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Removal of pollutants using organic/inorganic composite sorbents: a review

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ABSTRACT
Organic and inorganic contaminants (dyes, pesticides, phenol, aldehyde and heavy metal ions etc.) present in water have recently attracted much attention due to their toxic effect to human health and other organisms present in the environment. Persistent organic pollutants (POPs) are a matter of great concern because of their bioaccumulation, transformation and toxicity. Recently, organic/inorganic composite sorbents have demonstrated their capability as effective absorbents for the removal of these types of pollutants from aqueous medium. The present review focuses on the removal of organic and inorganic pollutants using organic/inorganic composite sorbents. It also discusses their photocatalytic property, adsorption mechanisms, thermodynamics and reaction kinetics.

Keywords: Heavy metals; Persistent organic pollutants; Nanocomposite; Kinetics

Introduction

Water has a broad impact on all aspects of human life including food, energy and economy. Every day, about 5000–6000 children die due to the water-related problem[1,2]. Currently, more than 0.78 billion people around the world did not have the access of safe water resources, resulting in major health problems [3]. Several countries that suffer from water shortage have been using groundwater for living which is contaminated with a variety of pollutants, for instance heavy metals, nutrient ions and toxic elements that are released from contaminated soil.

Heavy metals are considered to be toxic or carcinogenic because these ions are not biodegradable and tend to accumulate in living organisms. Zinc, copper, nickel, mercury, cadmium, lead and chromium are of particular concern in the treatment of industrial wastewaters[4-9]. The removal of these toxic metal ions from industrial effluents, water supplies and mine waters are a major global challenge for the 21st century. An increased level of lead in blood leads to increase in blood pressure, fertility problems, nerve disorders, muscle and joint pain, irritability and memory or concentration problems. Nickel exceeding its critical level might bring about serious lung and kidney problems aside from gastrointestinal distress, pulmonary fibrosis and skin dermatitis[10].

In addition to heavy metals, wastewater contain large amount of organic content that should be removed. Among them, persistent organic pollutants (POPs) and recalcitrant products are very hard to remove due to their complex structure. Persistent organic pollutants (POPs) are carbon-based chemical compounds and mixtures that includes polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins, dibenzofurans (PCDD/Fs), and some organochlorine pesticides (OCPs), such as hexachlorobenzene (HCB) or dichloro-diphenyl-trichloroethane (DDT), dibenzo-p-dioxins (dioxins) and dibenzo-p-furans (furans)[11] that persist in the environment, bio-accumulates through the food web, and poses a serious threat to human health and the environment.

Compounds of this nature are highly resistant to degradation by biological, photolytic and chemical means[12]. PCDD/Fs are released in the environment as by-products of waste incineration or metal production[13]. Some POPs are given in Figure. 1. Many of these compounds are continued to be used in large quantities, and due to their environmental persistence, they have the ability to bioaccumulate and biomagnify[14]

