CHAPTER II
2. Literature Review

2.1. Removal of Phenol and Phenolic Compounds

Removal of the phenolic compounds from industrial wastewater becomes necessary to protect the aqueous environment. The tolerance limit for phenolic compounds in drinking water is 0.001 mg.dm\(^{-3}\) according to the Bureau of Indian Standards [1]. Although many post-practices that resulted in substantial releases of these contaminants to the environment have been corrected, treatment technologies for their removal from aqueous waste streams are still needed [2]. There are various treatment technologies available, but the applicability of a particular method depends on the concentration or the load of phenols introduced into water [3].

Among the various physicochemical methods liquid-liquid extraction is one of the most simple and useful techniques. Solvent extraction with organic solvents such as benzene, heptane, toluene, methyl isobutyl ketone, isopropyl ether, isopropyl acetate was known for phenol recovery [4]. Extraction of phenols from the aqueous phase to organic solvents, such as chloroform [5], aliphatic alcohols (hexanol, octanol) [6], phosphoric acid esters [7, 8] has been studied. In general, such extraction is not very efficient, especially for the most hydrophilic phenols and therefore, mixed solvents are often used to enhance distribution coefficients [5, 8, 9]. Phenol being a weak acid (pK\(_a\) = 9.98) can be efficiently extracted with various basic and solvating reagents, including trialkyl phosphine sulfide, tributyl phosphate (TBP) and trialkyl phosphine oxides [10-15].

The extraction/removal of phenolic compounds (phenol, m-cresol, resorcinol) from alkaline medium via reaction with benzoyl chloride dissolved in toluene, as the solvent, under two phase conditions using hexadecyl tributyl phosphonium bromide as a phase transfer catalyst has been investigated [16]. Two types of experiments were performed to assess the utility of the reaction scheme for treatment of industrial wastewater. Results of stirred cell experiment
showed that the reactions of phenols conform to a diffusion-limited fast pseudo-first order kinetics. The rate enhancement of the reaction was reasonably low as compared to that reported when Aliquat 336 was used as the catalyst. The specific rate of extraction decreased in the order: phenol > m-cresol > resorcinol. Experiment conducted in a batch agitated reactor with individual phenolic compounds as well as their mixtures, representing compositions typical of industrial wastewater, showed that the volumetric rate of extraction was dependent on stirring speed under otherwise identical conditions. Conversion of phenols in a batch agitated reactor was >99.5% under suitable conditions of stirring speed and reaction times [16].

Coupling of extraction with subsequent voltammetric detection of phenols typically requires back-extraction or addition of background electrolyte, as common organic solvents are not conductive. However, the room temperature ionic liquids (RTILs) might be a convenient medium for both extraction and direct voltammetric analysis of the extracts. These RTILs are low melting, have high conductivity and are immiscible with water. Additionally, they have negligible vapor pressure which makes them environment friendly alternatives to conventional solvents [17-19]. Recently several phenolic compounds like phenol, 4-nitrophenol (4-NP), 2,4-dinitrophenol (2,4-DNP), 2,6-dinitrophenol (2,6-DNP), 1-naphthol, 2-naphthol and 4-chlorophenol (4-CP) are extracted nearly quantitatively from aqueous solution into RTIL, viz. 1-butyl-3-methylimidazolium hexafluoro phosphate (BMImPF₆) in molecular form at pH < pKₐ. The electrochemical window of BMImPF₆ at various electrodes was determined and voltammetric oxidation of phenols and reduction of nitrophenols in BMImPF₆ were studied by Khachatryan et al. [20].

There are important drawbacks to classical dispersive extraction, for instance, third phase formation, emulsification, dissolution of reagent and diluent in the aqueous phase as well as incidental leakage. As a result, solvent extraction may cause significant contamination of aqueous stream with spent chemicals. These
problems can be eliminated using membrane process. Membrane process seems to be natural successor of traditional extraction process [21]. Membrane assisted solvent extraction of phenols combined with large volume injection – gas chromatography was investigated by Schellin et al [22]. Hollow fiber modules were used by several authors to recover toxic substances, including phenol, from various aqueous effluents [23-28]. Methyl isobutyl ketone, isopropyl acetate and methyl tert-butyl ether were used as carriers for phenol recovery. Garea et al [29] had used Cyanex 923 for phenol extraction with a supported liquid membrane.

A setup with two parallel hollow-fiber modules was used to study for the recovery of phenol from aqueous solutions. Cyanex 923, Amberlite LA-2 and trioctylamine (TOA) in aliphatic kerosene were used as carriers. It was found that each of the studied carriers permitted the effective removal of phenol. Cyanex 923 showed the best performance in removing phenol in the shortest time, giving the highest fluxes and the highest mass-transfer coefficients [30].

Liquid-liquid extraction (LLE) is, however, limited by the specific choice of solvent, high cost and generation of large volume of organic solvent, long analysis time and tedious process. Among the various available technologies for the removal of organic pollutants, solid phase extraction (SPE) has become the choice of analytical chemists for removal or separation of various toxicants. The popularity of SPE is due to the availability of different kinds of adsorbents (both natural and synthetic), applicability to wastewater with wide range of phenol concentration (dilute and moderate), precise result, simplicity and quick operation. Adsorbents may be classified broadly as conventional and non-conventional.

Among the conventional adsorbents polymeric resin, activated carbon, silica based polymer are widely used for removal of phenol and its derivatives. The reported studies mostly deal with adsorption characteristics of phenolic
compounds on different activated carbons [31-41]. However, the demanding regeneration and poor mechanical rigidity of activated carbon pose limitations to its wider application. Girgis et al. [42] [14] studied the removal capacity of activated carbons, modified with H$_3$PO$_4$ treatment under flowing gases, for removal of wide variety of pollutants, viz. 4-NP, methylene blue dye and lead ions from aqueous solutions.

The efficiency of synthetically designed calcium and calcium-iron alginate gel beads in removing some nitrophenols was studied by Peretz and Cinteza [43]. Adsorption behavior of various phenol analogues by Amberlite XAD-4 resin under different conditions revealed that the removal is feasible in acidic conditions, but decreased significantly with increasing pH of the solution [44]. The extent of adsorption was, however, correlated with the presence of functional groups on the benzene ring of various phenols. Pan et al. [45] studied the removal of 4-NP using a hyper-cross-linked polymeric adsorbent (NDA-701) in fixed bed column and compared its adsorption capacity with those of Amberlite XAD-4 and a granular activated carbon GAC-1. It was found that NDA-701 exhibited better performance than both XAD-4 and GAC-1. Single component adsorption study of phenol as well as 2-, 3- and 4-NP from water on cobalt loaded carboxymethyl diaminoethane sporopollenin was made by Ayar et al. [46]. The nitro-substituted phenols were found to be less strongly adsorbed than the phenol. Both the binding strength and theoretical saturation capacity are correlated with the position of nitro substituent, which follows an order: phenol < 4-NP < 3-NP < 2-NP, while a reverse order is followed for binding strengths. Tewari and Kamaluddin [47] studied the removal of o-aminophenol and o-nitrophenol from aqueous solution using copper, zinc, molybdenum and chromium ferrocyanides in the pH range 2-10 at 27°C, where molybdenum ferrocyanide exhibited the highest sorption capacity and chromium ferrocyanide the lowest. It was further noted that adsorption of o-nitrophenol was more than that of o-aminophenol on all the metal ferrocyanides studied. Burleigh et al. [48]
investigated the adsorption capacities of 4-NP, 4-CP and 4-methylphenol in both batch and column mode using synthesized arylene- and ethylene-bridged polysilsesquioxane materials, where the former one exhibited a much greater affinity for all the three solutes. A novel hydrophilic adsorbent was prepared by Sayilkan et al. [49] by modification of hydrophobic pyrophyllite by treatment with prehydrolyzed N-(2-aminoethyl)-3-aminopropyltri-methoxysilane for the removal of 4-NP from aqueous solutions.

Adsorption study of phenols and substituted phenols on different adsorbents like hydrous ZnS [50], amorphous alumina [51] and soil [52] are well established. Sorption mechanism and retention characteristics of some nitro-phenols onto unloaded polyurethane foams (PUFs) were also demonstrated [53].

In recent years, there has been an increasing interest in utilizing clay minerals such as bentonite, kaolinite, diatomite and Fuller's earth to adsorb various solutes, both inorganic and organic in nature. Phenol removal from aqueous solutions on bentonite was studied by Banat et al. [54]. Removal of trichlorophenol (TCP) was investigated with calcium montmorillonite (pure clay), montmorillonite-humic complexes, and natural soils [55]. The differential behavior in adsorption-desorption characteristic of the solutes was explained in terms of nature and composition of organic matter as well as their interaction with the mineral fraction. Adsorption of phenol in granite residual soil and kaolinite indicated that the residual soil possesses greater adsorption capacity compared to that of kaolinite [56]. The adsorption of phenol by organoclays and a coal/mineral complex was studied by Ramos-Vianna et al. [57].

Adsorption extent of phenolic compounds are substantially improved by modifying the clay materials, viz. modified Clarion clay and clinoptylolite [58]. Alumina pillared montmorillonite and mesoporous alumina aluminum phosphates were used to remove 2,4-dichlorophenol (2,4-DCP), 2,4,6-TCP and pentachlorophenol (PCP) [59]. The removal of chlorophenols increases with
increasing chlorine substitution in their molecules. Removal of phenol was studied by Shen [60] using various organosmectites modified with quaternary ammonium surfactants, viz. benzyltrimethylammonium ion and hexadecyltrimethylammonium ion. The exchanged organic cations affected the adsorptive behavior of modified smectite which is appeared to be dependent on the size and molecular arrangement of the surfactant used. The adsorption of phenol and dichlorophenols by a porous clay heterostructure (PCH) was reported [61]. The adsorption capacity of PCH was explained in terms of both hydrophobic and hydrophilic characteristics, due to the presence of silanol and siloxane groups introduced during the pillaring and preparation of the PCH. The adsorption of dinitrophenol herbicides, 4,6-dinitro-o-cresol and 4,6-dinitro-o-sec-butyl phenol, by two reference smectite clays was evidenced from FTIR spectroscopy, XRD and molecular dynamic simulations [62]. Adsorption of phenol and 2-, 3- and 4-CP from water by tetramethylammonium (TMA)-smectite and tetramethylphosphonium (TMP)-smectite was compared [63]. TMP-smectite was found to be a better adsorbent than TMA-smectite. The selectivity appeared to be size and shape dependent, and not strongly influenced by solubility parameters of the solutes. Adsorption of phenol on mono, bis and tris(2,2'-bipyridine)nickel(II)- and tris(ethylenediamine) nickel(II)-saponite intercalated compounds from aqueous solution shows that the latter was less effective than the former [64]. This suggests that the interactions between pyridine rings and phenol played an important role in the adsorption of phenol. Okada and Ogawa [65] studied removal of phenol using 1,1'-dimethyl-4,4'-bipyridinium-smectites as adsorbent.

