resin was developed by Soylak et al in 2007 [90]. The quantitative sorption of gold^{3+}, effect of flow rates, pH, sorption capacity, eluent types, and the effect of diverse ions on the sorption of Au^{3+} were investigated to find optimum experimental conditions [55]. In their work, for more than 100 cycles of sorption–desorption, the chelating resin was reused without any considerable change in sorption of Au^{3+} [90]. In their work, the preconcentration factor was calculated to be 31. Detection limit (LOD) of Au was greater than 1.60 µg L^{-1} and the recovery values for Au^{3+} was greater than 96% [90]. The adsorption capacity of the resin was 8.1 mg.g^{-1}. Their proposed approach has been determining Au^{3+} in some real soil and water samples were used and showed the best results [90]. For characterizing As(III) biosorption from aqueous solution, green algae (*Ulothrix cylindricum*) biomass was used by Soylak et al in 2009 [91]. According to their studies, the biosorption capacity of *Ulothrix cylindricum* biomass was equal to 67.2 mg g^{-1} [91]. The outcomes of their work indicated that the processes of biosorption of As^{3+} followed well pseudo-second-order kinetics [91]. Separation of Cu^{2+} in environmental matrixes by using solid phase extraction on multi-walled CNT (carbon nanotubes) was studied by Soylak and Ercan in 2009 [92]. The optimum adsorption was obtained on MWNTs column in their study when pH was equal to 7.0. The preconcentration factor was equal to 60. Also, the detection limit for Cu^{2+} was equal to 1.46 µg L^{-1} [92]. For atomic absorption spectrometry, separation of trace heavy metals in sediment, urine, and dialysis concentrates by coprecipitation with samarium hydroxide was

carried out by Elci et al in 2003 [93]. In their study, the optimum pH for collecting trace heavy metals on samarium hydroxide was equal to 12.2. Also, coprecipitation occurs after 30 minutes, and when quantitative recovery is governed, and the precision is about 5% for the analytes [93]. Determining heavy Metals in plants, soil, and groundwater which followed high-rate sewage sludge was studied by Speir et al in 2003 [94].The pH of samples was less than 4. Also, during five years, the concentration of Zn in the soil reduced from 27 mg kg^{-1} to 0.04 mg kg^{-1}. Moreover, based on their study, there is a direct relation between the concentration of heavy metals in plants and the concentration of heavy metals in the soil [94]. An advanced biological treatment plant for removing heavy metals in groundwater was presented by Scheeren et al in 2007. Groundwater below the zinc production plant was contaminated with sulphate and heavy metals. To avoid contamination of nearby drinking-water aquifers in the future, a treatment plant for extracting contaminated ground water was established by them [95]. Effluent treatment based on activity of Sulphate Reducing Bacteria (SRB) for excess sulphide in solids for achieving the discharge criteria was designed by them. The reducing the sulphate to sulphide and thereby, precipitation of metal sulphides were obtained when anaerobic bacteria are there in the soil or the bacteria are injected [95].

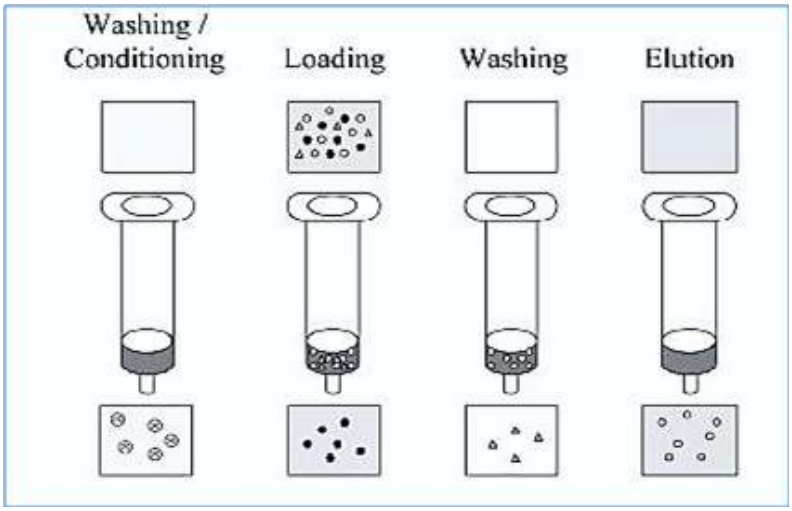
Determination of trace heavy metals in harvested rainwater by ICP-MS was used by Malassa et al in 2018 [96]. Inductively coupled plasma mass spectrometry (ICP-MS) was used to quantify the content of each trace heavy metal (Cr, Co, Mn, Ni, Cu, Zn, Mo, Ag, Cd, Bi, and Pb) in a few rainwater samples. Their results indicated that that the concentrations of Cr, Mn, Ni, Ag, and Pb are more than the WHO limits in drinking water [96]. Contamination of heavy metals in sediments of the Karasu spring in Nigde, Turkey has been investigated by Yalcin and Narin in 2007 [97]. A few sediment matrixes were collected from contaminant sites along the spring. Moreover, concentrations of heavy metals have been determined by X-ray Fluorescence Spectrometer [97]. The amount of Co, Cu, As, Sn, Ni, Zn, Ca, Pb, Al, Fe, Ti, Cr, and Mn contents of the Karasu creek sediments were equal to 18.30–69.00, 12.40–595.0 5.50–345.3, 5.80–15.1, 10.9–64.1, 28.90–103,300, 4.1–356.2, 7.70–37,840, 13,460–109,400, 11,740–62,900, 22.18–59.04, 41.70–369 and 12.09–3,480 mg/kg respectively. Moreover, according to their results, the presence of a contamination in the Karasu creek is obvious. In the case study, all the metal concentrations are more than acceptable limit values. In addition, in the Karasu creek and the Akkaya dam, eutrophication has been being developed. Also, it sounds that the accumulation of heavy metal in the creek is come from the discharge of mine quarries, domestic, and industrial wastes [97]. Separation of arsenic(III) and arsenic(V) by using *Streptococcus pyogenes* which has been immobilized on Sepabeads SP 70 resin has been considered by the approach of solid-phase extraction by Uluozlu et al in 2010 [98]. In sample solutions, hydride generation atomic absorption spectrometry (HGAAS) has been used to quantify the arsenic levels [98]. Their procedure has been governed when recovery of As^{3+} was more than 95%. Moreover, recovery of As^{5+} which was obtained was less than 5%. By using KI and ascorbic acid, As(V) has been reduced; in addition, after 1 hour later, for determining total arsenic, their system has been applied. As^{5+} has been calculated by subtracting the total As from As(III) content [98,99]. Some experimental parameters such as pH, amount of microorganism, sample volume have been assessed in their study. The capacity of biosorbent for As^{3+} has been equal to 7.3 mg g^{-1}. The preconcentration factor has been found to be equal to 36 [99]. The relative standard deviation has been obtained less than 8% [99]. Moreover, the contamination of trace heavy metal ions in drinking water samples has been investigated by Tuzen et al in 2005. According to their studies, if the amount of lead in drinking water samples is more than 10 microgram per liter, brain tissues and kidneys will be damaged [100]. Assessment of the amount of each metal in Drinking Waters from the

Tokat-Black Sea Region of Turkey was studied by Tuzen and Soylak in 2006. In their study, atomic absorption spectrometry was used to determine the amount of Cr, Ni, Cu, Mn, Zn, Fe, Co, and Al ions. According to their study, the amount of the heavy metals was lower than the maximum acceptable limits which were set by the World Health Organization [101-138]. In this review paper, the amounts of heavy metals and their toxicity in water, soil, air, and human bodies which have been studied and quantified by other researchers during the last decade are considered.

2. Experimental

Kaipei Qiu used ultrafine mesoporous magnetite nanoparticles (UFMNPs) for removal of heavy metals from waters (Scheme 1). Ultrafine magnetite NPs(UFMNPs, Fe_3O_4) were synthesized by co-precipitation method and successfully used as adsorbents for the removal of Pb^{2+}, Cd^{2+}, Cu^{2+}, and Ni^{2+} ions from contaminated river water. Also, the adsorption/desorption tests demonstrated that the ultrafine Fe_3O_4 NPs were reusable and can be used several times [139].