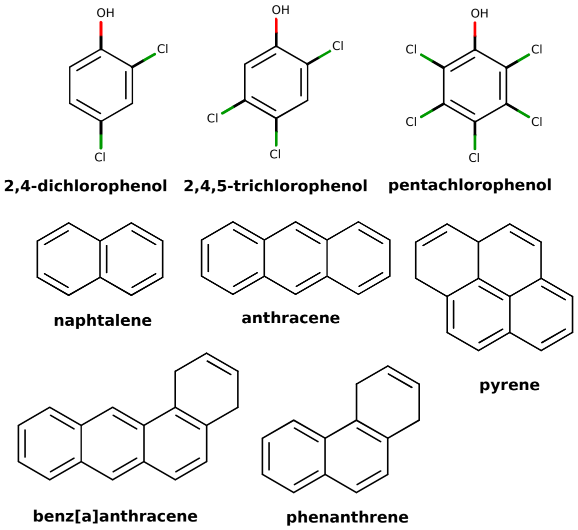


Figure 1. *Some Persistent organic pollutants*

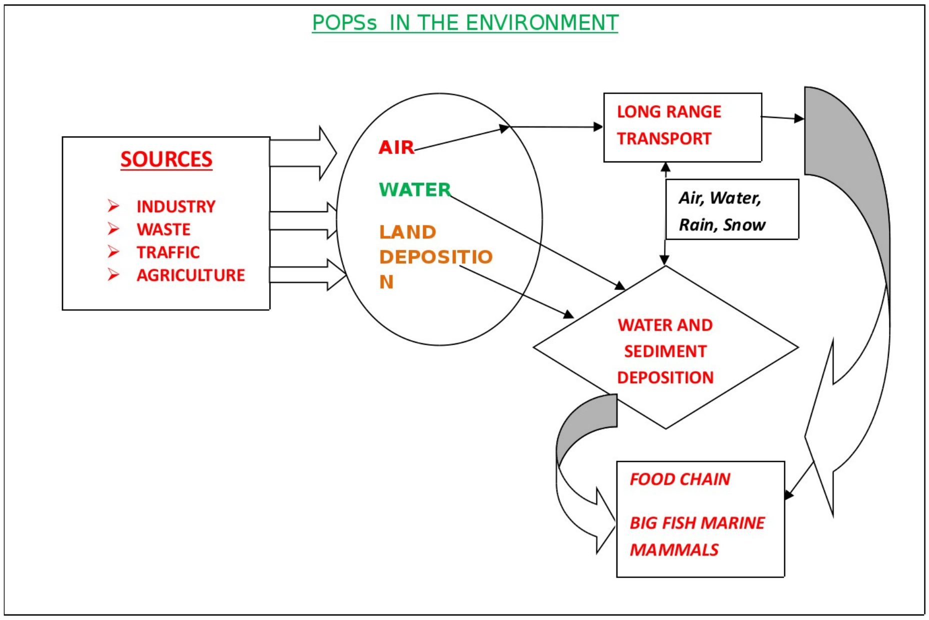


Figure 2. *Sources and pathways of POPs in the environment*

These substances affects the development and growth of plants and animals and also results in reduced reproductive success, birth defects, behavioural changes and death. They are suspected human carcinogens and disrupt the immune and endocrine systems. POPs work their way through the food chain by accumulating in the body fat of living organisms and becoming more concentrated as they move from one creature to another. This process is known as "biomagnification". The POPs are found in small amounts at the bottom of the food chain which biomagnify and pose a significant hazard to predators that feed at the top of the food chain.

This means that even small releases of POPs can have significant impacts. It is deposited in marine and freshwater ecosystems through effluent releases, atmospheric deposition, runoff, and by other means. Due to their semi-volatile nature[15], they are transported over long distances in the atmosphere that results in the widespread distribution of POPs across the globe, including regions where they have never been found (Figure 2).

The Great Lakes (Superior, Michigan, Huron, Erie and Ontario) and their connecting channels constitute the largest system of fresh surface water in the world. Until the 1970s, a variety of POPs, heavy metals and other agricultural and industrial pollutants was routinely discharged into the Great Lakes through waste sites, river runoff, and atmospheric deposition. Despite of many pollution control efforts, still some POPs exist at significant concentrations, indicating the possibility of continued contamination, particularly from long-range atmospheric transport of POPs from other areas.

In general, the presence of organic and inorganic pollutants in the environment even at trace level is believed to be somewhat risky for whole mankind, so treatment of wastewater for the removal and recovery of these pollutants has become a global concern[16-22]. Various techniques such as chemical precipitation, coagulation-flocculation, flotation, ion-exchange, membrane filtration and adsorption have been applied for the removal of organic and inorganic pollutants from wastewater[23-29].

Among them, adsorption is the most effective method because it is simple, highly efficient and easy to operate[30-38]. Adsorption through composite ion exchange materials has gained popularity due to the high selectivity, functionality, chemical and thermal stability of composite ion exchange material. Recently, a great deal of attention has been focused on the application of nano-structured materials as adsorbents to eliminate harmful organic substances from wastewater[39]. The present review discusses the removal efficiency of pollutants through nanocomposites and their adsorption mechanisms, thermodynamics and reaction kinetics.

Removal of pollutants through ion exchange materials

The Composite ion-exchangers formed by the combination of inorganic materials (multivalent metal acid salts) and organic polymer (polyaniline, polypyrrole, polythiophene, poly-o-toluidine, poly-o-anisidine etc.) were found to be very attractive for the purpose of creating high performance or high functional polymeric materials with better chemical, mechanical, and thermal stabilities, reproducibility and possessing good selectivity for heavy metals, indicates its useful environmental applications. The preparation of composite ion exchange materials was carried out by using various chemical routes. However, the sol–gel method is generally applied for the synthesis of these materials[40-46]. Few such excellent ion-exchange materials have been synthesized and successfully used in the environmental analysis. Composite cation-exchangers such as poly-o-toluidine Th(IV) phosphate and poly-o-anisidine Sn(IV) phosphate were prepared by mixing poly-o-toluidine and poly-o-anisidine with inorganic precipitate gels of Th(IV) phosphate and Sn(IV) phosphate under varying experimental conditions.