Experimental investigation on the adsorption characteristics of phenol and m-chlorophenol (3-CP) by organobentonites, prepared by modifying natural bentonite with several quaternary amines, was conducted [66]. Multistage adsorption of phenol and chlorophenol by organobentonites was compared with that calculated theoretically. Bouras et al. [67] investigated the removal ability
of different surfactant-modified iron-pillared bentonite for PCP removal from aqueous stream. Yaneva and Koumanova [68] found that the adsorption capacity of yellow bentonite for nitrophenols increases in the order: 2-NP < 2,4-DNP < 4-NP. Zhu and Chen [69] prepared a series of anion-cation organobentonites by incorporating both cationic (DTMAB) and anionic (SDS) surfactants to bentonite and studied their efficiency in removing 4-NP from water. The adsorption capacity depends greatly on the amount of incorporated SDS and DTMAB on bentonite.

The adsorption of 2,4-DCP in a batch technique on organoclays (surfactant/clay complexes), synthesized by partial modification of Na-montmorillonite with different surfactants showed greater efficiency for dialkylammonium-modified organoclays [70]. Zhou et al. [71] showed that the adsorption of 4-NP on surfactant modified montmorillonite is greater than that of untreated montmorillonite. Rytwo et al. [72] reported adsorption ability, compared to activated carbon, of naphthalene and several phenolic derivatives on organoclays prepared by adsorption of crystal violet or tetraphenylphosphonium ions on montmorillonite. Recently, a hybrid process of adsorption (on clay) and ultrafiltration has been reported to remove the phenolic compounds (phenol and o-cresol) from water [73]. Modification of clay by placing quaternary ammonium cations on smectite by cation exchange was made to examine their ability to adsorb phenol and several of its chlorinated congeners [74]. The complexes containing long chain alkyl (hexadecyl) groups, being more hydrophobic, adsorbed more phenols from water. The extent of adsorption is explained in terms of solute hydrophobicity that increases with chloro-substitution of phenol.

The adsorption of p-chlorophenol (4-CP) from aqueous solutions on bentonite and perlite indicated higher adsorption capacity for bentonite than perlite [75]. The adsorption of 4-CP and 4-NP on organophilic bentonite was studied as a function of solution concentration and temperature by Akcay and Akcay [76]. The amount of adsorption was found to be dependent on the relative energies of
adsorbent-adsorbate, adsorbate-solvent and adsorbate-adsorbate interaction. The removal of phenol from aqueous solutions using three different adsorbents, clinoptilolite, montmorillonite, and hydrotalcite, as well as their modified forms was studied to find the efficiency [77-79].

There is an increased demand to use natural siliceous adsorbents, such as silica beads, glasses, alunite, perlite and dolomite, for wastewater treatment because of their abundance, availability and low price. Silica beads, modified with various functional groups, deserve particular attention for removal of phenolic compounds [80-84]. However, due to their low resistance toward alkaline solutions their usage is limited to pH less than 8 [85]. Removal of phenol using alunite, a low cost siliceous material, indicates that the surface charge on the adsorbent and the pH have influence on the capacity of alunite. Experiments have been conducted to examine the adsorption of phenol from water by silica gel, HiSiv 3000, activated alumina, activated carbon, Filtrasorb-400 and HiSiv 1000 [86]. The influence of particle size, temperature and thermal regeneration on adsorption of phenol was evaluated.

Zeolites, the highly porous aluminosilicates with different cavity structures, have been intensively studied recently in removing phenolic compounds [87]. The adsorption capacity was found slightly higher at low phenol concentration (< 6 g.dm\(^{-3}\)) than that of activated carbon. A relationship between adsorption properties of zeolite catalyst was correlated with its composition by Kozhevnikov et al. [88] for the removal of phenol. The adsorption characteristic of phenol and 4-CP by surfactant-modified zeolite was investigated by Kuleyin [89]. Su et al. [90] reported that zeolite-templated porous carbons with different pore structures and surface properties have high adsorption characteristic for phenol. The adsorption capacity of phenol on the porous carbons after thermal treatment was markedly increased in spite of reduced surface area and pore volume, possibly due to formation of water molecular cluster, \(\pi-\pi\) dispersive interaction, electron donor-acceptor mechanism, and micropore structure. The
adsorption of o-, m- and p-nitrophenols on clinoptilolite type natural zeolite has been studied as a function of the solution concentration and temperature [91]. The adsorption rate was fitted to the first-order kinetics. The activation energies of adsorption were estimated using the Arrhenius equation. Adsorption isotherms were found to follow either Freundlich or Langmuir model. Removal of phenol using Indonesian natural zeolite in presence of microbial growth was studied in a column mode [92]. The bed was inoculated with *Pseudomonas putida*, which slowed down the adsorption as it contributed in increasing the mass transfer resistance. Shu *et al.* [93] utilized a novel class of aluminosilicate-based microporous materials, viz. pillared clays, silicalite and zeolite beta, in order to adsorb phenols selectively from aqueous solution. Factors which are important in determining the selectivity and adsorption capacity of these adsorbents are the hydrophobicity of the adsorbent, the size of the organic solutes and the pore diameter of adsorbent particles which are accessible to the adsorbate. Ghiaci *et al.* [94] utilized modified organo-zeolites modified with hexadecyltrimethylammonium (HDTMA) bromide and n-cetyl pyridinium bromide (CPB) as well as MCM-41 molecular sieve for the removal of phenolic compounds.

Bioadsorbents or biosorbents are now-a-days examined for the accumulation and concentration of pollutants from aqueous solutions. The different functional groups present in the biological materials, such as chitin, chitosan, peat, yeasts, fungi or bacterial biomass, undergo chelating and complexing interactions with phenolic compounds effecting their removal from solutions. Chitin and chitosan are the popular biopolymers used for the removal of phenols, even at low concentration (ppm or ppb levels). Chitin is found in a wide range of natural sources such as crustaceans, fungi, insects, annelids and molluscs. However, chitin and chitosan are only commercially extracted from crustaceans (crab, krill, and crayfish) primarily because a large amount of the crustacean's exoskeleton is available as a by-product in food processing. The chitosans
exhibited a high affinity to phenolic compounds [95]. Dursun and Kalayci [96] studied the adsorption of phenol onto chitin. The ability of chitin to bind phenol was tested using equilibrium, kinetic and thermodynamic aspects. A two-step approach for removing phenolic compounds, viz. cresol and catechol, from aqueous solutions by the enzyme mushroom tyrosinase was investigated [97]. In the first step, weakly adsorbable phenols are converted to quinines, which are then chemisorbed onto chitosan finally. The evaluation of applicability of chitin and chitosan for solid phase extraction of phenol and chlorophenols was studied by Rhee et al. [98]. In order to improve the adsorption capacity of phenol, chitosan was immobilized with matrix *P. putida*. Biodegradation of phenol by *P. putida* (NICM 2174) has been investigated for its degrading potential under different conditions [99]. The adsorption isotherms are described by Langmuir, Freundlich and Redlich-Peterson models. Subsequently the adsorption capacity, energy of adsorption, number of layers and the rate constants were evaluated. Intraparticle diffusion was found to be the rate-limiting step. Cell growth contributed significantly to phenol removal rates especially when the degradation medium was supplemented with an utilizable carbon source.

Peat is a porous and rather complex soil material with variable contents of organic matter and is formed through various stages of microbial decomposition. Chemical processes are used to improve adsorption properties and selectivity of peat. For example, Sun and Yang [100] prepared modified peat-resin by mixing oxidizing peat with polyvinylalcohol and formaldehyde. Various pollutant-binding mechanisms are thought to be involved in the bioadsorption process on peat, including physical adsorption, ion-exchange, complexation, adsorption-complexation and chemisorption [101]. Batch kinetic and isotherm studies were carried out to determine the adsorptive characteristics of peat and bentonite mixtures in different ratios for removal of PCP [102]. Batch isotherm studies showed that the adsorption of PCP by the peat-bentonite mixture from aqueous solution was best described by the Freundlich isotherm
Batch adsorption studies using peat at various dissolved oxygen (DO) levels in water showed that higher POP removal can be attained at elevated DO levels [103]. This effect can be quantified by a comparison of the adsorption capacities of peat from linearized Freundlich isotherms developed for different oxygen levels.

