Chapter 9
Removal of Pharmaceuticals from Water Using Adsorption

V. Arya and Ligy Philip

1 Background

Drinking water should be free from any kind of contamination. The source of water can be surface water or groundwater. The conventional water treatment plant takes care of most of the organic contaminants and pathogens. However, analysis of water samples by various researchers showed that the water bodies are contaminated with more complex compounds which are toxic at very low concentrations. Extensive research on these compounds started in mid 1990s with the use of more sophisticated instruments (Santos et al. 2010). These compounds are known as emerging contaminants (ECs) which are widely being studied because of their potential to cause long-term effects to living organisms. Even at very low concentration (μg/L to ng/L), these compounds have very high hazard quotient. Many studies have reported the presence of ECs in surface water and ground water. There is lack of knowledge of their impact in long-term effect on human health, environment and aquatic environments (Deblonde et al. 2011).

Emerging contaminants include endocrine disrupting compounds (EDCs), pharmaceutically active compounds (PhACs) and personal care products (PCPs). ECs can cause serious health effects to the ecosystem (Daughton and Ternes 1999). The removal of these compounds become difficult as these are present at very low concentrations. There is no regulation in the water quality standards for these contaminants. Hence, there is no measure to monitor these compounds in the effluents of wastewater treatment plants (WWTPs). Besides, complete information about the toxicity of these compounds is also not available. These compounds are getting into the water through municipal sewage. Major part of the ingested

V. Arya • L. Philip (✉)
Environmental and Water Resources Engineering Division, Department of Civil Engineering, IIT Madras, Chennai 600 036, India
e-mail: ligy@iitm.ac.in

F. Kurisu et al. (eds.), *Trends in Asian Water Environmental Science and Technology*, DOI 10.1007/978-3-319-39259-2_9

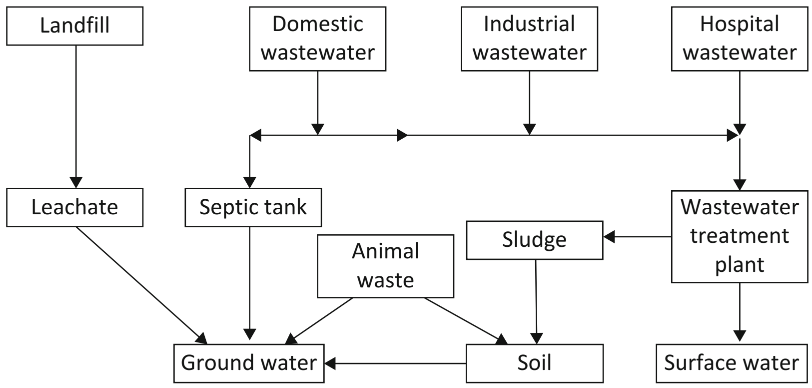

Fig. 9.1 Major sources and pathways of ECs in the environment

pharmaceuticals is excreted from the body, and subsequently gets discharged into the wastewater. Most of the conventional WWTPs are incapable of removing these contaminants (Petrovic 2003). As a result, these compounds will be present in WWTP effluent discharged into the water bodies. Many a time, this water will be used as the source for water supply in the cities located downstream. As a result, human beings are getting exposed to these compounds very regularly. Many studies have identified the presence of these compounds in WWTP effluent (Kumar et al. 2008; Mutiyar and Mittal 2014), surface water (Selvaraj et al. 2014; Shanmugam et al. 2014), groundwater (Sacher et al. 2001), and even in drinking water (Benotti et al. 2009). Figure 9.1 shows various sources and pathways of ECs in the environment.