Pandit and Chudasma[47] have synthesised o-chlorophenol Zr(IV) tungstate and p-chlorophenol Zr(IV) tungstate for the removal of pollutants from aqueous medium. Khan et al. have reported the polyaniline Sn(IV) arsenophosphate[48] and polystyrene Zr(IV) tungstophosphate[49] for the selective separation of Pb^{2+}, Cd^{2+} and Hg^{2+} respectively, and the ion-exchange kinetics of M^{2+}-H^{+} exchange and adsorption of pesticide[50] have also been carried out successfully on these materials. These materials are also used as ion-exchange membrane/ion selective electrodes.

Recently Khan et al.[51, 52] reported the use of polyaniline titanium(IV) phosphate and poly-o-anisidine Sn(IV) arsenophosphate as a methanol and humidity sensors. Kinetic modeling analysis for the removal of cesium from aqueous solutions using polyaniline titanotungstate has been reported by Naggar et al.[53]. The adsorption behavior of gadolinium ion from aqueous solutions by a composite adsorbent has also been investigated[54]. Nickel–potassium ferrocyanide ion exchanger has been immobilized in highly porous discs of chitin for the sorption of Cs(I) from near neutral solutions[55]. Cesium, cobalt and nickel were successfully removed from aqueous solutions by using nano zirconium vanadate as reported by Abd El-Latif[56]. Styrene supported Zr(IV) phosphate and fibrous ion-exchange materials polymethyl methacrylate, polyacrylonitrile, styrene and pectin based Ce(IV) phosphate, Th(IV) phosphate and Zr(IV) phosphate have been reported by Varshney et al[57, 58] have numerous analytical applications.

Some recently synthesized composite cation exchange materials viz. polyaniline Zr(IV) molybdophosphate[59], poly-o-toluidine Zr(IV) iodate[60], polyaniline Ti(IV) arsenate[61], polyaniline Zr(IV) sulphosalicylate[62], acetonitrile stannic(IV) selenite[63] and acrylonitrile stannic(IV) tungstate[64] have been utilized for the treatment of pollutants. Besides their use as ion-exchanger, conducting polyaniline Ti(IV) arsenate composite material has been successfully applied for the photochemical degradation of industrial dye. Polyaniline Zr(IV) sulphosalicylate nano-composite material has shown more significant activities against many bacteria and fungi than other known antibiotics. Due to their good ion-exchange capacity along with their optical and electrical properties, the nano-composite cation exchange materials are the promising candidate for utilizing as transparent electrodes in solar cells.

The practical utility of poly-o-toluidine Zr(IV) iodate is demonstrated by analyzing Zr^{4+} and Cd^{2+} ions from real samples and synthetic mixtures. The practical usefulness of polyaniline Zr(IV) molybdophosphate was revealed in the analysis of metal ions (e.g., Pb^{2+}, Hg^{2+}, Cd^{2+}, Cr^{2+} and Fe^{3+} etc.) from synthetic mixtures as well as environmental samples. Acetonitrile stannic(IV) selenite was used for the quantitative binary separations of metal ions, namely, Pb^{2+}–Th^{4+}, Ni^{2+}–Th^{4+}, Ni^{2+}–Zn^{2+}, Cu^{2+}–Ce^{4+}, Al^{3+}–Bi^{3+}, and Al^{3+}–Zn^{2+}. Acrylonitrile stannic(IV) tungstate was conveniently utilized for the removal and isolation of heavy toxic metal ions released from wastewater stream.

Inamuddin and Ismail[65] synthesized poly-o-methoxyaniline Zr(1V) molybdate composite cation-exchanger which is found to be selective for cadmium (toxic metal ion) indicating the utility of this material in the removal of cadmium from waste stream. Ion exchange kinetic parameters have also been determined for the poly-o-methoxyaniline Zr(IV)molybdate and polyaniline Ce(IV)molybdate composite cation exchanger [66, 67].The practical usefulness of celluloseacetate Zr(IV)molybdophosphate and polyaniline Sn(IV)molybdate have also been demonstrated[68, 69] in quantitative determination and separation of Ca^{2+} and Pb^{2+} from commercially available vitamin and minerals formulation namely Recovit and standard reference material (Rompin Hematite) of lead. A polystyrene based strongly basic anion exchange resin