Removal of phenolic compounds by biomass (dead or living), white-rot fungi and other microbial cultures [104] gains popularity. Microbial biomass is produced as a by-product in fermentation processes during synthesize of various antibiotics and enzymes. Recent literature focuses on the removal of phenol and its analogues from wastewater through microbial adsorption / biodegradation process [105-108]. Certain species, like *Pseudomonas* sp., under very controlled conditions of pH, temperature and in the presence of some specific nutrients, affect biodegradation of phenol. *Pseudomonas* strain, capable of degrading PCP has been isolated around tannery soil and characterized as *Pseudomonas aeruginosa* [109, 110]. The potential use of the fungus *Phanerochaete chrysosporium* to remove phenol and chlorophenols from aqueous solutions was evaluated by Denizli *et al.* [111]. The kinetics of both adsorption and desorption of phenolic compounds, viz. 2,4,6-TCP, 4-CP and 2-CP was rapid. The affinity was found to follow the order : 2,4,6-TCP > 4-CP > 2-CP > phenol. Desorption of phenol and chlorophenols was achieved using methanol solution (30% (v/v)). *Phanerochaete chrysosporium* is found suitable for reuse for more than ten cycles without any noticeable loss of adsorption capacity. Wang *et al.* [112] investigated the adsorption behavior of PCP from aqueous solution to activated sludge biomass. The experimental results indicated that the initial pH value and biomass concentration are important parameters affecting the adsorption capacity that increased with decreasing biomass concentration. The adsorption and biodegradation of phenol from aqueous solution using chitin-immobilized with bacteria has been investigated under different reaction conditions in batch equilibrium mode [113]. The kinetics followed pseudo-first order rate
expression and intraparticle diffusion played a significant role. Adsorption and desorption of PCP to microbial biomass were studied at varying pH, ionic strength and the concentration of dissolved organic matter [114]. A simple mathematical model, considering separate adsorption coefficients for the neutral and dissociated fraction of PCP was developed. The capacity of the fungus *Pleurotus sajor caju* to remove phenols (viz. phenol, 2-CP, 4-CP and 2,4,6-TCP) from aqueous solutions was evaluated by Denizli *et al.* [115]. The affinity order was found to follow: 2,4,6-TCP > 4-CP > 2-CP > phenol. This showed that the presence of electronegative group in the phenolic compounds affects the adsorption capacity. The solid biomass is reported to be suitable for reuse for more than five cycles. The use of sulphuric acid pre-treated cells of *Aspergillus niger* to remove phenol from an aqueous solution was studied in column mode by Rao and Viraraghavan [116]. The adsorption of phenol was best described by the Brunauer-Emmet-Teller model. The bioadsorption of phenol, 2-CP and 4-CP on *Sargassum muticum* has been investigated using the batch technique [117]. A chemical pre-treatment with CaCl₂ has been found to improve the stability as well as the adsorption capacity of the algal biomass. Batch experiments were conducted to study the biosorption of chlorophenols from aqueous solutions by non-living *P. chrysosporium* mycelial pellets [118, 119]. The adsorption capacity on mycelial pellets was in the order: phenol << 2-CP < 4-CP << 2,4-DCP. The adsorption increased with decreasing water solubility and increasing octanol-water partitioning coefficient. The presence of 2CP or 4CP and the initial concentrations of 2-CP or 4-CP had no significant effect on the adsorption of 2,4-DCP on fungal mycelial pellets, demonstrating that simple surface adsorption might not be responsible for the adsorption of phenolic compounds. Biosorption of phenol by the marine seaweeds *Lessonia nigrescens* Bory and *Macrocystis integrifolia* Bory was investigated as a function of pH [120]. It has been explained that a polar mechanism is involved in the formation of hydrogen bonds with the hydroxyl groups, spatially arranged in the polysaccharic chains of seaweed structure.
Abel et al. [121] compared the ability of biological and non-biological adsorbents to remove 2-NP and 2-CP from aqueous solutions at room temperature using marine seaweeds (viz. *Macroystis integrifolia* Bory (S1) and *Lessonia nigrescens* Bory (S2)), crosslinked with CaCl$_2$, and natural bentonite, chemically exchanged with hexadecyltrimethylammonium bromide (B1) and bencyltriethylammonium chloride (B2). It was found that the maximum adsorption capacity of 2-NP followed the order: S1 > S2 > B2 > B1 within the range of 97.37-18.64 mg.g$^{-1}$ whereas for 2-CP, it ranged between 24.18 and 9.95 mg.g$^{-1}$ with the trend : S1 > S2 > B2 =B1.

The agriculture based waste materials and industrial by-products are attempted as low-cost adsorbents since they are abundant, inexpensive, and require little processing. Commercially available activated carbons (AC) are usually derived from natural materials such as wood, coconut shell, lignite or coal, but almost any carbonaceous material may be used as precursor for the preparation of carbon adsorbents. Adsorption isotherms for mono-, di-, and tri-chlorophenols from aqueous solutions on wood-based and lignite-based carbons have been studied [122]. The capacity for activated carbon for adsorption of 2,4-DCP was found to be 502 mg.g$^{-1}$. Particle size did not appear to play a significant role on chlorophenol adsorption; although, larger particles were associated with a slightly diminished adsorption capacity. Isotherms for 2,4-DCP adsorption onto activated carbon were generated and the Freundlich model was used to fit the experimental data [123].

The kinetics of adsorption of phenols by granular activated carbon was studied by Zogorski et al. [124]. It was observed that 60-80% of the ultimate adsorption occurs within the first hour of contact followed by a very slow approach to the final maximum equilibrium concentration. The extent of adsorption of 2,4-DCP as a function of pH was investigated and explained in terms of pKa [125, 126]. Order of adsorption extent for phenol and chlorophenols on activated carbon reported by Caturla et al. [127] and Jossens et al. [128] is somewhat different.
possibly due to difference in the source, nature and properties of AC used. High-surface-area activated carbons were prepared by chemical activation of coconut shell with KOH as active agent [129]. The influence of activation parameters on the final products was studied by varying the KOH-to-shell ratio, activation temperature and pre-heat temperatures. Pre-treatment at 600°C favored the yield of the product with high surface-area. The activated carbons exhibited a much higher adsorption capacity for phenol, 4-CP and 4-NP from aqueous solution than did a commercial activated carbon. Radhika and Palanivelu [130] studied the adsorptive removal as well as desorption of PCP and 2,4,6-TCP from aqueous solutions on coconut shell activated carbon treated with different chemicals, viz. KOH, NaOH, CaCO₃, H₃PO₄ and ZnCl₂. The adsorption equilibria of phenol from water onto activated carbons with different surface functional groups were studied as a function of temperature by Seidel et al. [131]. Moreover, the presence of dissolved oxygen increased the adsorptive capacity of activated carbons for phenolic compounds [132]. The increase was attributed to the oligomerization of the compounds through oxidative coupling reactions. The presence of acidic functional groups on the surface of the carbons impacted the ability of activated carbon to adsorb phenolic compounds under oxic conditions. The presence of oxygen-containing basic groups such as chromene-type and pyrone-type was reported to be a key factor in promoting irreversible adsorption. The presence of molecular oxygen was found to increase the adsorptive capacity of granular activated carbon (GAC) for phenolic compounds by three fold with an appreciable amount of oxygen consumed during the adsorption [133]. The acidic oxygen surface complexes of GAC decreased the chemisorption of phenols [134]. The adsorption of phenols was found to greatly decrease due to the hydration of the surface functional groups of AC, due to blocking of the pore entrances, thus reducing the surface area available for adsorption. At high adsorbate concentrations, it was found that the interactions between the adsorbate molecules affected the adsorption process more than the adsorbent-adsorbate forces [135].
Studies have been performed on the removal of substituted phenols by carbonaceous adsorbents obtained from fertilizer waste [136]. Adsorption equilibria of phenolic compounds over a wide range of concentrations onto activated carbon were demonstrated by Juang et al. [137]. Higher adsorption capacities were found for the chlorinated phenols when compared to the methyl-substituted phenols. This may be due the presence of electronegative group in the chlorinated phenols. Activated carbon prepared from agricultural waste by-products, like rubber seed coat and tamarind nutshell has been used for the adsorption of phenol from aqueous solution [138, 139]. The removal of 3-CP from water by carbon derived from burning of rice straw was evaluated [140]. The adsorption occurred most strongly when CP existed as a neutral species. Activated carbons prepared from date pits have been examined for the adsorption of phenol from aqueous solutions [141]. The kinetic model and adsorption capacity were evaluated. Removal of phenol and 4-CP from aqueous solutions by chemically activated olive stones was studied [142]. The adsorption capacity was determined by fitting the data to Langmuir isotherm model and compared with that of commercial-grade powdered activated carbons. El-Hendawy [143] studied the influence of HNO₃ oxidation on the structure and adsorptive properties of corncob-based activated carbon and found its efficiency for removal of phenol and nitrophenols.

Efforts have been made to convert fertilizer waste and steel industry waste into low-cost potential adsorbents, which was used for the removal of aminophenol from aqueous solutions and wastewaters. The effects of temperature, initial adsorbate concentration, particle size of the adsorbent and solid-to-liquid ratio were evaluated [144]. It is found that activated carbon developed from fertilizer waste exhibits better performance than activated slag developed from blast furnace slag. Srivastava and Tyagi [145] studied the competitive uptake of various phenols, viz. 2,4,6-TNP, 4-NP, 4-CP and 1,3-dihydroxybenzene, from industrial wastewater by a carbonaceous adsorbent developed from fertilizer
waste. Adsorption studies were conducted to study the removal of 2,4-DCP from aqueous solution on palm pith carbon [146]. Thermodynamic study showed that adsorption of 2,4-DCP on palm pith carbon was more favorable. Namasivayam and Kavita [147] studied the removal of phenol, 2,4,6-TCP and PCP from aqueous solution on coir pith carbon and the suitable isotherm model was evaluated. It is indicated from the pH effect and desorption study that chemisorption plays a major role in the adsorption process. Namasivayam and Sangeetha [148] examined the adsorption capacity of ZnCl₂ activated coir pith carbon for the treatment of wastewater, contaminated with toxic anions, heavy metals, dyes and phenolic compounds. The results showed that the adsorbent was effective for removal of toxic pollutants from water. Daifullah and Girgis [149] tested the removal of phenol, m-, p-cresol, 2-CP, 4-NP, 2,4-DCP and 2,4-DNP by adsorption onto activated carbon prepared from apricot stone shells by chemical treatment with H₃PO₄. Disubstituted phenolic compounds were well correlated with respective increase in molecular dimensions, acidity and decrease in solubility of the sorbates. Activated carbon derived from beet pulp, a major low value by-product in sugar industry, was used for phenol adsorption in terms of kinetic and thermodynamic parameters [150]. Wu et al. [151] prepared the carbonaceous adsorbents with controllable pore sizes from carbonized fir wood (i.e., char), either by KOH treatment or by steam activation, for the removal of phenols. As the different treatments result activated carbon with different surface area and pore volume, the adsorption efficiency varies widely. The adsorption capacity of the activated carbons produced from palm oil mill effluent (POME) sludge was evaluated for phenol removal by Alam et al. [152]. Batch adsorption studies showed an equilibrium time of 6 h for the activated carbon of POME 800. Activated carbons prepared from Tectona grandis sawdust, a timber industry waste, and treated with ZnCl₂, have been examined for the removal of phenol from aqueous solutions by Mohanty et al. [153].
Low-cost adsorbents, such as coal, can also be used for the removal of phenolic compounds. Coal is a porous material and is known to have micro porosity and thus high surface area. There is a significant increase in capacity when coal is activated with either steam or carbon dioxide or their mixture as activated gases or with iron. Teng et al. [154] used phosphoric acid impregnation followed by carbonization in nitrogen at 400°C-600°C to obtain activated carbon from Australian brown coal. Moreno-Castilla et al. [155] prepared activated carbon from Spanish bituminous coal by a two-stage pyrolysis at 850°C in nitrogen flow followed by steam activation at 840°C for different periods of time and was used for the adsorption of phenol, p-cresol, 3-CP, m-aminophenol and 4-NP from aqueous solutions. The adsorption capacities for the solutes were explained in terms of surface area and porosity of the carbon, the solubility of the phenolic compound and the hydrophobicity of the substituent. Haghseresth and Lu [156] studied the adsorption of phenolic compounds onto coal-reject derived adsorbents. It was found that nitric acid pre-treatment significantly enhanced the surface properties and consequently the adsorption capacity. It was also observed that the Redlich-Peterson equation fitted the experimental data best. Hobday et al. [157] used a range of Victorian brown coal-based material to remove nitrophenol from aqueous solution. The influence of particle size, presence of buffer solution components, other electrolytes and pH on the kinetics of adsorption of nitrophenol were investigated. A Lakhra coal sample (Sindh province) was treated with various leachants like NaOH and HCl and used for adsorption of environmentally objectionable phenol by Ishaq et al. [158]. NaOH treated coal may be best-suited for phenol adsorption compared to other coal samples. Studies on the adsorption of phenol from aqueous solution using pre-treated non-coking low-grade bituminous coal are reported by Das and Sharma [159]. The coal showed better adsorption after oxidation for more than 6 h. Extraction with quinoline and ethylenediamine showed a remarkable increase in phenol adsorption. Ahmaruzzaman and Sharma [160] investigated the possible use of coal, residual coal and residual coal treated with H$_3$PO$_4$ as
adsorbents for removal of phenol from the wastewater and the kinetic model was evaluated. A raw lignitic coal was investigated for phenol removal from wastewaters [161]. Hydrogen-bonding of phenolic –OH with the oxygen sites on lignite surface is the most likely mechanism for adsorption. Cheap adsorbents were also produced from lignites for the removal of phenolic compounds by Finquensel et al. [162]. Othman et al. [163] evaluated the efficacy of three activated carbons and two chars made from low rank coal to remove 4-NP and natural organic matter from aqueous systems. The adsorption was improved with decreasing particle size and higher carbon mass loadings. Gupta et al. [164] converted the waste slurry generated in fertilizer plant into a cheap carbonaceous adsorbent material and investigated its practical applicability in column operations for the removal of 2,4,6-TCP, 4-NP, 4-CP and 1,3-dihydroxybenzene. Recovery of phenols and chemical regeneration of the spent column showed that 70 cm$^3$ of 5% w/w NaOH or 50 cm$^3$ of acetone were sufficient for almost complete desorption of phenols. After regeneration with 1M HNO$_3$ the sorption capacity of the column was almost the same as that of virgin adsorbent material.