The ECs were first identified in surface water three decades ago in USA. After that, numerous studies were carried out in USA, Europe and some parts of Asia which reported the presence of various ECs in surface water posing threat to human and aquatic life. There are only a few studies reporting the concentration of emerging contaminants in surface water in India. The most significant study was the analysis of pharmaceuticals from the effluents of pharmaceutical industries in Patancheru (Larsson et al. 2007), which is one of the leading production sites in world market. Studies reported the presence of antibiotics and EDCs in WWTP effluents and in hospital wastewater (Diwan et al. 2010; Kumar et al. 2008; Mutiyar and Mittal 2014). Ramaswamy et al. (2011) analyzed antiepileptic, antimicrobial and preservative compounds in surface water and sediment from the Kaveri, Vellar and Tamiraparani rivers, and in the Pichavaram mangrove in Tamil Nadu, India. Recent studies reported the presence of bisphenol A, alkylphenol ethoxylates and non-steroidal anti-inflammatory drugs, namely, diclofenac, ketoprofen, naproxen, ibuprofen, and acetylsalicylic acid in ng/L in the above locations (Selvaraj et al. 2014; Shanmugam et al. 2014).

2 Adverse Effects of ECs

Pharmaceuticals are extremely important as emerging contaminants because continuous consumption through drinking water even at very low concentrations can cause irreversible effect on human health. Studies have been conducted on aquatic organisms to measure toxicity in terms of growth rate, bioaccumulation, reproduction, geno-toxicity and morphological and physiological abnormalities (Santos et al. 2010). There have been evidences on feminization of fish and significant changes in physiological functions due to the presence of EDCs in surface water and wastewater effluent (Beijer et al. 2013; Larsson et al. 1999). Antibiotics are widely studied because of their utmost importance. Continuous exposure to antibiotics may lead the microbes to become resistant against these medicines. There have been evidences on the presence of antibiotic resistant bacteria in wastewater effluents (Diwan et al. 2010; Kümmerer 2004). Studies have reported the undesired effects of ECs, in particular EDCs, in higher organisms such as rats and alligators (Guillette Jr. et al. 1994; Kumar et al. 2008). All these data show that even in trace amounts, ECs can cause significant effects to the environment. There is not much data available on the toxicity to humans due to consumption of water containing ECs (Daughton and Ternes 1999; Stackelberg et al. 2004). However, possibility of future generations getting affected irreversibly cannot be ignored.

The fate of the compound during treatment depends on the nature of compound and treatment schemes adopted. Even though the compound is not identified in effluent, it may be present in some other form as a metabolite (Daughton and Ternes 1999). Hence, it is important to understand the fate of these compounds in generally adopted treatment schemes. The increased toxicity at very low concentrations, bioaccumulation, antibacterial resistance and the persistence of ECs after conventional WWTP necessitates the use of advanced treatment technologies or modifying the existing treatment schemes for water treatment. Various treatment technologies are available for the removal of emerging contaminants from water. Depending on the technology adopted, the compounds get completely mineralized, converted to intermediate forms, adsorbed to material used for removal or become more hydrophilic and more persistent. Hence, suitable technology should be selected considering the objective.

3 Treatment Technologies

Even though the treatment plants are efficient in removing the pollutant load and nutrients from wastewater, the removal of ECs is not promising. The removal of ECs in conventional treatment is complex because of their diverse physicochemical properties. Removal efficiencies in WWTPs range from 20 to 90 % depending on the technology adopted and the compound to be removed. A lot of studies have been conducted to assess the ability of the conventional treatment methods to

Table 9.1 Removal of ECs by various conventional treatment technologies

Treatment	Advantages	Disadvantages	References
Adsorption using activated carbon	Efficient in removing non-polar compounds (log Kow > 2). It can be coupled with ozonation and coagulation to improve the efficiency.	Polar compounds are not removed. Presence of DOM, solubility of compounds and contact time affect the efficiency.	Kim et al. (2007), Snyder et al. (2007), and Westerhoff et al. (2005)
Activated sludge process	Commonly used in WWTPs and cheapest treatment option. Only less number of ECs are removed efficiently.	Most of the compounds present as ions at neutral pH bypass the treatment. Increase in SRT enhances the removal.	Bolong et al. (2009) and Clara et al. (2005)
MBR	Flexibility to operate at high MLSS concentration and increased SRT. MBR coupled with RO shows higher removal efficiency. More diversity of microbes, over effluent quality is improved.	Removal due to biosorption requires further sludge treatment, high capital and operating costs.	Clara et al. (2005), Dolar et al. (2012)
Advanced oxidation processes	Use of reactive oxygen species with high oxidation potential. Can be used as tertiary treatment for the compounds escaping the pretreatment processes.	Needs UV for most of the treatments which makes the system expensive. High doses are required for efficient removal of ECs.	Adams et al. (2002), Andreozzi et al. (2004), and Pereira et al. (2007)