Gollavelli et al and Luo et al used Magnetic Graphene and magnetic chitosan/cellulose microspheres for removal of heavy metal from dinking waters, waters [140,141]. Mahmoudi ,Chen and Neyaz can be extracted heavy metals from different matrix by iron oxide nanoparticles (SPIONs), Fe_3O_4 @ SiO_2 and functionalized iron oxide nanomaterials [142-144]. Tuzen et al showed a novel method based on switchable hydrophilicity microextraction syringe system (μS-SHS*)* by electrothermal atomic absorption spectroscopy (ETAAS). The proposed method was developed for separation and determination of vanadium in waters by complexing 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol (5- Br-PADAP). In this study, LOD, EF, and RSD were achieved 7.5 ng L^{-1}, 120 and 2.91 %, respectively. In addition, the μS-SHS is consisting of micropipette tip and syringe system was designed. First, the 10 mL of real sample was placed on beaker and then, 5- Br-PADAP solutions as ligand were used by sucking into syringe system. Finally, 0.1 mL of decanoic acid as a hydrophobic effect sucked into to solution which was followed by 500 μL of 1.0 mol L-1 Na_2CO_3 solution as a switchable hydrophobicity for the decanoic acid ($CH_3(CH_2)_8COOH$) in liquid phase. The surface response methodology was used to calculate response surface between [pH]/[V of SHS] and [pH]/[V of Na_2CO_3] of the vanadium. The results showed, high recovery based on 112 μL of SHS and 624 μL of Na_2CO_3 was obtained at pH=3.28. The design of experiments (DOE) was used for analyzing data and optimizing by surface response methodology [102]. Xiaogang Luo et al explained a novel sorbent for absorption heavy metals from waters. The carboxyl decorated magnetite (Fe_3O_4) nanoparticles (MN-CA) were obtained by modifying the magnetite surface with



Scheme 1. SPE method for extraction heavy metals from liquids

citric acid. .In this research, the combination of specifically modified magnetic nanoparticles and activated carbon(AC) to cellulose may create new nanocomposite adsorbents, which possess high adsorption capacity for heavy metals removal and easy recovery by magnetic field. It could be deduced that electrostatic attraction between negatively charged magnetic cellulose-based beads (MCB) samples and positively charged Cu^{2+}, Pb^{2+}, and Zn^{2+} was the initial driving force of heavy metals binding to the adsorption site of the adsorbents [145]. Researcher such as Shannon, Luo, Gericke, Karami and Zhao et al worked for removal heavy metals from water, water Purification, wastewater treatment and methyl orange removal by novel technique with different sorbents such as; activated magnetic cellulose Microspheres, functional cellulose beads, magnetite nanoparticles,and hierarchical MWCNTs/Fe^3O_4/PANI magnetic composite [146-150]. For determining the amount of metals in drinking water samples, the Perkin Elmer Analyst 700 atomic absorption spectrometer was used by Tuzen and Soylak in 2006 [101]. A 10 cm long slot-burner head, a lamp and an air-acetylene flame were applied. In solid phase extraction (SPE) studies, a glass column with 100 mm high and 10 mm in diameter was applied [101]. The solid phase materials such as Amberlite XAD-1180, Amberlite XAD-4 and Diaion HP-2MG was purchased, and they were prepared with the washing steps as reported previously in literature. They collected the drinking water samples in prewashed (with detergent, doubly de-ionized distilled water, diluted HNO_3 and doubly de-ionized distilled water, respectively) polyethylene bottles from eight stations in Tokat and villages around Tokat in July 2004. The samples were obtained from the water pump directly after the water had run for at least twenty minutes. They filtered the samples by using a Millipore cellulose membrane with a 0.45 µm pore diameters [101]. After the process of filtration, nitric acid was used to acidify the samples to 1%, and then the samples were stored in 1 L polyethylene bottles. The samples were thereby stored at 4 °C for a short time, afterwards they were analyzed until the changes of the physicochemical form of the metals were minimized [101]. Electroplating industry, tanneries, electronics manufacturing industry, coal-fired power plants and mining operation are key sources of heavy metal pollution in water [151]. Lead (Pb) is discharged into water sources from various industries and is highly toxic to human beings even at trace concentrations. Maximum contaminant level of Pb(II) in drinking water is set at 15 µg L−1 by US Environmental Potential Agency (US EPA). Chromium(Cr), another toxic heavy metal pollutant, is mainly present in the effluents of leather tanning, electroplating and chromate preparations. Chromium is found in two oxidation states Cr(III,VI) and Cr (VI) is more toxic. World Health Organization (WHO) guideline for Cr(VI) in drinking water is 50 µg L^{-1}. So determination and separation this pollutant from waters with novel technique based on sorbent adsorption is very important [151]. Santhosh et al showed lead and Cr simply extracted from water solutions by PG-C and CNF-C [151]. By using thermal process, cobalt ferrites ($CoFe_2O_4$) paste on porous graphene (PG) and carbon nanofibers (CNF)), which was named PG-C and CNF-C nanocomposites as magnetic adsorbents [151]. In Figure 2, removal of heavy metals using nanographene is shown.

Sarika Singh et al used a functional oxide nanomaterials and nanocomposites for the removal of heavy metals and dyes in liquid phase. They showed that the oxide-based nanomaterials, such as Fe_3O_4, ZnO and TiO_2 for the removal of different toxic metals and organic dyes at optimized pH. Magnetic nanoparticles as excellent sorbent can be used as highly effective, efficient and economically-viable for removal toxic metals with advantages of easy separation under a magnetic field for reuse. Shen et al have observed that the adsorption efficiency of Ni^{2+}, Cu^{2+}, Cd^{2+} and Cr^{6+} ions by Fe_3O_4 nanoparticles is strongly dependent on pH, temperature, and the amount of the adsorbent. In optimized conditions, 3.5 mg mL^{-1} dose of nano-adsorbent with an optimum pH=4 was used for removal heavy metals from contaminated water [152]. Phoebe Zito Ray et al studied on Inorganic

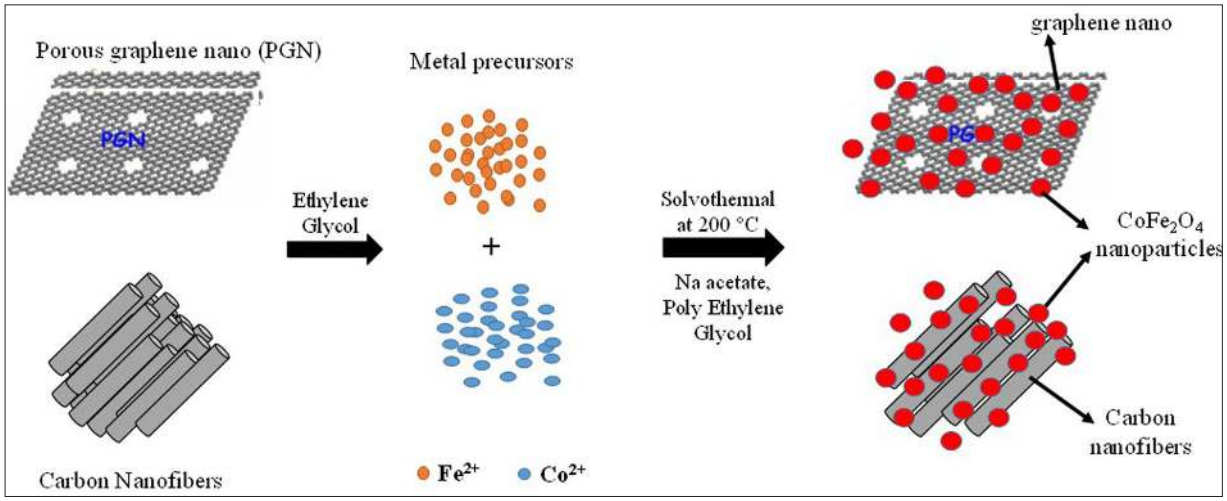


Fig. 2. Removal of heavy metals using nano-graphene [151].