The role of sawdust materials, an agricultural solid waste, in the removal of pollutants, particularly phenol, from aqueous solutions has been reviewed by Shukla et al. [165]. Dutta et al. [166] carried out the studies on adsorption of p-NP on charred sawdust. Adsorption equilibrium data was found to fit most satisfactorily with the Langmuir adsorption isotherm. Nenkova and Radev [167] showed that wood sawdust, barks and technical hydrolysis lignin (THL) can be used for the removal of dissolved phenols from waters. The adsorption ability was found to decrease in the order: sawdust > wood barks > THL. The adsorption of phenol on sawdust, polymerized sawdust and sawdust carbon was also studied by Jadhav and Vanjara [168].

Edgehill and Lu [169] investigated removal of phenol using carbonized slash pine bark as a substitute for activated carbon. Similar studies on Pinus pinaster
barks has been reported by Vázquez et al. [170]. The influence of variables such as solid/liquid ratio, pH and initial concentration of phenol in the solution on the adsorption capacity of the bark has been analysed. A kinetic model based on phenol diffusion within the pores of the adsorbent was in agreement with the results obtained for high initial concentrations of phenol, allowing the determination of diffusion coefficients. The influence of flow rate on the breakthrough curves using a column packed with pretreated P. pinaster bark was analyzed further [171]. Brás et al. [172] showed the uptake of PCP by pine bark to be faster in the initial phase followed by a slower process. The neutral PCP species showed to have higher binding capacity to pine bark than the anionic PCP, which depends on pH. Rice husk, an agricultural waste produced as by-product of the rice milling industry, has been used for phenol removal [173, 174]. The adsorption capacity of chemically treated rice husk (RHCT) and thermally treated rice husk (RHT) for the removal of 2,4-DCP from aqueous solutions was evaluated showing higher capacity of RHT than both RHCT and rice husk untreated (RHUT) [175]. Mahvi et al. [176] reported that adsorption equilibrium of phenol on rice husk and rice husk ash was reached within 6 h and rice husk ash is much effective than rice husk. Ahmaruzzaman and Sharma [160] also investigated the potential of rice husk and rice husk char for the removal of phenolic compounds from wastewater. Rice husk ash obtained from a rice mill in Kenya has been used as an inexpensive and effective adsorbent for the removal of some phenolic compounds in water [177]. Other industrial waste products such as pith, date pits, wheat straw, and wood chips etc have also been successfully employed for the removal of phenolic compounds from wastewater.

Because of their low cost and local availability, industrial solid wastes / by-products such as metal hydroxide sludge, fly ash and red mud are classified as low-cost materials and can be used as adsorbents for the removal of phenolic compounds. Bagasse fly ash generated in the sugar industry has been widely
used for adsorption of phenolic compounds [178, 179]. Khanna and Malhotra [180] first reported the use of fly ash for phenol removal. The kinetics and mechanism of phenol removal were investigated. They also provided useful data in the design of phenol-fly ash adsorption systems. Adsorption of phenol and cresol and their mixtures from aqueous solutions on activated carbon and fly ash were compared [181, 182]. The effects of contact time, pH, temperature and isotherm parameters were evaluated. Isotherm analysis for phenol, 3-CP and 2,4-DCP adsorption onto fly ash revealed the capacity of 67, 20 and 22 mg.g\(^{-1}\) respectively [183]. The affinity of phenolic compounds for fly ash is above the expected amount corresponding to a monolayer coverage. The isotherms for the contaminants studied were favorable, indicating that adsorption becomes progressively easier as more solutes are taken up. Aksu and Yener [184, 185] compared the loading capacity of phenol and chlorophenols for fly ash and that for granular activated carbon. The adsorption of phenolic compounds on a mixture of bottom and fly ashes has been investigated [186]. Bagasse fly ash has been converted into a low-cost adsorbent and used for the removal of phenol and p-NP [187]. Adsorbent prepared from fly ash was successfully used to remove cresol from an aqueous solution in a batch reactor [188]. The performance of the adsorbent prepared was favorable compared with that of commercially available activated carbon.

Kao et al. [189] utilized fly ash for the removal of 2-CP and 2,4-DCP, which was reported to be affected by particle diameter, carbon content, specific surface area of the ash used and pH of the solution. The adsorbed amount of chlorophenol is not influenced by the matrix in the wastewater from a synthetic fiber plant but with breakthrough times, being inversely proportional to flow rates. Viraraghavan and de Maria Alfaro [190] examined the effectiveness of less expensive adsorbents such as peat, fly ash and bentonite in removing the phenol from wastewater. Sarkar et al. [191] investigated the kinetic aspects of adsorption of some priority organic pollutants (phenol, hydroxyl and
nitrophenol) on fly ash indicating the process to be of complex nature consisting of both surface adsorption and pore diffusion and the extent of each being estimated from the diffusion coefficient value. Activation parameter data for the ultimate adsorption as well as the pore diffusion are also evaluated.

Batch shaking adsorption experiments conducted with fly ash (FA) and impregnated fly ash (IFA) in removing the phenols from aqueous solution indicates that IFA has better efficiency than FA [192]. It was observed that polar substituted phenols having less steric hindrance are adsorbed more than others. Substituted phenols with large hindered group are less adsorbed than phenol. The removal mechanism of phenols is suggested due to chemical coagulation with metallic oxides. Singh et al. [193, 194] investigated the adsorption of 2,4-DCP and tetrachlorocatechol by bagasse fly ash (BFA), rice husk fly ash (RHFA) and activated carbon (AC). Economic evaluation of the adsorbents BFA and RHFA with the AC shows that use of BFA and RHFA is viable. Removal of nitro-substituted phenols and dimethyl phenol on fly ash was investigated [195, 196]. Srivastava et al. [197] studied the adsorption of phenol on carbon rich bagasse fly ash (BFA). The overall adsorption process is controlled by intraparticle diffusion of phenol. Mukherjee et al. [198] investigated the use of bagasse ash (BA) as adsorbent for removal of phenol from water. The effect of the load of nitrate ion and EDTA in the solution was found to be insignificant; however, the chloride ion has considerable negative effects on the removal by BA. Phenolic compounds from paper mill industry wastewaters was investigated by using fly ash, raw sepiolite and heat-activated sepiolite as adsorbent [199]. Heat-activated sepiolite is found to be more effective than raw sepiolite and fly ash. The efficiency of adsorption decreases with increasing adsorption temperature for both fly ash and untreated sepiolite. Fly ash has also been used for the removal of a typical alkyl dinitro phenol compound, 2-sec-butyl-4,6-dinitrophenol (DNBP), from aqueous solution [200]. The thermodynamic parameters were calculated based on a statistical model.
Kinetic studies have been performed to understand the mechanism of adsorption.

The potential use of Mowital B30H resin immobilized on dried activated sludge as a substitute for granular activated carbon for removing phenol from aqueous solution was examined in a continuous packed bed reactor as function of flow rate and inlet phenol concentration [201]. The maximum specific uptakes, total adsorbed quantities, and total removal of phenol related to the effluent volumes were determined by evaluating the breakthrough curves obtained at different flow rates and compared with GAC and dried sludge. Simultaneous adsorption of phenol and Cr(VI) ions to Mowital®B30H resin immobilized activated sludge from binary mixture was studied and compared with single phenol or Cr(VI) adsorption in a continuous packed bed column [202]. The column adsorption capacity of immobilized dried activated sludge for phenol and Cr(VI) decreased notably due to the presence of other component. The single and multi-component adsorptions in packed bed were evaluated. The adsorption of phenol, o-CP and p-CP from aqueous solutions on dried activated sludge has been investigated [203]. The adsorption capacity of silica gel sludge for phenol removal from aqueous solution was studied [204]. Surplus biological sludge from wastewater treatment operations was converted into activated carbon and then added to the aerated vessel of an activated sludge process treating phenol [205]. The addition of activated carbon, either sludge-based or commercial, enhanced phenol removal from 58 to 98.7%. Adsorption of phenol, 2-CP and 4-CP from aqueous solutions onto granular activated carbon and dried activated sludge was investigated [206]. The synthetic wastewater containing 4-CP was treated in an activated sludge unit at different sludge ages [207] as well as in an upflow anaerobic sludge blanket reactors [208]. The adsorption behavior of PCP from aqueous solution to activated sludge biomass was studied by Wang et al. [209]. Thawornchaisit and Pakulanon [210] investigated the removal of phenol on dried sewage sludge. It is interesting to note that the adsorption capacity of
sludge decreased from 94 to 5 mg g\(^{-1}\) when sludge dose was increased from 0.5 to 10 g dm\(^{-3}\), possibly due to the competitive effect of leachable heavy metals from the sludge. Experimental data on the adsorption of phenols on paper mill sludge showed that particle diffusion was involved in the adsorption process though was not the only rate limiting mechanism [211]. With an objective of production of carbonaceous adsorbent for industrial effluent treatment, physical activation of biological sludge by steam was studied [212]. The activation step shows an improvement of pore and adsorption characteristics of the adsorbent and subsequently the adsorption capacities of phenol. The adsorbents produced from sewage sludge via chemical activation and pyrolysis treatment was used for phenol removal [213]. Das and Patnaik [214] used blast furnace flue dust and slag for the removal of phenol from wastewater. Removal efficiency was obtained after equilibrium period of 8 h. Column experiments indicate that the amount of phenol adsorbed decreases with increasing flow rate and decreasing bed height. The breakthrough time and bed-depth data show the applicability of the bed depth service time (BDST) model. A comparative study of the adsorbents prepared from several industrial wastes for the removal of 2-bromophenol, 4-bromophenol and 2,4-dibromophenol has been carried out by Bhatnagar [215]. It is reported that as compared to the carbonaceous adsorbent, prepared from fertilizer industry waste, the other three adsorbents (viz., blast furnace sludge, dust, and slag) adsorb bromophenols to a much smaller extent probably due to higher porosity and surface area of carbonaceous adsorbents.