remove ECs. Comparison of different treatment technologies is presented in Table 9.1. Previous studies reported that coagulation and flocculation are not effective in removing ECs from water (Adams et al. 2002; Westerhoff et al. 2005). However, Snyder et al. (2007) reported that compounds with log Kow value greater than 5 can be removed by coagulation if they are present in anionic form. Adsorption, membrane processes and advanced oxidation are reported to remove ECs from water to some extent.

4 Clay as Adsorbent

There are many studies on the removal of pharmaceuticals using activated carbon (Westerhoff et al. 2005; Snyder et al. 2007). However, the fate of pharmaceuticals during adsorption depends on their partition coefficient, pH of solution and sorption coefficient. Clay is a natural adsorbent for most of the pollutants. Use of clay as an alternative to conventional adsorbents can reduce the cost of the treatment. Clay minerals are hydrous aluminum or magnesium phyllosilicates containing iron, magnesium, alkali and alkaline earth metals and other cations present either in the interlayer space or in the clay lattice (Zhou and Keeling 2013). The layered structure of clay minerals makes them good adsorbent by adsorbing guest species to the interlayer space. The ions present in the interlayer spaces are Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} etc. These ions have high hydration energies thereby making clay minerals hydrophilic in nature.

Clay minerals obtained considerable attention in adsorption due to their large surface area, swelling properties, strong electrostatic interactions and micro to nano sized particles (Zhou and Keeling 2013). There are a number of methods to change the adsorption properties and surface characteristics of clay particles. Commonly used method is modifying clay minerals by cationic or anionic surfactants and the clay synthesized using organic molecules is termed as organo clay. Organo clay is synthesized by intercalation of organic molecule to the interlayer space of clay. This happens mainly through cation exchange mechanism. During the preparation of organoclays, organic cations replace the inorganic cations in the interlayer spaces and on the external surfaces of clay particles (Wu et al. 2014). This leads to an increase in interlayer spacing, thereby accommodating large organic molecules from water. Changes in the interlayer structure of clay are shown in Fig. 9.2. While modifying clay using surfactant, surfactant retention occurs within the interlayer space of clay and other layers of silicates present. These modified clay exhibits hydrophobicity and can adsorb organic contaminants. Adsorption of non-polar organics will be followed by the uptake of counter ions and these counter ions further enhance the adsorption of anionic pollutants from water (Xu and Boyd 1995). A number of studies using organo clay for the removal of contaminants from water have been conducted in the past. However, studies aiming at the removal of pharmaceuticals from water are less. Table 9.2 lists studies conducted using different types of clays in removing pharmaceuticals from water.

Proper selection of treatment is important in the removal of ECs from the environment. Low cost adsorbents can be an alternative to conventional adsorbents. Clay adsorbents are proven to be efficient in batch studies and as adsorption column. Modified adsorbents can be applied in field as permeable barrier which can improve the natural treatment processes. Research in this area requires more attention. The main problem faced in adsorption is the regeneration of adsorbent. Thermal regeneration is not feasible in most of the cases as it can affect the stability of the adsorbent. Other methods such as biodegradation, photo-oxidation and