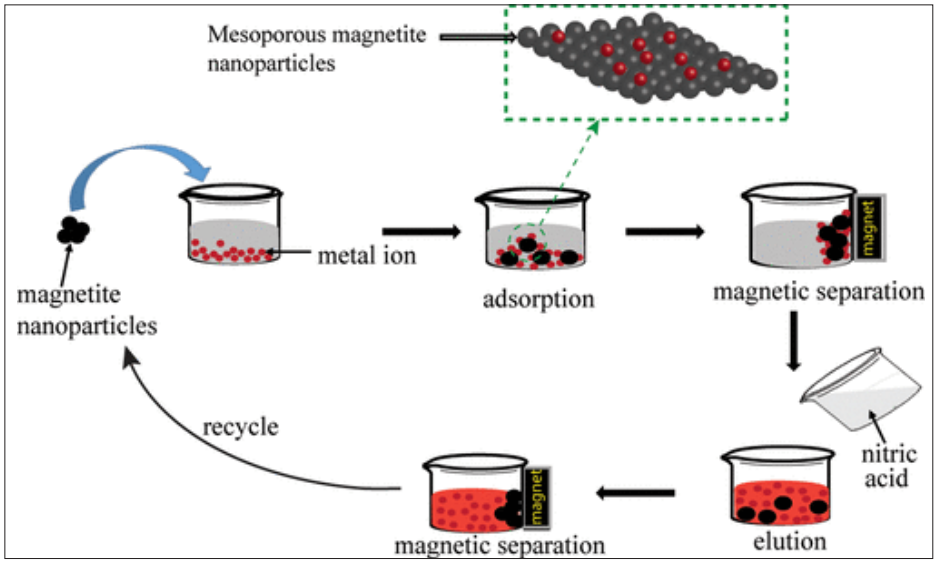
nano-adsorbents for the removal of heavy metals and arsenic in aqueous solutions. They were explained that metal oxides and CNTs as nanoadsorbents were used for heavy metal removal in aqueous solutions. Phoebe Zito Ray et al used the iron oxide (hematite, magnetite and maghemite), carbon nanotubes (CNT), and metal oxide based (Ti, Zn) and polymeric nanoadsorbents for this study. Based on reults, metal oxides can have increased surface area and possess favorable sorption to heavy metals. ZnO nanoplates showed complete removal of Cu^{2+} in aqueous solutions [153]. Recently, CNTs and nZVI synthetized by coupling these nanomaterials and was efficient used for removal of Cr(VI), Se and Co from polluted water by Giorgio Vilardi et al. Regeneration studies were performed fixing CNTs-nZVI concentration and the initial metal concentration equal to 10 mg L^{-1}, as already reported in a previous study [154]. Experimental results of adsorption batch tests showed that the removal efficiency of nanomaterials was in decreasing order: CNTnZVI>nZVI>CNTs>CNTs-nZVI, except for the Cr(VI) that nZVI was the most efficient material. Furthermore, the removal of Cr(VI) was found to not be affected by varying the pH in the case of using nZVI, but decreased with increasing pH when using the other three nanomaterials [154]. Also, Majed Alrobaian and Hassan Arida studied on Assessment of Heavy and Toxic Metals in the Blood and Hair of Saudi Arabia Smokers Using Modern Analytical Techniques. The levels of some selected heavy and toxic metals (e.g.; Hg, Pb, Cd, As, Se, Mn, Zn, Ni, and Cr) were determined using inductively coupled plasma-atomic emission spectrometer (ICP-AES). Prior to the analysis, the blood and hair samples of Saudi Arabia smokers were collected, treated, and digested by microwave digestion system. The validation measurement of ICP-AES was performed using working calibration solutions of the investigated toxic heavy metal ions (Hg, Pb, Cd, As, Se, Mn, Zn, Ni, and Cr) [155]. Kaiser, Zheng and Feng was introduced a novel two-dimensional polymers synthesis with nano size in water which was different application such as heavy metal removal. They reported the controlled synthesis of few-layer two-dimensional polyimide crystals on the surface of water through reaction between amine and anhydride monomers, assisted by surfactant monolayers [156]. Heavy metals such a lead or cadmium has devastating health effects on human body. So, removal of heavy metals from industrial wastewater and drinking water is very important. Rosillo-Lopez et al showed that carboxylated graphene nanoflakes (cx-GNF) and nano-graphene oxide (nGO) can be extracted Fe^{2+}, Cu^{2+}, Fe^{3+}, Cd^{2+} and Pb^{2+} ions from water sample. The sorption capacity for Pb^{2+}, , is more than six times greater for the cx-GNF compared to GO which is attributed to the efficient formation of lead carboxylates as well as strong cation–π interactions [157]. Zhao et al introduced a novel multi-throughput dynamic microwave-assisted leaching

(MDMAL) combined with ICP-AES was used for the simultaneous determination of Cu, Mn, Zn and Pb in soil. The MDMAL method was more rapid than the simple digestion method or microwave digestion process and could be an alternative approach for the analysis of heavy metals in solid samples [158]. Aaron et al reported an efficient chemical strategy for the crosslinking of polymer chains based on the N- and C- of proteins(CPC→N/C-P), producing hybrid hydrogels which was related to biomolecules. This compound is largely independent of the protein's sequence; it can in principle be used to incorporate of polypeptide into a polymer based on uniform linkages. They used cysteine for this strategy to convert metallothioneins into a recyclable polymer gel that can remove heavy metals from water samples [159]. Shirkhanloo et al reported a novel method based on amine-functionalized mesoporous silica UVM-7 as nanoadsorbent for manganese (II) and manganese (VII) extraction in waters by ultrasound assisted-dispersive-micro-solid phase extraction (US-D-μ-SPE) procedure. They were used NH2-UVM7 for speciation of Mn(II) and Mn(VII) ions at pH of 8 and 5, respectively which was determined by(AT-F AAS. The validation of the method was also performed by the standard reference material [160]. Also, Shirkhanloo et al introduced a carboxyl-functionalized nanoporous graphene (NG-COOH) as solid phase sorbent for speciation of trace Hg (II) and R-Hg (CH_3Hg^+ and $C_2H_5Hg^+$) in waters by US-D-IL- μ-SPE (pH=8). Ionic liquid was used for trapping of sorbent from water sample. After back extraction, Hg (II) concentration determined with flow injection-cold vapor-atomic absorption spectrometry (FI-CV-AAS) [161]. Also they were reported a new method based on ultrasound assisted-dispersive solid-liquid multiple phase microextraction (USA-DSLMPME) for speciation of trace amounts of inorganic arsenic (III and V) and total organic arsenic (TOA) in waters and human urine samples. By procedure NH2-UVM7 were immersed in ionic liquid (IL) as an extraction phase. Then, the mixture of NH2-UVM7 and IL/acetone [HMIM][PF6]/AC) was injected to sample at pH of 3.5. After ultrasonic, As(V) anion extracted by binding to amine group. Total amount of inorganic arsenic (TIA) was determined after oxidization of As(III) to As(V) by ETAAS and As(III) was calculated by the subtracting TIA and As(V) content [162].

3. Results and Conclusions

Kaipei Qiu was introduced a novel adsorption process for heavy metals from waters. In the adsorption process, the desorption and repeatability are significant parameters for developing new adsorbents for practical applications. The heavy metals such as, Pb^{2+}, Cd^{2+}, Cu^{2+}, and Ni^{2+} were adsorbed by UFMNPs which was shown in Scheme 2. The adsorption kinetics is one of the important characteristics defining the effectiveness of an adsorbent, which describes the solute uptake rate by controlling the diffusion process and the residence time of an adsorbate uptake at the solid/solution interface. The results in this quaternary Pb–Cd–Cu–Ni system indicated that the rate constant of Pb^{2+} (0.045 g mg^{-1} min^{-1}) was higher than the rate constants of Cu^{2+} (0.008 g mg^{-1} min^{-1}), Cd^{2+} (0.005 g mg^{-1} min^{-1}), and Ni^{2+} (0.003 g mg^{-1} min^{-1}), further demonstrating the strong affinity of Fe_3O_4 NPs for Pb^{2+}[139].

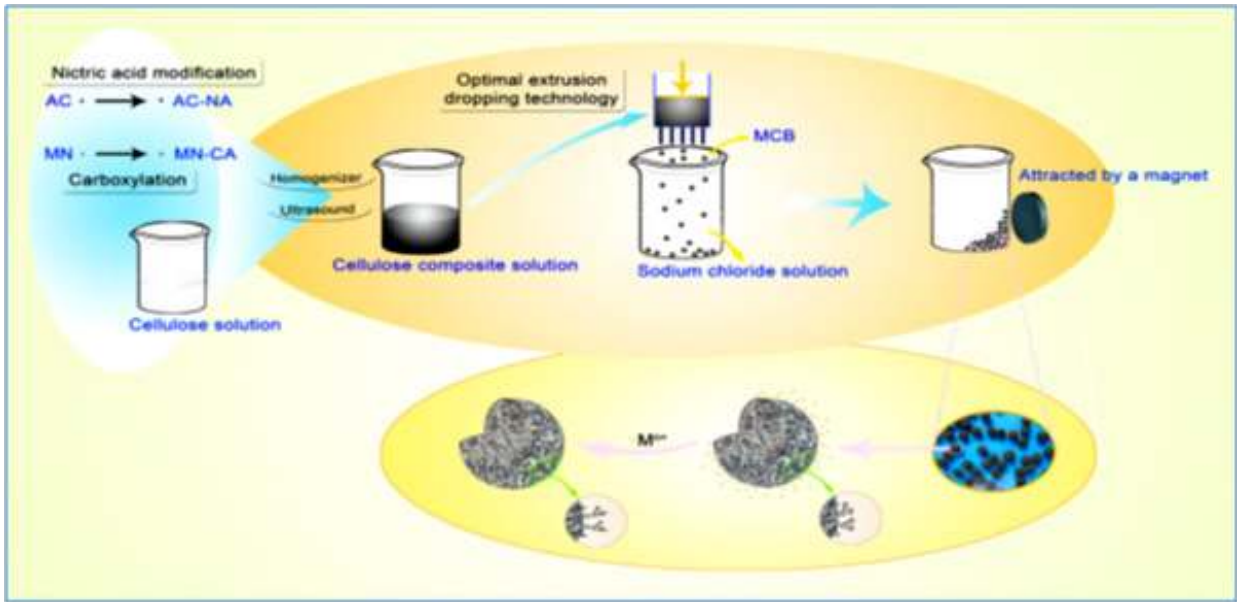
Soylak and Tuzen studied on the amounts of Cr, Cu, Ni, Zn, Mn, Fe, Co, and Al in drinking water samples based on novel extraction technique using atomic absorption spectrometry in Turkey. According to their studies, the concentration of Cr in natural water was often very small. Based on results, the hexavalent form of chromium (Cr_{VI}) is ranged between 3.14 and 6.08 μgL^{-1}. The mean of Cr levels in the waters of the area of Turkey was equal to4.40 μgL^{-1}. Maximum tolerable limit of concentration of total chromium in drinking water was less than 50 μg L^{-1} (Tlv of chromium by WHO > 50 μg L^{-1}) [101]. The permissible value of Ni in drinking water was less than 20 μg L^{-1}. The mean level of Ni in the water samples, in the area of Tokat, Turkey was equal to 3.82 μg L^{-1} which was lower than standard references such as EPA, WHO. Also, according to their study, the drinking water sample from Turhal was the highest nickel value