Red mud, an aluminum industry waste was converted into a low-cost adsorbent and has been used for the removal of phenol, 2-CP, 4-CP, and 2,4-DCP from wastewater [216]. The removal of phenols and its derivatives was achieved up to 98% by column experiments at a flow rate of 0.5 cm\(^3\).min\(^{-1}\). The order of removal was 2,4-DCP > 4-CP > 2-CP > phenol, and the removal takes place through a particle diffusion mechanism. Gupta and Ali [217] utilized red mud as adsorbent for the removal of 2,4-DNP. The removal was achieved up to 95% by
batch and 96% by column experiments at the flow rate of 0.5 cm$^3\cdot$min$^{-1}$. The adsorption was found to be endothermic in nature. Recently, Tor et al. [218] studied removal of phenol from aqueous solution by using the neutralized red mud. The influence of addition of salt on phenol removal depends on the relative affinity of the anions for the red mud surface and the relative concentrations of the anions. Adsorption of methylphenols on adsorbents prepared from several industrial wastes was also studied [219]. The results show that extent of adsorption has been found to follow an order: 2-methylphenol $>$ 4-methylphenol $>$ 2,4-dimethylphenol $>$ 2,4,6-trimethylphenol. Industrial waste products, such as, waste slurry, Fe(III) hydroxide from industry, etc have also been utilized for the removal of phenolic compounds from wastewater.

Besides the various adsorbents, discussed above, a number of other materials, such as starch, cyclodextrin, cotton waste, human hair, chicken feathers, spent oil shale, pine bark, petroleum coke, coke breeze, etc have also been utilized as low cost adsorbents for the removal of phenolic compounds. In a typical experiment Akbal [220] investigated the adsorption of phenol and 4-CP on pumice modified with the cationic surfactants hexadecyltrimethyl-ammonium bromide and benzyltrimethyltetradecylammonium chloride. Jordanian spent oil shale was used for the adsorption of phenol from wastewater [221]. The effects of pH in the presence of KI and NaCl were studied for a possible interaction between salts and solution pH. Adsorption of 4-NP by pyrolysed and activated Jordanian oil shale was studied by Al-Asheh et al. [222]. Human hair was also tested as an adsorbent for the removal of phenol from aqueous solutions [223]. The presence of NaCl salt in the adsorption system had only a marginal effect on phenol adsorption. Banat and Al-Asheh [224] used chicken feather for the removal of phenol from aqueous solutions. Batch kinetics and isotherm studies were performed. The adsorption equilibrium was well represented by the Freundlich and Langmuir adsorption isotherm models. The effects of bed-depth, feed flow rate and feed concentration on the breakthrough behavior were further
investigated for removal of phenol in a fixed-bed system packed with chicken feather [225].

Experiments have been conducted to study the adsorption of chlorinated phenols by sediments and aquifer materials [226]. The adsorption was found to be strongly influenced by the organic carbon content of the sorbent and by the ionic strength of the aqueous medium. The adsorption of phenol, 2-CP, 4-CP and 2,4-DCP by aged-refuse has been investigated [227]. The chlorinated phenols are adsorbed more strongly than the phenol. The experiment data suggests that both the partition function and the chemical adsorption involve in the adsorption process. More than one step involves in the adsorption process and the overall rate of the adsorption process appears to be controlled by the chemical reaction. The thermodynamic analysis indicates that the adsorption is spontaneous and endothermic. Ahmaruzzaman and Sharma [160] investigated the removal of phenolic compounds from wastewater using petroleum coke and coke breeze. Asyhar et al. [228] utilized the modified petroleum coke treated with KOH for the removal of phenolic compounds. Daifullah et al. [229] investigated the potential use of pyrolysed residue from animal bones for removing p-NP from aqueous solutions by adsorption. The maximum adsorption capacity was found to be 111 mg·g⁻¹.

Starch as the low-cost adsorbent has been used for the removal of phenolic compounds [230, 231]. Cahn [232] investigated the adsorption of heavy metal ions (CrO₄²⁻ or Pb²⁺) and phenol from solution with a highly cross-linked amphoteric starch containing phosphate anionic group and tertiary amine cationic group. The adsorption mechanism confirms that the Na⁺ of the sodium phosphate group and the Cl⁻ of the tertiary amine group are used to exchange Pb²⁺ and CrO₄²⁻ ions respectively, and the tertiary amine group is used to adsorb phenol. Two series of cross-linked starch polymers were tested for their ability to adsorb organic pollutants in aqueous solutions as influenced by pH, polymer structure and the kinetics of adsorption [233]. Results of adsorption experiments
showed that the starch-based materials exhibit high adsorption capacities towards phenolic derivatives. The study of the kinetics of pollutant uptake revealed that the adsorbents presented a relatively fast rate of adsorption. The cyclic derivative of starch, cyclodextrin has also been utilized for the removal of phenolic compounds from wastewater [234]. The adsorption properties of cross-linked cyclodextrin carboxymethylcellulose gels toward β-naphthol were studied by Crini et al. [235]. The influences of the quantity of cyclodextrin, crosslinking agent and pH were also studied. The proposed adsorption mechanism involves several interactions, viz. hydrogen bonding, interaction due to crosslinking agent, physical adsorption and inclusion complex. Macroporous cyclodextrin has been utilized for removal of 4-NP from aqueous solution [236]. Allen and colleagues [237] investigated the removal of 2-NP on technical hydrolysis lignin (THL), a low-cost and abundantly available material. The sorption characteristics and the calculated sorption capacity of the lignin proved the feasibility of its use as a potential and alternative sorbent for 2-NP removal.

2.2. Removal of Arsenic from Water

The arsenic problem is of particular concern for small communities in rural areas, where groundwater comprises the main drinking water source. In villages, where most groundwater sources are polluted by high arsenic, provision for arsenic free water supply is urgently needed. Some possible options may be:

I. Treatment of contaminated tube-well water,
II. Use of alternate safe water source, and
III. Artificial water recharge of contaminated aquifer.

However, proper awareness program is needed to popularize the use of alternate water sources. Due to limited facility in use of other alternatives, ‘tube-well water treatment’ is, in fact, the only option to remove arsenic from drinking water. Several arsenic removal technologies have been adopted under laboratory
and field conditions. The use of any particular technique depends on the load of arsenic and its specific form together with the composition of water and wastewater. The conventional remediation processes include:

1. Coagulation and Flocculation
2. Precipitation
3. Adsorption and Ion Exchange
4. Membrane Filtration
5. Oxidation
6. Biological Remediation
7. Electrochemical Treatment

Coagulation and flocculation are among the most common methods employed for removal of arsenic from water. Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Cationic coagulants provide positive electric charges to reduce the negative charge (zeta potential) of the colloids. As a result, the particles collide to form larger particles. Rapid mixing is required to disperse the coagulant throughout the liquid. Flocculation is the action of polymers to form bridges between the larger mass particles or flocs and bind the particles into large agglomerates or clumps. Bridging occurs when segments of the polymer chain adsorb on different particles and help particles aggregate. An anionic floculant will react against a positively charged suspension, adsorbing on the particles and causing destabilization either by bridging or charge neutralization.

Aluminium-based coagulation with disinfection by chlorination is one of the commonly used treatment methods. McNeill and Edwards [238] reported a wide range (6-74%) of decrease of soluble As(V) concentrations for five alum coagulation treatment plants. Gregor [239] performed his studies on drinking-water treatment plants (that extract water from the river) and observed the variation of states and concentrations of arsenic through aluminium-based coagulation treatment method. Soner Altundoğan and Tümen [240] studied the
removal of As(V) from wastewater using a waste material – liquid phase red mud (LPRM). In their experiments, they mixed As(V) solution with LPRM in several volumetric ratios, neutralized the mixtures with acid solution followed by air-agitation and again neutralized those mixtures with CO₂ gas. As(V) was removed by co-precipitation with aluminium present as aluminate in the LPRM. For an efficient removal, Al/As(V) molar ratio of 6-8 was suggested. Yuan et al. [241] studied a combination system of ferric sulphate coagulation and sand filtration in arsenic removal. Zouboulis and Katsoyiannis [242] employed modified coagulation/flocculation process for the removal of arsenic using alum or ferric chloride as the coagulant agent enhanced by some organic polymers achieving up to 99% arsenic removal efficiency. Karcher et al. [243] and Guo et al. [244] reported the uses of ferric chloride and lime-polyferric sulphate as the coagulants. Han et al. [245] used ferric chloride and ferric sulphate as flocculants. The results showed considerable arsenic removal through adsorption onto the ferric complexes present. Wickramasinghe et al. [246] reported that ferric based coagulant is highly efficient in treating the city groundwater, contaminated by arsenic.

The precipitation processes can be accomplished via alum coagulation, iron coagulation, lime softening, and iron (and manganese) assisted precipitation for arsenic removal.