De-Acidite FF-IP was utilized for the removal of malathion from aqueous solution by Naushad et al. [70]. More recently, Bushra et al. synthesized polyaniline Ti(IV) arsenophosphate and poly-o-toluidine Zr(IV)tungstate[71,72]. Electrically conducting polyaniline Ti(IV) arsenophosphate help in the exclusion of heavy metal ions and organic pollutants (dyes). Photocatalytic degradation for Acid Blue 29 by using this composite material was found to be higher than that of MB (Methylene blue) owing to the presence of more number of sulphur attaching functional group compared to MB. It was also found, that polyaniline Ti(IV) arsenophosphate shows 76% decolorization of Acid Blue 29 and 47% for MB in 180 min. The adsorption of dye on the material follows both pseudo first and second order kinetics but it best fits with pseudo second order kinetic as it shows relatively higher value of the regression coefficient. Their good electrical conductivity, antimicrobial screening and photochemical degradation results show that polyaniline Ti(IV) arsenophosphate can be successfully used as conducting material, antimicrobial agent as well as a photocatalyst for the degradation of textile industry dye besides its use as ion exchanger. Poly-o-toluidine Zr(IV) tungstate show selective behaviour for Ba^{2+}, Hg^{2+} and Pb^{2+}ions and their use in determination of Pb^{2+}metal ions from tap water and electroplating wastewater samples by FAAS demonstrates its practical utility. Poly-o-toluidineZr(IV) tungstate composite cation exchanger thus, exhibits the characteristics of a promising ion-exchanger as well as conducting material.

Photocatalytic behaviour of nanocomposites in the elimination of organic pollutants

Endocrine disrupting chemicals (EDCs) are the organic compounds which includes substituted phenols, alkanes, alkenes, carboxylic acids, aromatics and their halogenated derivatives are normally found in surfactants, dyes and pesticides/herbicides poses a serious threat to ecology as well as human health[73] due to its low degradation ability and toxicity [74]. The effluent from the textile industry accounts for the largest proportion of dye effluent pollution worldwide[75]. Photocatalytic system is considered to be a desirable method for exclusion of environmental pollutants, due to its certain characteristic features such as ambient temperature and pressure, complete mineralization of the parent as well as their intermediate compounds without secondary pollution and low operation costs [76, 77].

The efficiency of various processes was assessed by percent decolorization. The percentage of decolorization was estimated by the following equation:

$$\text{Decolorization (\%)} = (1 - C_t/C_o) \times 100$$

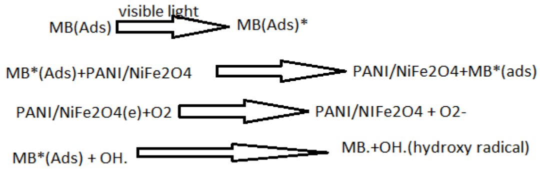
where C_t was the dye concentration in aqueous solution at time t and C_o was initial dye concentration.

From functional point of view, the photocatalysis is one of the so-called advanced oxidation technology (AOT). This technology involved the generation and use of powerful redox transient species i.e hydroxyl radical (HO•) which is very effective in the oxidation of organic matter. An important parameter in the photocatalytic reactions taking place on the particulate surfaces is the pH of the solution, since it dictates the surface charge properties of the photocatalyst and size of aggregates it forms. Effect of different concentration of photocatalyst also plays a very important role in the degradation kinetics of pollutant.

Titanium dioxide (TiO_2) is a suitable photocatalyst for degradation of environmental pollutants because of its outstanding photocatalytic performance[78,79]. The main advantages of TiO_2 is its high chemical stability towards acidic and basic compounds, its nontoxicity, its relatively low cost and highly oxidizing power which make TiO_2 a competitive candidate for many photocatalytical applications. The highly oxidizing effect of TiO_2 makes it suitable for decomposition of organic and inorganic compounds at very low concentrations ranging from 0.01to 10 ppm. Polyaniline (PANI) has also received much attention in various fields due to its better mechanical, electrical and thermal properties[80]. TiO_2 coated PANI enhance the photocatalysis of reactive dyes[81]. The photodegradation of reactive black dye 5(RB-5) was investigated for both the uncoated P25-TiO_2 as well as the PANI coated P25-TiO_2[82]. The PANI coated TiO_2 show an improved performance in both the photocatalysis and adsorption of reactive black dye 5(RB-5) as compared to the uncoated TiO_2. Adsorption also plays a very important role in photocatalytic process. Photodegradation rate of reactive black dye 5 by PANI coated TiO_2 increases at low pH values, because at high pH the surface is negatively charged and the PANI/TiO_2 catalyst repels the anionic RB-5 dye. Increase in the amount of catalyst increases the activation site for the reaction[83] which in turn increases the photodegradation efficiency of dye. Concentration of dye also plays a very important role in photocatalysis. Increase in initial concentration of RB-5 dye decrease the efficiency of photocatalysis. Equilibrium studies show that low pH and high sorbent mass would favour the adsorption. So PANI coated P25-TiO_2 nanocomposite can be successfully applied for the removal of dye from real water samples from textile industries.