Scheme 2. Removal of heavy metal Ions by desorption process [139]

(5.35±0.28 µg L^{-1}) and the city center of Tokat was the lowest (2.16±0.19 µgL^{-1}) [101]. They showed, the amount of Cu was in the range of 4.44-7.43 µgL^{-1}. In Erbaa, Turkey, Cu was substantially lower than the permissible limit defined by WHO (1.0 µgL^{-1}) in drinking waters [101]. In addition, mean level of concentration of Cu was equal to 6.01 µg L^{-1}. Therefore, no contamination of Cu was there in the drinking water samples. The guideline value for zinc in drinking-water is given as 5.0 mg/l by WHO. The concentration of Zinc ranged from 4.16 to 8.44 µg L^{-1} in the drinking water samples. The mean level of zinc was obtained 6.12 µg L^{-1}, which was more than the permissible limit value (5.0 mg/L^{-1}) [101]. Many published methods were reported for determination and sample preparation of heavy metals in water and biological samples [Table 1-3]. Chromium speciation based on acetylcysteine (NAC) by dispersive liquid–liquid bio-microextraction was achieved in human blood samples by shirkhanloo et al. By method, Ionic liquid (1-hexyl-3-methylimidazolium hexafluorophosphate) was rapidly injected into the blood samples containing Cr^{3+}, which have already complexed by NAC at pH from 5 to 8. By optimizing, the linear range, limit of detection and preconcentration factor were achieved 0.03–4.4 µg L^{-1}, 0.005 µg L^{-1}, and 10 respectively [163,164]. Also, chromium speciation was reported by other researcher [165-172]. Xiaogang Luo et al explained a novel sorbent for absorption heavy metals from waters by syntesis of MCB. The carboxyl decorated magnetite (Fe_3O_4) nanoparticles (MN-CA) were obtained by postmodifying the magnetite surface with citric acid. The nanoparticles of Fe_3O_4 were added to 0.1 M citric acid under ultrasonic condition for 45 min, and the reaction was kept for 4 h at room temperature. A magnet was used to separate the MN-CA, and then the prepared MN-CA samples were rinsed thoroughly with acetone and double distilled water. The proposed method based on MN-CA followed by Scheme 3 for adsorption heavy metals from waters [145].

Naeemullaha et al showed, the effect of main parameters on extraction of vanadium in waters was evaluated by µS-SHS procedures [102]. For optimizing, Statistical assessment of µS-SHS method, Screening and optimization of experimental variables and selectivity of the µS-SHS method was studied and finally, the method was validated by CRM (SLRS-4 Riverine water samples). The optimization of experimental variables followed with screen out of the volume of SHS, pH, volume of Na_2CO_3 and volume of H_2SO_4 solution as a extraction efficiency with t-value (95 %) of 2.365. The simple, fast and switchable hydrophilicity microextraction (SHM) couple with ETAAS through micropipette tip



Scheme 3. depiction of preparation of MCB and the adsorption mechanism of heavy metal ions by MCB [145].

syringe system (μS-SHS) was used for separation and determination of vanadium in food and water samples. The μS-SHS method introduced an ideal sample preparation for vanadium extraction. The simple, fast and applied method based on SHM had good efficiency as compared with conventional methods for extraction of vanadium [102]. Also, the proposed method based on μS-SHS compared with published method and results showed high precision and accuracy results with low LOD and RSD (Table 1). Moreover, the graphical abstract of the μS-SHS was shown in Figure 3.

Many separation methods were used for determination of ultra-trace metals in different matrix, such as Liquid-liquid microextraction, dispersive liquid–liquid microextraction, solid-phase microextraction, selective dispersive micro solid-phase extraction, traditional organic solvents, and switchable solvent, ultrasound assisted-dispersive-ionic liquid-micro-solid phase extraction and ultrasound assisted-dispersive solid-liquid multiple phase microextrbased on action [Table 1-3]. Kaiser, Zheng and Feng used a novel two-dimensional polymers crystals (TDPC) synthesis with nano size in waters through reaction between amine and anhydride monomers by surfactant monolayers. They showed high crystallinity polymers (CsP) with thickness (2 -3 nm) and an crystal size (3.5 μm^2). The molecular structure of the materials, were characterized using X-ray scattering and TEM. The structure and TEM was shown in Figure 4. The formation of CsP is attributed to the pre-organization of monomers at interface phase (water- surfactant). Finally, micrometre-sized and few layer TDPC were grown. This material was used in different application such as removal heavy metals [156].

Rosillo-Lopez et al used carboxylated graphene nanoflakes (CX-GNF) and nanographene oxide (GO) for extracting of heavy metals such as, Fe^{2+}, Cu^{2+}, Fe^{3+}, Cd^{2+} and Pb^{2+} in waters. The carboxylic acid groups (cx-GNF) have strong binding with heavy metal cations. CX-GNF with additional chemical-functionalization procedures can easily compete

Table 1. The proposed method based on μS-SHS compared with published method [102]

Sample prepration	Technique	SV	RSD%	LOD (μg.L^{-1})	EF/PF	References
SPE	ICP-OES	10	3.4	0.06	45	68
CPE approach	Spectrometric	….	….	1.4	….	70
CPE	ETAAS	50	….	0.042	125	71
μS-SHS	ETASS	10	2.2	0.0075	120	76

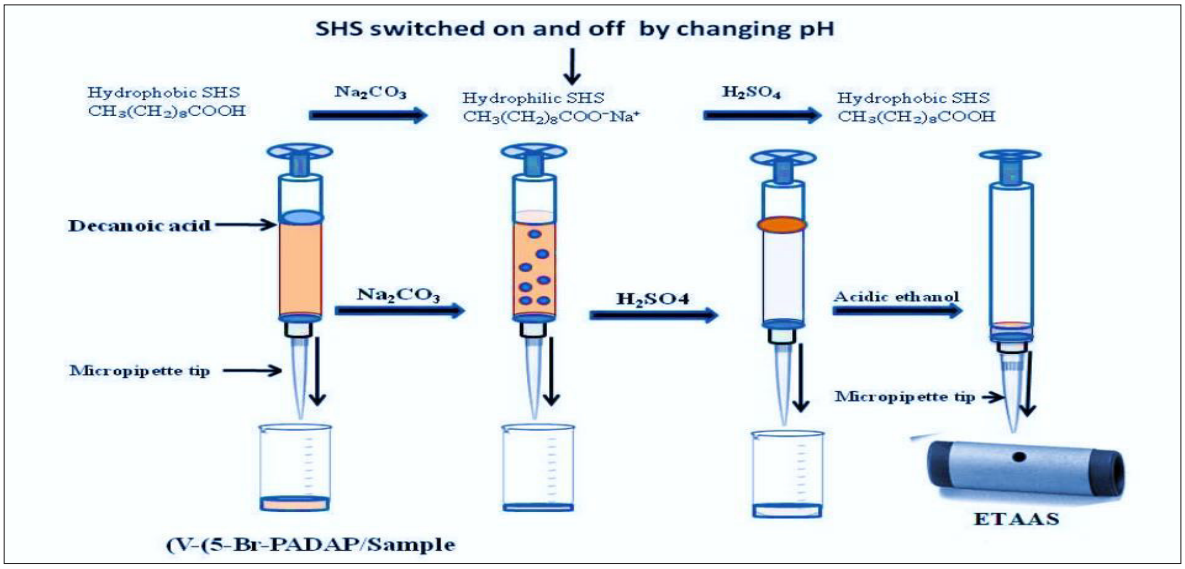


Fig. 3. The graphical abstract of the μS-SHS [102].