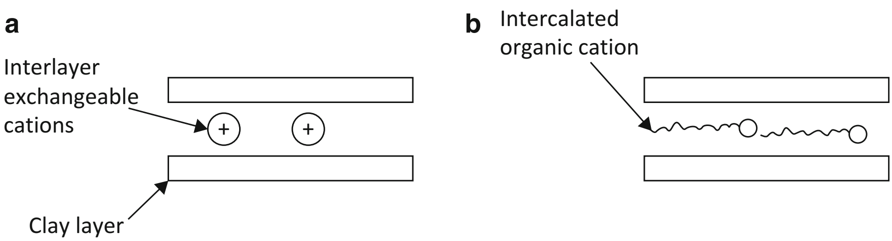

Fig. 9.2 Layered structure of clay before (**a**) and after (**b**) modifying using organic cations

Table 9.2 Selected studies on removal of pharmaceuticals using different clay adsorbents

Material used	Target pollutants	Observations	References
BDMHDA modified montmorillonite	Tetracycline and sulfonamide antibiotics	Micelle-clay adsorption column was efficient compared to activated carbon column.	Polubesova et al. (2006)
Organo clay modified using tetrabutyl ammonium	Flurbiprofen	High adsorption capacity, mainly chemisorption and was found to be exothermic.	Akçay et al. (2009)
Montmorillonite and rectorite	Tetracycline	Clays can remove hydrophilic compounds by intercalation, adsorption is highly dependent on the pH.	Chang et al. (2009)
Aluminum pillared K10 and KSF (Al-K10 and Al-KSF)	Trimethoprim	Removal was dependent on pH of the solution, electrostatic interactions dominated adsorption process.	Molu and Yurdakoç (2010)
Montmorillonite, illite and rectorite	Ciprofloxacin	Adsorption was due to the electrostatic attraction of functional groups and hydrogen bonding.	Wang et al. (2011)
Zeolites and pure and modified clays using organic cations and transition metals	Salicylic acid, acetylsalicylic acid and atenolol	Adsorption capacities are dependent on the characteristics of the pharmaceuticals such as hydrophobicity and functional groups present.	Rakić et al. (2013)

chemical extraction of pollutants for regeneration of organo clay are reported (Zhu et al. 2009).

5 Experimental Studies on Organo Clay in Adsorbing Ciprofloxacin from Water

Previous studies have reported considerable adsorption of ciprofloxacin on montmorillonite minerals (Wang et al. 2011). Ciprofloxacin is a commonly used antibiotic. More than 70 % of the concentration consumed is excreted (Mompelat et al. 2009). Studies were done to compare the adsorption capacities of Na-Bentonite and organically modified bentonite. Surfactant CTAB (Cetyltrimethyl ammonium bromide) $[C_{16}H_{33}(CH_3)_3NBr]$ was used to modify bentonite which had a CEC of 70 meq/100 g. Intercalation of the surfactant into the clay layer was verified by FTIR spectroscopy. Figure 9.3 shows the FTIR spectra of Na-Bentonite before and after modifying with CTAB. The common bands present in both the samples include -OH stretching of Al-OH and Si-OH at

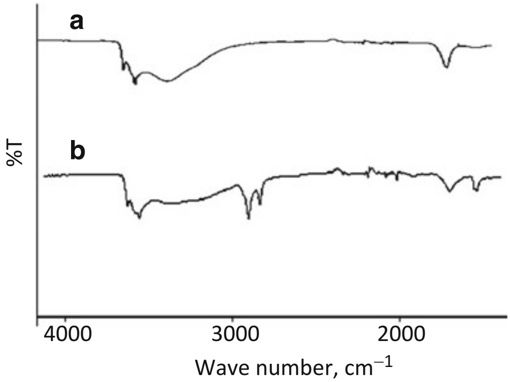

Fig. 9.3 FTIR spectra of bentonite (**a**) and modified bentonite (**b**)

3622 cm^{-1} and 3695 cm^{-1}, respectively (Suchithra et al. 2012). The bands near 2927 cm^{-1} and 2850 cm^{-1} represents the symmetric stretching vibrations of $–CH_2$ bonds and asymmetric stretching vibration of C-H bonds (Praus et al. 2006). This clearly indicates the intercalation of modifier in the interlayer space of clay. CTA ions get adsorbed on the clay due to electrostatic forces causing ion exchange (Praus et al. 2006). Further, it was reported that longer the surfactant chain length and higher the charge density of the clay, interlayer spacing of the clay will be increased (Rakic et al. 2013). Moreover, charge density of the layer would determine the orientation of organic cations in the clay lattice. Orientation of exchanged cations in organo clay could be identified by XRD analyses by observing the basal spacing.