In removal of arsenic, alum is found most effective if an oxidizing agent, such as chlorine, is added ahead of the flocculator and clarifier and the pH is reduced to 7 or less. It would probably be necessary to use a number of chemicals in order to treat the arsenic in the drinking water. However, the arsenic removed from the water would be contained in the alum sludge [247]. Arsenic removal by iron precipitation necessarily needs addition of an iron compound (e.g. ferric chloride or ferric sulphate) and adjustment of pH of the contaminated water. The arsenic combines with the iron to form a precipitate in the form of sludge, which settles out in the clarifier. A filter, attached to the bottom of the clarifier.
removes iron / arsenic particles. The best arsenic removal rates are obtained at pH less than 8.5 with or without chlorine [247]. In practice ferric chloride is more frequently used rather than ferric sulphate. Jones et al. [248] studied the removal of As(V) and found that ferrous iron provides an effective treatment giving residual dissolved arsenic concentrations below 1.0 mg.dm$^{-3}$ over a range of compositions along with 99.9% removal. They also noticed that ferric iron treatment is more effective in conjunction with mixed lime and magnesium hydroxide. Fields et al. [249] reported in detail on arsenic treatment for drinking water by lime softening. Arsenic removal efficiency of this process strongly depends on the pH and presence (or absence) of chlorine in the solution. Chlorine is required to oxidize arsenic and the acid lowers the pH of the treated water to acceptable drinking water levels. Eberhard et al. [250] had patented the method of removing arsenic from a sulphur dioxide-containing solution using lime precipitation. Huang and Rong [251] also reported the uses of calcium breach and lime in the treatment of sewage with high arsenic content.

Sorg [252] reported the importance of selection of suitable media in arsenic removal by filtration. Different media are found to have different removal capabilities. However, pH in source water, competitive ligands such as Si, PO$_4^{3-}$ etc, and concentrations of arsenic and other ligands influence the removal of arsenic. Sorg and Lytle [253] proposed arsenic selection guide based on Fe/As in the source water. The removal efficiency was found to increase with the addition of iron oxide to the treatment system. Kartinen and Martin [247] reported a process in which iron and/or manganese are frequently removed along with arsenic from water using “manganese greensand” coated with manganese dioxide. They showed that arsenic removal rates of 90% may be obtained from this process. However, when permanganate is applied intermittently to the greensand during backwash, the process will form a layer of MnO$_2$ on the filter media. Palfy et al. [254] studied the treatment of arsenic using H$_2$O$_2$, calcium oxide, ferric sulphate, portland cement as the precipitating
agents and arsenic waste neutralizers. Further the leachate analysis showed that lime precipitation in combination with cement solidification can provide relatively safe material. The solubility of arsenic was reduced from original value of 6430 to 0.823 mg.dm\(^{-3}\) in leachate from the produced solidificate. Combination of lime and ferric compounds used in the treatment of arsenic via precipitation are also reported [255-264].

Adsorption as an important solid phase extraction technique is quite popular for removal of pollutants due to its simplicity as well as availability of wide range of adsorbents and applicability to most natural, physical, biological, and chemical systems [265]. Jackson and Miller [266] reported adsorption of both As(V) and As(III) by ferrihydrite and the role of sulphate as competitive anions. The process is highly dependent on pH. Desorption study of sorbed As(V) from ettringite \([\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}]\) phase in presence of concentrated sulphate and high ionic strength was investigated by Myneni et al. [267]. It is found that adsorption of both As(V) and As(III) on hydrous ferric oxide decreases in presence of sulphate in the pH range of 4-7 [268].

Among the different adsorbents used in arsenic treatment, activated carbon is the most commonly used one [265, 269-271]. Eguez and Cho [271] studied the adsorption of As(III) and As(V) using activated carbon at various pH values. The isoteric heat of adsorption was determined from the effect of temperature. In some of the experiments [272-275] activated carbon has been impregnated with various metal ions in order to improve its arsenic adsorption capacity. The iron oxide impregnated activated carbon has shown higher removal capacity both for As(III) and As(V) compared with the non-impregnated carbon. Rajakovic [273] found that carbon pretreated with Ag\(^{+}\) or Cu\(^{2+}\) ions improved As(III) adsorption but reduced As(V) adsorption. Evdokimov et al. [274] reported that arsenic adsorption can be improved by impregnating carbon with ferric hydroxide or tartaric acid. Rajakovic and Mitrovic [276] showed that
chemically treated activated carbon exhibits high adsorption capacity for arsenic. Lorenzen et al. [277] studied several factors (such as solution pH, carbon type and carbon pretreatment) that affect the mechanism of adsorption of arsenic species on activated carbons as well as the elution of arsenic from loaded carbon. It is found that As(V) is more effectively removed from solution when using activated carbon with high ash content and pre-treatment of the carbon with Cu(II) solutions further improves the arsenic removal capacity. Gu et al. [278] designed granular activated carbon-based, iron-containing adsorbents (As-GAC) for the effective removal of arsenic from drinking water. Column studies showed that both As(V) and As(III) could be removed to below 10 µg.dm⁻³ within 6000 empty bed volume when the groundwater containing approximately 50 µg.dm⁻³ of arsenic was treated. Mondal et al. [279, 280] compared the efficiency of removal of arsenic from a contaminated ground water (simulated) by adsorption onto Fe³⁺ impregnated granular activated carbon (GAC-Fe) and that onto untreated granular activated carbon (GAC). The pH and temperature of the study were 7±0.1 and 30°±1°C, respectively and Fe³⁺ impregnated GAC shows high removal capacity than untreated GAC.

Singh and Pant [281] studied the removal of As(III) from contaminated water using activated alumina. However, iron oxide impregnated activated alumina showed an improved efficiency for the removal of As(III) [282]. A novel adsorbent prepared in situ precipitation of Fe(OH)₃ on the surface of activated Al₂O₃ demonstrated adsorption efficiency of 0.1-0.4 mmol.dm⁻³ for arsenate and arsenite ions from solutions [283]. Tripathi and Raichur [284] reported that alum-impregnated activated alumina is more efficient than activated alumina for the removal of As(V) from drinking water at different pH values and successively removed As(V) to below 40 µg.dm⁻³ from an initial concentration of 10 mg.dm⁻³. However, As(V) adsorption is strongly influenced by the presence of phosphate. Nakajima et al. [285] investigated a novel method for removal of inorganic As(III), monomethylarsonate (MMA), and
dimethylarsinate (DMA) from aqueous media, by combined use of adsorption on activated alumina and photo-irradiation in presence of TiO₂-photocatalyst. The results show a removal of 89% for inorganic As(III), 98% for MMA and 97% for DMA.

Zhang et al. [286] found that natural iron ore, e.g., hematite, is very effective for the adsorptive removal (100 times) of As(V) from contaminated water. Meng and colleagues [287, 288] demonstrated in batch and column studies the efficacy of Fe(0) filings to remove arsenic from arsenic-spiked solutions as well as arsenic-contaminated groundwater. In presence of dissolved oxygen (DO) and at a low pH the rate of iron corrosion together with arsenic removal was increased. It is noticed that As(V) removal was greater and faster than As(III). The column results indicate that Fe(0) fillings column and a sand filter could be used for treatment of arsenic in drinking water. Kanel et al. [289, 290] reported that nanoscale zero-valent iron was fairly effective for the removal of both As(V) and As(III) from groundwater. Leupin et al. [291, 292] employed filtering of contaminated water through sand and zero-valent iron. As(V) adsorbed on hydrous ferric oxides formed as a result of oxidation of iron. Jang et al. [293] proposed that hydrous ferric oxide incorporated into naturally occurring porous diatomite is quite effective for the removal of arsenite and arsenate from contaminated water. A variety of adsorbent materials, viz., amorphous iron hydroxide [294], ferric hydroxide [295-297], ferrihydrite [298], silica containing iron(III) oxide [299], Ce(IV)-doped iron oxide [300], iron(III)-poly(hydroxamic acid) complex [301], ferric chloride [257], Fe(III)-doped alginate gels [302], nanocomposite adsorbent based on silica and iron(III) oxide [303], and iron oxide-coated polymeric materials [304] have also been used for arsenic treatment.

Pierce and Moore [294] studied the removal of arsenite and arsenate by amorphous iron hydroxide adsorbent. A maximum of 92% removal can be achieved by proper selection of the relative concentration of arsenic and
amorphous iron hydroxide, and pH. Arsenic removal technology by adsorption with a commercial granular ferric hydroxide (GFH) has been developed in the early 1990s [296, 305]. It can be applied in simple fixed bed reactors, similar to those for activated alumina or activated carbon. Simplified operation is a key benefit of the system, which will operate without the need for chemical pre-feed or pH correction. GFH has a high adsorption capacity in natural waters. The work carried out by Driehaus et al. [296] showed that GFH possesses high treatment capacity of 30,000-40,000 bed volumes. Jekel and Seith [306] compared the methods for the precipitation/flocculation by iron(III)-chloride and iron(II)-sulphate as well as adsorption on GFH in a full scale water treatment plant. Their findings also show that adsorption on granulated iron hydroxide has been proven to be the effective method in terms of greater operational reliability with easy maintenance and monitoring. Among the three arsenic treatment techniques, viz. direct filtration with FeCl₃, adsorptive filtration with FeSO₄ and adsorption on granulated ferric hydroxide adopted by Ruhland and Jekel [307], the adsorption on granulated ferric hydroxide has been found to be the most preferential process.

A combination of adsorption system using ferric oxy hydroxide and ion exchange using SORB 33 and Bayoxide® E33 was designed for arsenic removal [308]. The removal was effective and arsenic concentration is reduced to a level below the permissible limit of 10 µg dm⁻³. However, the removal efficiency is reduced under high pH and high levels of vanadium, phosphate and silica. Deliyanni et al. [309-311] synthesized a novel adsorbent, akaganéite-type β-FeO(OH) in the laboratory by precipitation from aqueous solution of Fe(III) chloride and ammonium carbonate for arsenic removal. The adsorption is found much higher compared to other adsorbents, like hydrous iron oxides, ferrihydrite and goethite. Lenoble et al. [312] used synthesised iron(III) phosphate to remove arsenic from water. Results showed that adsorption capacities were higher towards As(III), leading to Fe²⁺ and HAsO₄²⁻ leaching.
The high release of phosphate and iron excludes its application in drinking water plants, which is the main drawback. Arsenic is frequently associated with sulphide minerals and typically forms its own minerals like arsenopyrite (FeAsS). Such affinity of arsenic towards sulphide minerals raises a potential use of the sulphide minerals for arsenic removal from water. Jingtai and Fyfe [313] examined the feasibility of these minerals to adsorb arsenic from arsenic spiked waters through bench scale experiments. They found that iron sulphide minerals like pyrite and pyrrhotite are effective adsorbents for arsenic removal from water and are much more efficient than other geologic materials like hematite, feldspar and clay. Zhang and Itoh [314] synthesized iron oxide loaded municipal solid waste melted slag for removal of both arsenate and arsenite showing its effectiveness much for arsenate than for arsenite. However, when iron oxide and TiO₂ were loaded on municipal solid waste melted slag arsenite removal increased due to photocatalytic oxidation of arsenite to arsenate [315]. Kundu and Gupta [316-318] examined the efficiency of iron oxide-coated cement for the removal of As(III) from aqueous solution through batch and column studies and observed that it can be used repeatedly up to three cycles without noticeable loss of capacity. Lakshmipathiraj et al. [319] investigated the effectiveness of goethite synthesized from the oxidation of ferrous carbonate precipitated from the double decomposition of ferrous sulphate doped with sodium lauryl sulphate and sodium carbonate in aqueous medium for the removal of As(V). Guo et al. [320-322] performed batch and column tests utilizing naturally formed hematite and siderite for the removal of As(V) and As(III) from water. Column studies were conducted using siderite-coated quartz sand and/or hematite-coated quartz sand columns. Further study on H₂O₂ activated siderite-hematite filter [323] showed improved adsorption for As(V) than the originals in batch experiments. Iron oxyhydroxide loaded bead cellulose and iron oxide/activated carbon (FeO/AC) composite adsorbent material with special ferric oxide microcrystal have been successfully applied for the elimination of arsenic from aqueous solutions [324, 325]. The rate of
arsenic removal by iron-containing ordered mesoporous carbon (FeOMC) was found high, and is recommend to apply in point-of-use systems [326]. Mayo et al. [327] evaluated the capability of nanoscale iron oxides, specifically magnetite (Fe₃O₄) nanoparticles as potential adsorbents for both As(III) and As(V), where adsorption on Fe₃O₄ nanocrystals and magnetic separations offered a promising method for arsenic removal from groundwater.