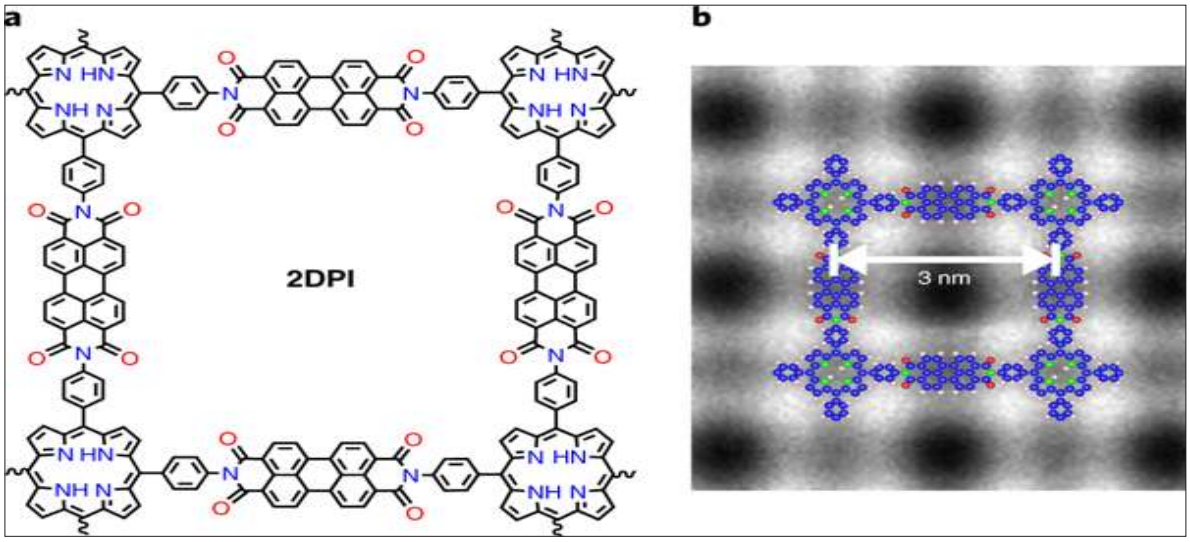


Fig. 4. The structurea and b) TEM of two-dimensional polymers crystals (TDPC)[156]

with other carbon materials such as G and GO for heavy-metal extraction (Fig. 5). Furthermore, the cx-GNF material extracted Pb^{2+} ions in the presence of excess Ca^{2+} or Mg^{2+} cations which were already existed in environmental matrix. So, the CX-GNF material showed the highest potential for extraction of heavy-metal from water as compared to other graphene materials [157]. Zhao et al used multi-throughput dynamic microwave-assisted leaching (MDMAL) for determination of Cu, Mn, Zn and Pb in soil . This method combines the microwave and dynamic leaching technique for five samples within 15 min (Fig. 6). HNO_3 aqueous solution was

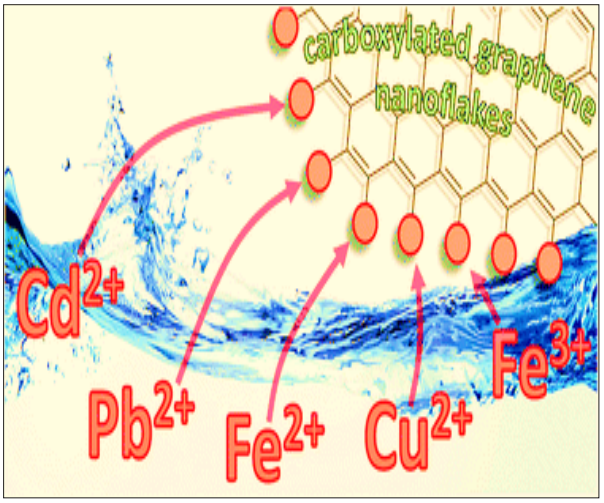


Fig. 5. Heavy metal extraction by cx-GNF.

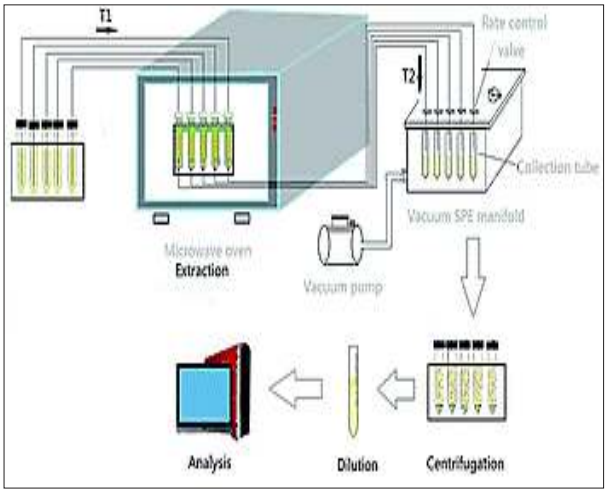


Fig. 6. Heavy metal extraction by MDMAL

employed as leachant at a flow rate of 1.5 mL min^{-1}. The leaching condition were above 95% for Cu, Mn, Zn, Pb and lower for Cr, Cd, Ni and Co, compared to the conventional method. The mean of RSD of intra- and inter-day of Cu, Mn, Zn, and Pb were 4% and 6%, respectively. The proposed method was more rapid than the conventional digestion method and could be an alternative approach for the analysis of heavy metals in complex solid samples [158].

Aaron et al, showed that, the crosslinking of polymer chains based on the N- and C- of proteins (CPC→N/C-P) was used as a key of the proteins which was captured trace amounts of heavy metals such as cadmium in the presence of innocuous ions in contaminated water sample. Protein-cross-linked hydrogels introduced for sequestration of heavy metal ions in water samples. As Figure 7, the Pea metallothioneins (PMTs) can capture toxic metal ions by condensing to form binding pockets. The synthetic route to access these materials involves the introduction of ketones on both protein termini. These groups are then used to cross-link alkoxyamine-substituted polymers through oxime formation [159]. Shirkhanloo et al used NH_2-UVM_7 based on US-D-μ-SPE method for speciation of manganese in water samples. The batch adsorption

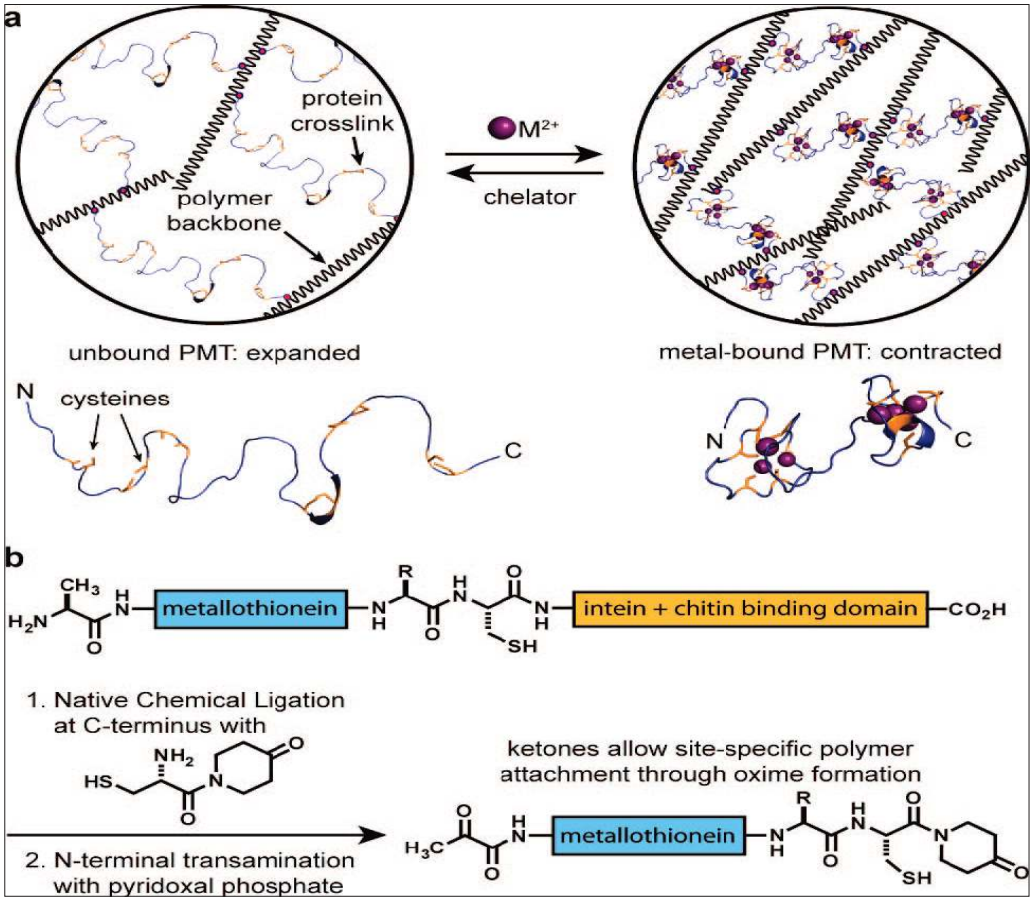


Fig. 7. Pea metallothioneins (PMTs) can capture toxic metal ions a) Condensing to form binding pockets b) Ketones used to cross-link alkoxyamine-substituted polymers [159]

capacity of NH_2-UVM_7 for Mn(II) and Mn(VII) ions was found to be 1733 µmol g^{-1} and 570 µmol g^{-1}, respectively. In optimized parameters, LOD (3Sb/m), and LOQ (10Sb/m) were 0.007 µg L^{-1} and 0.03 µg L^{-1} for Mn(II). The mean preconcentration factors for Mn(II) and Mn(VII) were calculated as 102.3 and 98.8 with RSD about 2.8%, respectively (Fig. 8). The regression equations for the calibration curves of Mn(II) and Mn(VII) were A=9.8438 C+0.0053 (R2=0.9997), and A=9.6922 C+0.0045 (R2=0.9995), respectively [160]. In addition, Shirkhanloo et al used NG-COOH for speciation of trace mercury in waters by US-D-IL- µ-SPE. Under optimized conditions, the linear range, LOD and PF/EF were obtained 0.03–6.3 µg L^{-1}, 0.0098 µg $L^{-1}$and 10.4 for caprine blood samples, respectively. The developed method was successfully applied to natural water and human/caprine blood samples. In order to validate the method described, two certified standard reference materials, NIST-SRM 995c (mercury species in caprine blood) and NIST-SRM1641e (total mercury inwater), were analyzed by US-D-IL- µ-SPE [161]. They used NH2-UVM7 based on USA-DSLMPME for speciation of trace amounts arsenic (III and V) in waters and human urine samples. The linear range, LOQ (3σ), RSD% and EF for As(V)were obtained 0.02–1.65 µg L^{-1}, 11 ng L^{-1}, 4.3% and 100.5. The recoveries (95–102%) was achieved by certified reference material in urine (NIST-SRM). The mean of LOD was obtained 3.3 ng L^{-1} and 2.7 ng L^{-1} for human urine and standard samples, respectively (intra-day, Mean of LOD = 3)[162].