In the present case, the surfactant loading was not exceeded above the cation exchange capacity (CEC) of the clay. It is evident that the properties of the clay will change with respect to the surfactant loading, chain length of the surfactant and clay mineral used. He et al. (2010) reported that the basal spacing of the clay minerals increased with increase in surfactant loading. However, for the experimental study, surfactant loading was not exceeded above CEC of the clay as it would increase the hydrophobicity. Depending on the requirement, optimized loading of the surfactant could be found out experimentally.

During kinetic adsorption studies, 1 g/L of adsorbent was used in solution containing 1 mg/L of ciprofloxacin. Adsorption equilibrium was reached within 6 h. Adsorption of ciprofloxacin was higher in modified bentonite. Nearly, 50 % of the compound was adsorbed to pure bentonite whereas 67 % of ciprofloxacin was adsorbed to organo clay as given in Fig. 9.4. Ciprofloxacin is polar in nature with low Kow values. In case of organically modified clay, hydrophilic head and hydrophobic tail of the surfactant in the interlamellar space of the clay will attract the polar and non-polar part of the molecules in the solution (Rakic et al. 2013). Ciprofloxacin would be present in zwitterionic form at neutral pH. Even then the main mechanism of adsorption to clay is assumed to be cation exchange, there could be limited amount of adsorption owing to the interaction of COO- group in ciprofloxacin with the cations in the interlayer space of clay (Wang et al. 2011).

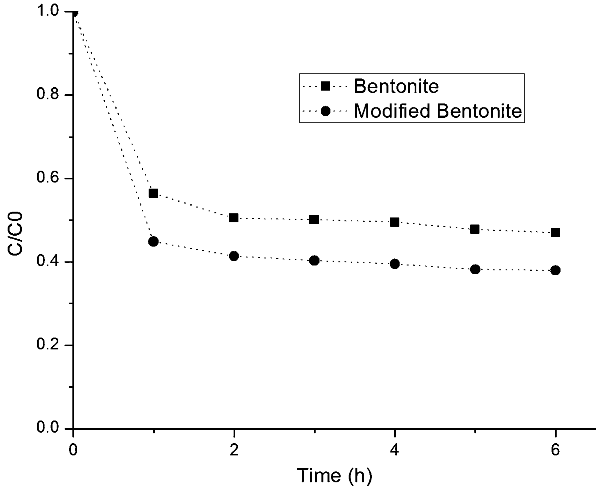

Fig. 9.4 Adsorption of ciprofloxacin on bentonite and modified bentonite

6 Conclusions

Removal of ECs from water and wastewater is not completely achieved in conventional treatment methods due to the complex nature of these compounds and their diverse chemical properties. Adsorption is found to be efficient in removing ECs from water and is used as a tertiary treatment. Modified clay adsorbents can be used to remove the pharmaceuticals from water if these materials possess the desired surface characteristics. Clay is mainly hydrophilic in nature which limits its applications in water treatment. Hydrophilic nature of the clay can be altered by incorporating surfactants into the interlayer space of the clay. Presence of surfactants significantly alters the hydrophilic-hydrophobic nature of the organoclay. Pharmaceuticals present in the water can get adsorbed onto the organo clay due to hydrophobic interactions or the bonding between the functional groups in the compounds to the clay surface. Surface characteristics of the organo clay can be controlled by the surfactant loading. However, extent of removal of the compound depends on the ionic form in which it is present at the desired pH. Column studies need to be done and a suitable method should be adopted for regeneration of adsorbents. The effect of DOM and presence of other ions in water should be considered before developing treatment scheme.

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