Haque et al. [328] investigated the removal of arsenate, As(V) from aqueous solutions by iron-coated light expanded clay aggregates (Fe-LECA) under both batch and column operations. Pokhrel and Viraraghavan [329] performed batch studies to examine the adsorption kinetics and adsorption capacity of iron oxide-coated biomass (IOCB) for As(III) and As(V). The adsorption of As(V) on IOCB was found to be rapid compared to that of As(III). Column studies [330] conducted with iron oxide-coated *Aspergillus niger* biomass showed adsorption capacity to be 1080 and 880 μg.g⁻¹ for As(V) and As(III) respectively. Zaspalis et al. [331] proposed an adsorption-filtration process using iron oxide in nanoparticles and microparticle form and porous ceramic membranes for the purification of water from As(V) ions. Efficiency of iron oxide-coated sand to remove arsenic from drinking water [332, 333] was examined in batch and column studies and the results were compared with those for uncoated sand. The maximum adsorption of As(III) for coated sand was found to be much higher than that for uncoated sand; the maximum As(III) removal efficiencies of 99 and 94% were obtained in batch and column experiments respectively for coated sand. Hsu et al. [334] also investigated the feasibility of arsenate and arsenite removal by reclaimed iron-oxide coated sands and concluded that the species can be considered as a viable and economic adsorbent. Batch experiments showed that under the same initial solution, pH and adsorbent dosage, the removal efficiencies were in the order: As(V) > As(T) > As(III). Chang et al. [335] investigated the applicability of manganese-coated sand (MCS) and iron-coated sand (ICS) for the treatment of As(III) and As(V) via
oxidation and adsorption processes. In the batch adsorption, the adsorption rate of As(V) onto ICS was greater than that of As(III), and ICS showed a greater adsorption capacity for the removal of As(V) than As(III). From a bench-scale column test, a column reactor packed with both MCS and ICS was found to be the best system for the treatment of As(III) due to the promising oxidation efficiency of As(III) to As(V) by MCS and adsorption of As(V) by both MCS and ICS.

Pagana et al. [336] used composite γ-Al₂O₃ ceramic membrane made by sol-gel method for the removal of As(V) and Cr(III) ions from contaminated water through combined adsorption-ultrafiltration processes. As(V) removal was achieved by a two-stage adsorption-ultrafiltration processes in series based on Fe₂O₃ adsorbent nanoparticles and a 0.2 wt% (w/v) adsorbent concentration was found sufficient to reduce the initial As(V) concentration of 1.0 mg.dm⁻³ down to the recommended permissible limit in drinking water. Other reported works on the metal oxide based adsorbents include manganese oxide [337-339], zirconium oxide [340-344] and alumina [345-349]. Most of these studies are carried out in low concentration of arsenic solution in batch experiments.

Deschamps et al. [350] explored adsorption capability of a natural oxide sample consisting basically of Mn-minerals (birnessite, cryptomelane, todorokite) and Fe-oxides (goethite, hematite) in batch and column experiments. The adsorption capacity was found higher for As(III) than that of As(V). Bang et al. [351] evaluated granular titanium dioxide for the removal of arsenic from water. the effect of anions on arsenic removal was also investigated. Pena et al. [352] evaluated the effectiveness of nanocrystalline titanium dioxide in removal of arsenic from aqueous systems. It was reported that in the presence of sunlight and dissolved oxygen, As(III) was completely converted to As(V) through photocatalytic oxidation within 25 minutes. Jeong and co-workers [353] found that the oxides of iron (Fe₂O₃) and aluminum (Al₂O₃), despite their relatively small surface area, may well be utilized as good and, of course, low-cost...
adsorbents for As(V) removal even up to 90%. It has also been found that Fe₂O₃ is a better absorbent than Al₂O₃ for achieving higher adsorption capacity and adsorption rate. Hristovski and co-workers [354] investigated the feasibility of arsenate removal by aggregated metal oxide nanoparticle media in packed bed columns. Batch experiments with 16 commercial nanopowders in four water matrices were conducted to select a metal oxide nanoparticle that both amply removes arsenate and can be aggregated using an inert binder. TiO₂, Fe₂O₃, ZrO₂ and NiO nanopowders, which exhibited the highest arsenate removal in all water matrices, were characterized with Freundlich adsorption isotherm parameters, and TiO₂ nanoparticles, aggregated with inorganic and organic binders, shown to have the highest arsenate adsorption. Qu and colleagues [355, 356] developed a unique Fe-Mn binary oxide from low cost materials for the efficient adsorption of As(III) as well as As(V) using a simultaneous oxidation and co-precipitation method.

You et al. [357] used layered double hydroxides (LDHs), also called hydrotalcite-like compounds or anionic clays for their arsenic removal experiments. LDHs, although rare in nature, are readily synthesized by co-precipitation method under laboratory conditions. The applicability of Zr(IV) loaded chelating resin with lysine-Na,Na diacetic acid functional groups for the removal of As(V) and As(III) was evaluated [341, 358]. A variety of zeolites, modified with aluminium and iron [359-363] were used for arsenic removal. Chitosan gel beads, modified with molybdate, was shown to be efficient in removing As(V) from acid solutions, even at low equilibrium concentration, whereas the sorption capacities were significantly lower for As(III) uptake [364, 365]. The adsorption study on ferruginous manganese ore revealed its efficiency to remove both As(III) and As(V) at a pH range of 2-8 without any pretreatment. The adsorption of As(III) was more than that of As(V) [366].

In a typical column study Thirunavukkarasu et al. [367] investigated the removal of organic arsenic (dimethylarsinate) spiked in tap water using
manganese greensand (MGS), iron oxide-coated sand (IOCS-1 and IOCS-2) and ion exchange resin in Fe$^{3+}$ form. The removal capacities were found to decrease in the order: ion exchange resin > IOCS-2 > MGS > IOCS-1. Valiente and co-workers [368] showed that inorganic arsenic species can well be removed through adsorption from aqueous media using an open cell cellulose sponge (Forager Sponge) with anion-exchange and chelating properties. Zouboulis and Katsoyiannis [369] examined the efficiency of biopolymers (alginate), as potential sorbent supports, for the removal of arsenic from contaminated water. Rau et al. [370] prepared a unique iron(III)-chelated iminodiacetate resin and investigated the adsorption of As(V) from arsenic-contaminated water with concentrations up to 1000 mg.dm$^{-3}$. Ghimire et al. [371] carried out batch and column tests to investigate the removal of arsenic with the iron(III)-loaded gels, prepared from orange waste and cellulose. Kundu et al. [372] used hardened paste of Portland cement as a low-cost adsorbent for the removal of arsenic from water achieving arsenate and arsenite removal up to 95 and 88% respectively. Seko et al. [373] synthesized a new Zr(IV) loaded fibrous phosphoric chelate adsorbent (Zr-FPA) by radiation-induced grafting and used it for removal of arsenic from aqueous media in column mode. The total capacity of As(V) was 2.0 mmol.g$^{-1}$ of adsorbent at pH 2. Maity et al. [374] carried out a detailed study on As(III) and As(V) adsorption on polymetallic sea nodule, comprising of iron, manganese and silicon with trace quantities of aluminium, copper, cobalt and nickel, and found effective in removing arsenic from six contaminated groundwater samples of West Bengal, India, containing arsenic in the range 0.04-0.18 mg.dm$^{-3}$. Makris et al. [375] described the utility of drinking-water treatment residuals (WTR), a waste by-product of the drinking-water treatment process, as an excellent adsorbent for removing both As(III) and As(V) from solution. Both Fe- and Al-based WTRs were found to exhibit high affinities for soluble As(V) and As(III). Decontamination of arsenic from water using shelled *Moringa oleifera* seeds was reported by Srivastava et al. [376]. Samples of clay minerals (natural metakaoline, natural clinoptilolite-rich tuff.
and synthetic zeolite) in both untreated and Fe-treated forms were tested for the adsorption of arsenate from aqueous solution [377]. Gupta et al. [378, 379] investigated the efficacy of the adsorbent, modified calcined bauxite, in removing As(V) and As(III) from aqueous environment by batch and column studies. The consistency in arsenic sorption over a wide pH range, availability and adaptability in the local environment, excellent sorption potential, least interference from most of the anions, negligible temperature effects and quality of the treated water makes it an ideal choice for arsenic removal. Boddu et al. [380] studied the removal of As(III) and As(V) at pH 4.0 under equilibrium and dynamic conditions through adsorption on a biosorbent prepared by coating ceramic alumina with the natural biopolymer, chitosan. Mohan and co-workers [381] reported that the bio-char, a by-product obtained from fast wood/bark pyrolyses, can fairly be used as an adsorbent for the removal of the different toxic metals including As(III) from water. The experiments were carried out using oak bark, pine bark, oak wood, and pine wood chars, where oak bark outperformed the other chars and removed about 70% of arsenic from aqueous solutions.

Lim and Chen [382] synthesized a novel calcium-alginate magnetic sorbent by an electrostatic extrusion technique and reported the adsorption capacity for arsenic ions as 6.75 mg.g⁻¹, which is much higher than that of commercial adsorbents. Vithanage et al. [383] investigated the retention of arsenic on goethite and gibbsite as a function of pH with similar site densities of >FeOH and >AlOH of natural red earth. It was found that arsenite adsorption was low for gibbsite (50%) than goethite (<95%), whereas arsenate adsorption was high (>90%) for both the solids. Selvakumar et al. [384] carried out the sorption of arsenic from aqueous solution using polyvinyl pyrrolidone K25 coated cassava peel carbon through batch experiments as well column studies. The batch sorption proved to be more efficient than the column sorption. Chen et al. [385] studied the sorption of As(V) onto bone char in an agitated batch adsorber and
inferred that bone char can be used effectively for the removal of As(V) from aqueous solution. The adsorption was found to be strongly dependent on pH, dosage of adsorbent, and contact time.