3.1. Chemistry techniques for heavy metals

Also, many chemistry techniques were reported in published papers for separation, extraction, preconcentration and speciation metals in different matrixes (Table 2). Recently, the liquid-liquid extraction methods (LLE) were used for separation and determination heavy metals from water and human biological samples. Some of LLE techniques such as, ultrasonic-thermostatic-assisted cloud point extraction procedure (UTA-CPE-FAAS), aqueous solvent-based dispersive liquid-liquid microextraction (AS-DLLME), cloud point extraction - slotted quartz tube-flame atomic absorption spectrometry (CPE-SQT-FAAS), surfactant-assisted dispersive liquid–liquid micro-extraction (SA-DLLME-FAAS), switchable liquid-liquid microextraction (SLLME-SQT-FAAS), surfactant-Based Dispersive Liquid-Liquid Microextraction based on FAAS(SB-DLLME-FAAS), vortex-assisted DLLME based on voltammetric (VA-DLLME-VM), microwave-assisted extraction - inductively coupled plasma-optical emission spectrometry (MAE-ICP-OES), Ionic liquid-based microwave-assisted dispersive liquid-liquid microextraction (IL-based MA-DLLME), Ionic liquid-based dispersive liquid-liquid microextraction (IL-DLLME), Ionic liquid

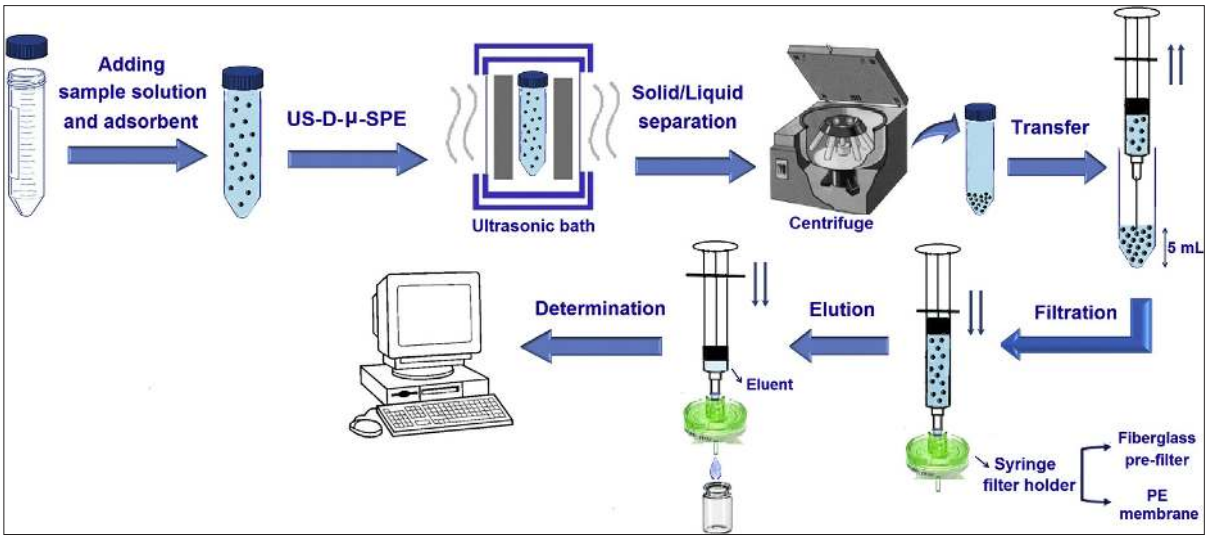


Fig. 8. Procedure of Mn speciation based on NH_2-UVM_7 by US-D-µ-SPE procedure [160].

Table 2. Solvent extraction for determination and separation of heavy metals in different matrix [173-197]

Sample	Metals	Method	Solvent /Ragent	EF/PF	LOD µg L^{-1}	Ref.
Wastewater	Cd	DLLME/SQT-FAAS	DPC	93.3	0.5	[173]
Milk Vegetables Foodstuffs	V(V) and Mo(VI)	UTA-CPE-FAAS	Nile blue A - PONPE	145 and 115	0.86 and 1.55	[174]
Parsley	Cd	CPE-SQT-FAAS	DPC	60	0.0007	[175]
Tap River Well water	Zn	SA-DLLME-FAAS	PAR	-----	0.5	[176]
Wastewater	Co	DLLME/SQT-FAAS	DPC	86.56	0.97	[177]
Tea vitamin B12	Co	SLLME-SQT-FAAS	Schiff base ligand	107.7	3.1	[178]
Food Water Samples	Cu(II)	SB-DLLME-FAAS	Triton X-114	50	1.61	[179]
Milk	Cd(II), Cu(II), Pb(II)	DLLME/FAAS	TDES	----	0.38–0.42	[180]
Chocolate	Ni	PV-IS-DLLME	APDC	17	100.0	[181]
Urine	Hg	VA-DLLME-VM	AuNPS-PE	---	1.1 - 1.3	[182]
human blood	Cr(III and VI)	CP-DILLME-ET-AAS	IICDET	25.2	0.0054	[183]
Human serum	Cd	DLLME-ETAAS	TSILs	10.2	0.005	[184]
Human blood	Cr(III and VI)	IL-DLLBME-ETAAS	NAC	10	0.005	[185]
Biodiesel	Na, K, Ca and Mg	RP-DLLME/FAAS	Iisopropanol,HNO_3,	----	0.006- 0.026	]186]
Water	Ta (I), Ta (III)	IL DLLME-ET-AAS	[C6MIm][PF6]	100	3.3 ng L^{-1}	[187]
Cosmetic	Hg (II), MeHg+ ,EtHg+	HPLC-ICPMS	[C6MIm][PF6]	760, 115, 235	1.3 ng L^{-1}	[188]
Wines	As (III)	DLLME-ETAAS	[C8MIm][PF6]	----	5.0 ng L^{-1}	[189]
Water	Cu(II)	DLLME-FAAS	[C4MIm][PF6] or [C16C4Im][Br]	54	3 300 ng L^{-1}	[190]
Water and leaves	Rh (III)	US-IL DLLME-FAAS	[C8MIm][NTf2]	----	0.37	[191]
Water	V (IV) and V (V)	TC-IL DLLME-ETAAS	[C4MIm][PF6]	----	0.0049	[192]
Tea, Soda Beer Milk	Se (IV)	USA-IL-DLLME-ETAAS	[C6MIm][NTf2]	150	12	[193]
Water	Au, Ag	MRTILs- DLLME-ETAAS	$[C_5(MIM)_2][NTf_2]_2$	245 and 240	3.2 and 3.7	[194]
Food	Zn, P, Cd, Pb, Fe, Mn, Mg, Cu, Ca, Al, Na, K	MAE -ICP-OES	MAE	----	0.01 mg kg^{-1} -7.8 mg kg^{-1}	[195]
Water	Pd and Pt	CPE-ICP OES	MBT	---	0.525 and 0.752	[196]
Water serum	Cu(II)	IL-mE-DLLME-CPE-ETAAS	Oxine-IL	70	0.132	[197]

EF: Enrichment Factor
UTA-CPE-FAAS: ultrasonic-thermostatic-assisted cloud point extraction procedure
AS-DLLME: Aqueous solvent-based dispersive liquid-liquid microextraction
DPC: Diphenylcarbazone
Nile blue A: 9-(diethylamino)benzo[a]phenoxazin-5-ylidene]azanium; sulfate-PONPE (polyoxyethylene-nonylphenyl ether
ETAAS: Electrothermal atomic absorption spectrometry
FAAS: Flame atomic absorption spectrometry
SQT-FAAS: Slotted quartz tube-flame atomic absorption spectrometry
CPE-SQT-FAAS: Cloud point extraction - slotted quartz tube-flame atomic absorption spectrometry
DPC: Diphenylcarbazone
SA-DLLME-FAAS : Surfactant-assisted dispersive liquid–liquid micro-extraction
PAR: 4-(2-pyridylazo) resorcinol
SLLME-SQT-FAAS: Switchable liquid-liquid microextraction
SB-DLLME-FAAS: Surfactant-Based Dispersive Liquid-Liquid Microextraction/FAAS
Triton X-114: Surfactant
TDES: Ternary deep eutectic solvent
APDC: ammonium pyrrolidine dithiocarbamate
VA-DLLME-VM: Vortex-assisted DLLME/ voltammetric
AuNPS-PE: gold nanoparticle-modified screen-printed electrodes
MAE-ICP-OES: microwave-assisted extraction - inductively coupled plasma-optical emission spectrometry
MBT: 2-mercaptobenzothiazole
Oxime-IL: 8-hydroxyquinoline-IL
UA-DLLME: Ultrasound-assisted dispersive liquid-liquid microextraction
UAE- IL-DLLME: Ultrasonic-assisted ionic liquid based dispersive liquid–liquid microextraction
USA-DLLME: Ultrasound-assisted dispersive liquid-liquid microextraction
USA-IL-DLLME: Ultrasound assisted ionic liquid dispersive liquid-liquid microextraction

ultrasound assisted dispersive liquid-liquid microextraction (IL-UA-DLLME), In-situ ionic liquid dispersive liquid-liquid microextraction(*in-situ* IL-DLLME), microwave-assisted extraction and dispersive liquid–liquid microextraction (MAE–DLLME), magnetic ionic liquid-based dispersive liquid-liquid microextraction) MIL-based DLLME), magnetic stirring-assisted dispersive liquid-liquid microextraction (MSA-DLLME), magnetic stirrer induced dispersive ionic-liquid microextraction (MS-IL-DLLME), microwave-assisted dispersive liquid-liquid microextraction(MWA-DLLME), ionic liquid dispersive microextraction (IL-DLLME), surfactant assisted dispersive liquid-liquid microextraction (SA-DLLME), switchable solvent-based dispersive liquid-liquid microex-

Table 3. Different sorbents for extraction of heavy metals in human and environmental samples [198- 218]

Sample	Method	Sorbent	Heavy metals	LOD (ng L^{-1})	EF/PF	AC(mg g^{-1})	Ref.
Serum Blood	USA-D-µSPE-ETAAS	NH_2-UVM_7	Cd	2.0	25	108.6	[198]
Waters	MCD-µSPE-ETAAS	GSH	Pb, Cd, Cr	8.9, 4.0, 10	17, 18,17	146.3, 132.5, 125.8	[199]
Waters River	USA-CP-MSPE	AFSA	Pb	10.0	102	---	[200]
Urine Water	USA-DSL-MPME	NH_2-UVM_7	As_{III}, As_V	1.1	100.5	---	[201]
Blood Water	US-D-IL- µSPE-AT-FAAS	NG-COOH	Hg, MHg, EHg	9.8	10.4	153.7, 125.8, 125.8	[202]
Water Tap W	US-D- µSPE	NH_2-UVM_7	Mn_{II} , Mn_{VII}	7.0, 8.0	102.3, 98.8	1733 and 570 µmol.g^{-1}	[203]
Serum Blood	USA-D- µSPE	GONPs	Al	20.0	25	187.5	[204]
Water Drinking	SPE-FAAS	CdSNPs	Pb, Cu	---	---	200, 166.7	[205]
Wastewater	FTIR	G+MGO	Pb^{2+}, d^{2+} ,Cu^{2+}	---	---	358.96, 388.4, 169.8	[206]
Waters	SPE-FAAS	GO	Pb, Ni	1400–2100	95-102.5	195, 178	[207]
Waters	ET-AAS	GO-NH_2	Pb (II)	9.4	100	479	[208]
serum urine	H-US-D-µ-SPE	G-COOH	As species	2.1	53	125.4	[209]
River water	CHD-µSPE	GO	Pb, Cd, Cr	110, 15, 38	15	----	[210]
Waters	SPE-ETAAS	MnO_2/ CNT	PB, Cd	4.4, 1.5	100	----	[211]
Waters Urine	DµSPE-TRXRFS	MWCNT	$Cr_{(VI)}$	3000	66	154.3	[212]
Soils Waters	SPE-ICPMS	Ti- MSN	Cu	3.9	10	----	[213]
Blood	M-SPµE-FAAS	Modified carbon cloth	Cd	150	10	----	[214]
FOOD	SPE-FAAS	Dowex Marathon C	Pb	130	250	----	[215]
Agricultur	SPE-FAAS	F-MOF	Zn	200	238	----	[216]
Foods	SPE-FAAS	B2O3/TiO2	Cd	1440	50	172.5	[217]
Waters	D-µSPE-ETAAS	NH_2-SiO_2-GO	Pb	9.4	100	----	[218]

AC: Absorption Capacity
EF/PF: Enrichment factor/preconcentration factor
ET-AAS: Electro-thermal atomic absorption spectrometry
FAAS: Flame atomic absorption spectrometry
GSH: Graphene-silica hybrid
USA-D-µSPE: Ultrasound assisted-dispersive-micro solid phase extraction
MCD-µSPE: Moderate centrifugation-assisted dispersive micro solid phase extraction
USA-CP-MSPE: Ultrasound-assisted cloud point-micro solid phase extraction
AFSA: Amine functionalized silica aerogel
USA-DSL-MPME: Ultrasound assisted-dispersive solid-liquid multiple phase microextraction
US-D-IL-µ-SPE: ultrasound assisted-dispersive-ionic liquid-micro-solid phase extraction
NG: Nanographene
CHD-µSPE: Coagulating homogenous dispersive micro-solid phase extraction
CdSPNs: Cadmium Sulfide Nanoparticles
TRXRFS: Total reflection X-ray fluorescence
GONPs: Graphene oxide nano-particles
M-SPµE: Miniaturized solid phase microextraction
SPE-FAAS: Solid phase extraction-flame atomic absorption spectrometry
GO-NH_2: Aminosilanized graphene oxide

traction (S-DLLME), temperature-assisted ionic liquid-based dispersive liquid–liquid Microextraction (TA-IL-DLLME), ultrasound-assisted dispersive liquid-liquid microextraction (UA-DLLME), ultrasonic-assisted ionic liquid based dispersive liquid–liquid microextraction (UAE- IL-DLLME), ultrasound-assisted dispersive liquid-liquid microextraction (USA-DLLME), ultrasound assisted ionic liquid dispersive liquid-liquid microextraction (USA-IL-DLLME) was used for heavy metal extraction in different matrixes (Table 2) [173-197]. Many researchers were reported other nanomaterial or sorbents for extraction metals and heavy metals from water, wastewaters, air pollution and human biological matrix which were shown in Table 3.

3.2. Nano particles for extraction heavy metals

The affinity of Hg towards Au was generally achieved by AuHg, AuHg3, and Au3Hg [219]. Lisha et al. reported the removal of Hg (II) with nanoparticles of Au (AuNPs) coated on aluminum [220]. NaBH4 helped to reduce Hg (II) to Hg (0) and removed by AuNPs with capacity of 4.0 g g^{-1}. Also, Jiménez et al. was used citrate-coated AuNPs for extraction mercury in water [221]. Absorption mercury with AuNPs was shown in Figure 9.

Magnetite (Fe_3O_4) as nanoadsorbent was used for heavy metal removal as environmental friendliness. Fe_3O_4 could be easily separated from liquid phase. Fe_3O_4 was used for heavy metals treatment in waters [222-224]. Giraldo et al. synthesized magnetite nanoparticles by using a co-precipitation method and were used for extracting of Pb (II) and Mn (II) in different samples [225]. In Figure 10, the removal of chromium was shown by chitosan–magnetite nanocomposite.