Some low cost adsorbents developed from agricultural wastes, like rice husk [386, 387], coconut husk [388], amine modified coconut coir [389], carbonized wood powder [390], sawdust [391], orange juice residues [392] and waste tea fungal biomass [393] were tested from arsenic removal from water. Diamadopoulos et al. [394] investigated the possible use of fly ash, a by-product of coal power stations, as a means of removing arsenic from water, or equivalently, of restricting its movement in the solid wastes or the soil. The results indicated that the degree of removal of arsenic on fly ash was quite pH dependent. The adsorption was almost irreversible and attained equilibrium in 72 h. Goswami and Das [395] modified the fly ash samples by treating with conc HCl and investigated the efficiency of the modified fly-ash bed in removing arsenic from drinking water. The effectiveness of the modified fly-ash bed for the control of arsenic has been demonstrated by taking different quantities of As(III) and As(V) salts. Pattanayak and co-workers [396] compared the adsorptive efficacy of a char-carbon (CC), derived from fly ash with those of a commercially available Darco activated carbon (DC) and a carbon produced by arcing of graphite rods (AC) for the removal of As(V) and As(III) from contaminated water. CC was fairly efficient for the removal of both As(V) and As(III) which showed its better prospects for arsenic fixation in several practical applications. Namasivayam and Senthilkumar [397] proposed that the use of recycled industrial non-toxic solid wastes as non-conventional adsorbents for removal of arsenic from wastewater can be quite effective as well as economical. Altundoğan et al. [398], in an attempt to improve the adsorption efficiency of red mud, activated it by heat treatment and acid treatment. The maximum removals observed for As(V) and As(III) were 96.52 and 87.54% respectively at optimum conditions.
Kamala et al. [399] demonstrated the ability of *Garcinia cambogia*, an indigenous plant found in many parts of India, in removing As(III) from solution through batch and column experiments. The excellent As(III) sequestering capability of fresh and immobilized *G. cambogia* biomass was indicated. Amin et al. [400] explored the prospect of using rice husk as a potential adsorbent for the removal of arsenic from groundwater. Mondal et al. [401] investigated the ability of arsenic removal by activated rice husk carbons (ARHC) produced from calcium chloride (CaCl$_2$)-impregnated rice husks. It was observed that the removal percentage of As(III) by CaCl$_2$-impregnated ARHC was higher than that without impregnation.

The process of phytoremediation as a promising alternative for removal of arsenic from contaminated soil and water was suggested by Rahman et al. [402] using *Spirodela polyrhiza* L., an aquatic macrophyte. The mechanism of arsenic uptake was also investigated. Vithanage et al. [403] utilized natural red earth (NRE) as a novel adsorbent for decontaminating natural water sources containing As(III) and As(V), As(V) having stronger affinity for NRE surface sites than As (III). Sorghum biomass can be used as an effective and economic adsorbent for the removal of arsenic from aqueous environments [404]. Anirudhan and Unnithan [405] assessed the effectiveness of an anion exchanger (AE) prepared from coconut coir pith, for the removal of As(V) from ground water and industrial wastewater.

Among different waste materials, viz., Atlantic Cod fish scale, chicken fat, coconut fiber and charcoal, studied for removal of As(III) and As(V) from aqueous streams, Atlantic Cod fish scale shows higher efficiency in removing both the species of arsenic [406]. The capability of laterite soil, a low-cost and natural geo adsorbent, was investigated for arsenic removal [407, 408]. Some orange waste, upon loading with Zr(IV), can be used as a unique adsorbent for both As(V) and As(III) from an aquatic environment [409]. Other low cost adsorbents, reported for arsenic removal, include clay [410], kaolin [411].
Membrane separation process commonly includes: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and hyperfiltration or reverse osmosis (RO). Separation of arsenic is reported to be accomplished by MF and UF membranes via mechanical sieving, while capillary flow or solution diffusion is responsible for separation in NF membranes and RO membranes [420]. Nanofiltration is considered as one of the methods that can be used for lowering of arsenic concentrations in drinking water [421]. Waypa et al. [422] studied the arsenic removal from synthetic freshwater and from surface water sources by NF and RO. The results show that both As(V) and As(III) are effectively removed from the water by RO and NF membranes (NF70, Dow/Filmtec) over a range of operational conditions. Both the membranes can achieve rejections of 99%. Removal of As(V) and As(III) are comparable, with no preferential rejection of As(V) over As(III). This suggests that size exclusion, rather than charge interaction, governed the separation behavior. Urase et al. [423] studied the pH effect on the rejection exclusion and the mechanism was proposed [423, 424]. The separation of arsenic species seems to be due to a combination of size exclusion, preferential passage of more mobile ions, and charge exclusion. Saitúa et al. [425] studied the effects of operating conditions in removing arsenic from water by nanofiltration. They showed that arsenic rejection is independent of transmembrane pressure, crossflow velocity and temperature. The co-occurrence of dissolved inorganics does not significantly influence arsenic rejection. Seidel et al. [426] used loose (porous) NF membranes to study the difference in rejection between As(V) and As(III). Oh et al. [427] studied the feasibility of removing the arsenic by a low pressure NF that was applied in rural areas with an electricity supply shortage. The NF is operated by using just a manually operated bicycle pump. Sato et al. [428] also investigated the performance of nanofiltration for arsenic removal. Reverse osmosis (RO)
membranes have been identified as another alternative to remove arsenic from water. Kang et al. [429] studied the effect of pH on removal of arsenic using reverse osmosis. They found that the removal of arsenic compound is almost proportional to the removal efficiency of NaCl. The removal of As(V) is much higher than As(III) over the pH range of 3-10. The removal of arsenic using RO membranes is strongly affected by the solution pH, especially for As(III). Ning [430] had reviewed the removal mechanism of RO and concluded that arsenic, in the commonly high oxidation states of (V), is very effectively removed by RO. Han et al. [245] studied the feasibility of combination of flocculation and microfiltration for arsenic removal from drinking water. Microfiltration of the flocculated water resulted in rejection of the flocs formed by the membrane, thus leading to low turbidity and arsenic removal in the filtrate. However, addition of small amounts of cationic polymeric flocculant can greatly increase the permeate flux during microfiltration. Shih [431] explored the parameters, viz. source water parameters, membrane material and membrane types, that may influence the arsenic removal efficiency. Brandhuber and Amy [432] carried out an intensive study on arsenic removal from drinking water using several membrane filtration methods via bench and pilot testing and summarized the guidelines for arsenic removal via membrane treatment. When arsenic contaminated water contains other dissolved solids, e.g. sulphates, nitrates, carbonates etc, the membrane technology method requires a pre-treatment. In practice, the combined use of in-line coagulation and a membrane treatment (MF or UF) provides very good performances [433, 434]. The impact of chemical pre-treatment on the performance of membrane systems and overall cost and benefits were evaluated [435]. Recent advances in membrane technology in arsenic removal following electro-ultrafiltration (EUF) [436] have been found effective in treating arsenic from water. The removal mechanisms adopted for As(V) are relied on electrophoretic force and electrochemical reduction.
Use of chemical oxidation process as well as oxidative separation of iron and arsenic for disinfection of water has been explored recently. Frank and Clifford [437] showed that under ambient conditions all the As(III) get completely oxidized with oxygen and chlorine within 61 days. Other researchers investigated the oxidation of arsenic in presence of oxygen and ozone [438, 439]. Kim and Nriagu [440] studied the rates of oxidation of naturally occurring arsenic in groundwater samples in presence of ozone, air and pure oxygen gas. Solar oxidation in individual units (SORAS) was explored by Garcia et al. [441] as an alternative technology to treat arsenic from groundwater. The process is based on photochemical oxidation of As(III) followed by precipitation or filtration of As(V) adsorbed on Fe(III) oxides. Swiss Federal Institute of Aquatic Science and Technology has currently developed SORAS in its laboratory and field tested in Bangladesh [442]. A coupled technology utilizing addition of an oxidant and a photoabsorber followed by irradiation with ultraviolet (UV) sources is used as an inexpensive and simple method for arsenic removal [443]. Jayaweera et al. [444] have shown that in the presence of colloidal TiO₂ photocatalyst and the UV radiation (or sunlight), As(III) can be readily converted to As(V) within a short period of time with no concomitant reduction of As(III) to metallic arsenic.

Biological treatment has been demonstrated to be a useful alternative to conventional treatment systems for the removal of toxic metals from dilute aqueous solution. Jong and Parry [445] treated arsenic and other acidic metals (Cu, Zn, Ni, Fe, Al and Mg), and sulphate contaminated waters in a bench-scale upflow anaerobic packed bed reactor by employing a mixed population of sulphate-reducing bacteria. Similar findings were reported by Simonton et al. [446] for removal of As and Cr using Desulfovibrio desulfuricans in columns containing silica sand. Studies on the removal of As(III) and As(V) during biological iron oxidation indicates that bacteria catalyzes the oxidation of trivalent arsenic and enhances overall arsenic removal [447, 448]. Mokashi and
Paknikar [449] studied As(III) oxidation using *Microbacterium lacticum* as a means of treatment of arsenic contaminated groundwater. Fungal, non-living biomass *P. chrysogenum*, an industrial waste with trade name Mycan, was studied by Loukidou *et al.* [419] for the removal of arsenates. The biosorption process is mainly influenced by pH of the solution.

Twardowski [450] reported a method for removal of As(III) from mineral acids by electrochemical reduction to arsenic, which was deposited on a three-dimensional carbon cathode, using a divided cell and cathode potentials that disfavored over-reduction to arsine. Bejan and Bunce [451] used a carbon cathode and IrO₂/Ti anode to study the electrochemical reduction of As(III) and As(V) in acidic and basic solutions. Reduction of As(V) is not efficient, only arsine is removed. However, efficiency can be improved by adding Pd-alumina catalyst. The speciation study of arsenic with respect to solution pH was also made [452]. Bisang *et al.* [453] studied the feasibility of removing the arsenic from acid electrochemically using various cathodes made of Cu, Pb, stainless steel or graphite. The best result was achieved with copper where the arsenic deposition takes place in a range of potentials without hydrogen evolution. Long-term experiments with a pilot plant electrochemical reactor with a three-dimensional cathode were also explored.
References


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