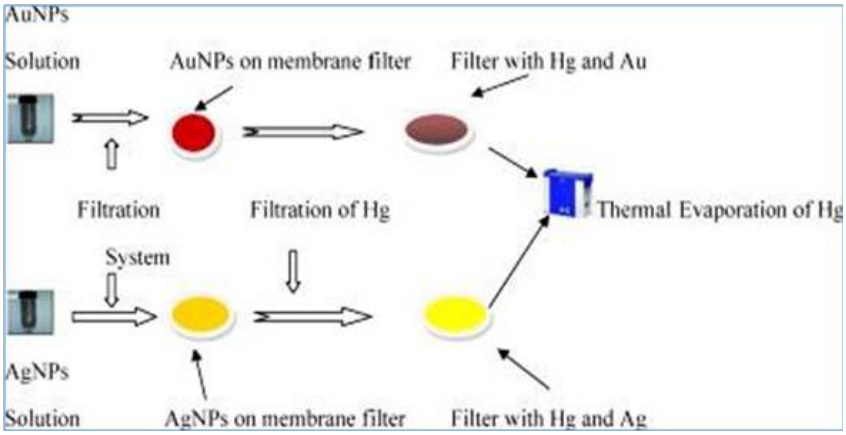


Fig. 9. The absorption mercury by AuNPs

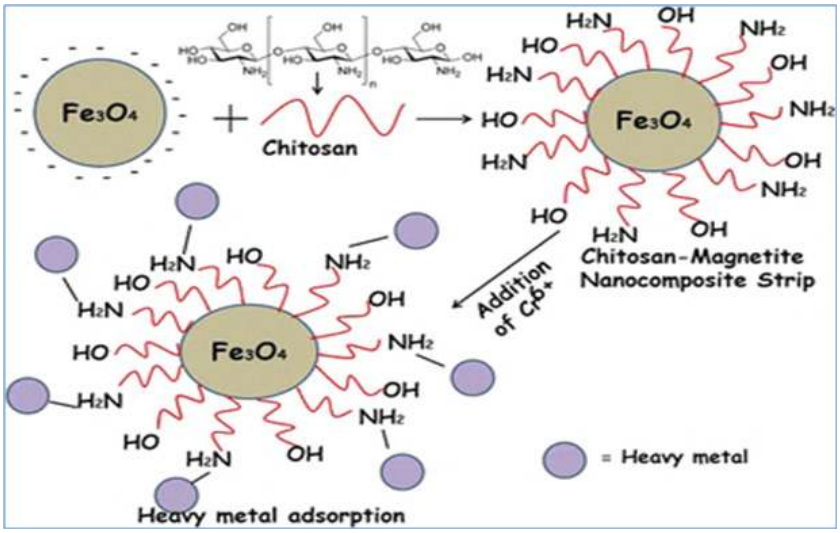


Fig. 10. The removal of chromium by chitosan–magnetite nanocomposite strip

Magnetite particles are modified with groups such as, MPs-NH2 [226], MPs–COOH [227], MPs–SH [228]. The core-shell structure of PI-b-PEG diblock copolymer encapsulated with iron oxide nanoparticles [229]. PI-b-PEG diblock copolymer was used for removal heavy metals from waters [230]. The nanostructures of amphiphilic diblock copolymers due to the inherent curvature of the polymer were shown in Figure 11 which was used for extraction lead and other heavy metals from different matrixes.

Zero valent iron as nanoparticles of is a Fe (0) and ferric oxide coating (nZVI) which was used for extraction heavy metals from different matrix (Figure 3) [231]. Also, nZVI as a novel adsorbent can be removed heavy metals (Fig. 12), such as mercury, chromium, copper, nickel, and cadmium from waters. [232-235]

The silica nanoparticles based on ligand of β-ketoenol–pyridine–furan (as a selective adsorbent was used for metal removal from waters (Pb,Cd,Zn,Cu) (Scheme 4). The engineered sorbent had high adsorption capacity for capturing toxic heavy metal in environmental samples [236-239].

4. Conclusions

In this review paper, constructive issues from novel published papers were selected for studying

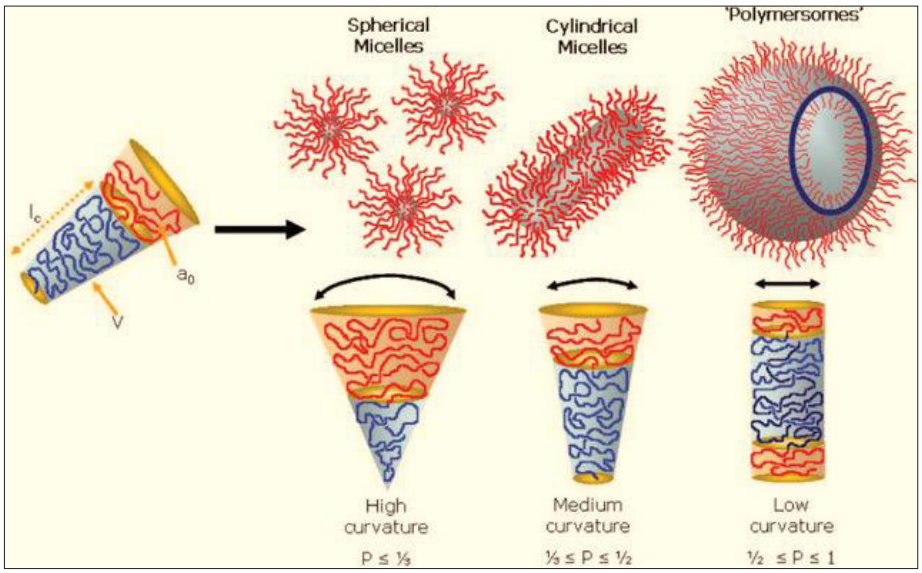


Fig. 11. The nanostructures of amphiphilic diblock copolymers for extraction lead ions

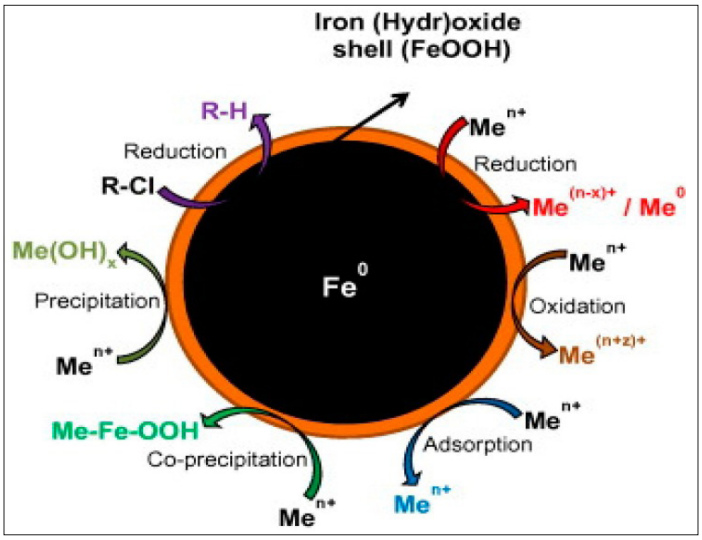
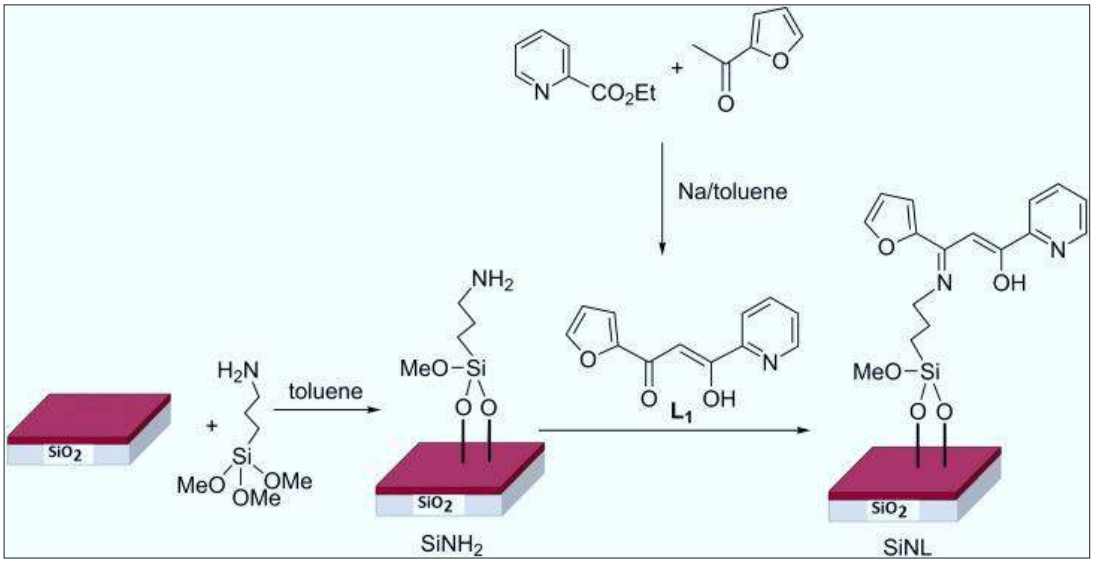


Fig. 12. The core-shell structure of nZVI used for extraction of metals [231]



Scheme 4. The Silica nanoparticles based on β-ketoenol–pyridine–furan as chelating agent for extraction heavy metals in liquid phase

of separation, preconcentration, and extraction of heavy metals from water, waste water, vegetable and human biologic samples. Recently, the SPE methods were coupled with spectrometry techniques such as atomic absorption spectrometry (AAS) based on various adsorbents included graphene, graphene oxide, activated carbon, carbon nanotubes (CNTs), zeolites, MOF, magnetic nanoparticles, carbon quantum dots (CQDs)a nd MSN which was used for ultra-trace determination of heavy metals in different matrixes. In addition, the liquid-liquid micro extraction techniques coupled with ET-AAS, F-AAS, ATF-AAS, SQT-FAAS, ICP-XRF, CV-AAS, ICP,ICP-AES, ICP-MS, ICP-OES, HPLC, voltammetry, UV-VIS, and FTIR were presented in this study by a lot of researchers. The proposed review showed us, the novel techniques based on nanotechnology had been developed in SPE and LLE methods since 2010 by authors. Also, SPE and solvent extraction based on different adsorbents and instrumental techniques were extended in various sciences such as, bio chemistry, nanotechnology, environmental analytical chemistry and human analysis during last decade.

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