Photocatalytic degradation studies are also carried out for water soluble carcinogenic methylene blue (MB) dye by employing polyaniline (PANI)-Nickelferrite ($NiFe_2O_4$) nanocomposite[84] in aqueous solution. Different parameters like dye concentration, dose of photocatalyst, contact time and pH have been studied to optimise reaction condition.

With increase in the concentration of PANI-$NiFe_2O_4$ nanocomposite, photocatalytic degradation of dye increases rapidly due to increase in the number of active sites of the catalyst. Photocatalytic degradation of dye is also increased with increase in pH but increase in initial concentration of dye decreases the photocatalytic efficiency. The photocatalytic degradation of MB dye on the surface of PANI-$NiFe_2O_4$ nanocomposite as shown in the Scheme 1 follows pseudo first-order kinetics. The optimum conditions for the removal of the MB dye is 30 ppm, photocatalyst dose 8 g/L and pH 8.5.



Scheme 1 *Photocatalytic degradation of MB dye on the surface of PANI-$NiFe_2O_4$ nanocomposite*

Degradation of malachite green (MG) with PANI/ZnO nanocomposite under ultraviolet irradiation was carried out by Eskizeybek et al[85]**.** The experimental results revealed 98% decolorization of Malachite green with 1.2 g/L of the nanocomposite at 180 min of irradiation. Decolorization efficiency of the dye is very high than corresponding dark conditions in the presence of the PANI/ZnO nanocomposite under illumination. Photocatalytic degradation of MG dye on the surface of PANI/ZnO nanocomposite follows pseudo first-order kinetics. The experimental results revealed that the prepared PANI/ZnO nanocomposites are good catalyst to remove organic pollutants under UV light irradiation.

Mechanism of Adsorption

The important models like Langmuir, Freundlich, Halsey, Henderson, Smith, Elovich liquid film diffusion, intraparticle diffusion, and Lagergren are used to explain the results of adsorption studies but here only few of them are described.

According to Langmuir model[86], the adsorption occurs on a homogenous surface forming monolayer of adsorbate with constant heat of adsorption for all sites without interaction between adsorbed molecules[87].The linear form of Langmuir model is given as

$$\frac{1}{q_e}=\frac{1}{q_m}\times\frac{1}{b}\times\frac{1}{C_e}+\frac{1}{q_m} \tag{1}$$

where C_e is the equilibrium concentration of metal ions in the solution (mg/L), q_e is the amount of metal ion adsorbed per unit weight of adsorbent (mg/g), q_m is the amount of metal ion required to form monolayer (mg/g) or maximum monolayer adsorption capacity and b is a constant related to energy of adsorption (L/mg) which represents enthalpy of adsorption and should vary with temperature.

The Freundlich isotherm model[88] is applied to multilayer adsorption with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface[89].The linear form of Freundlich model is represented as

$$\log q_e=\log K_f+\frac{1}{n}\log C_e \tag{2}$$

where C_e is the equilibrium concentration in mg/L and q_e shows that the adsorption seems to follow the Freundlich isotherm model as well as Langmuir isotherm, K_f is the Freundlich constant which indicates the relative adsorption capacity of the adsorbent related to bonding energy and n is the heterogeneity factor representing the deviation from linearity of adsorption and is also known as Freundlich coefficient.

Temkin isotherm[90] assumes that the decrease in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich isotherm[91].The linear form of Temkin equation is represented as

$$q_e=\left(\frac{\mathrm{RT}}{b}\right)\times\ln A+\left(\frac{\mathrm{RT}}{b}\right)\times\ln C_e \tag{3}$$

where (RT/b) = B, R is universal gas constant, T is absolute temperature and b is another constant. A (g/L) and B (J/mol) are Temkin constants related to adsorption potential and heat of adsorption.

Dubinin- Redushkeuich (D-R) isotherm [92] does not assume a homogenous surface or a constant sorption potential[93].

The Dubinin−Radushkevich model was chosen to estimate the characteristic porosity and the apparent free energy of adsorption. The linear forms of this equation are represented as

$$\ln q_e=\ln q_m-\beta\varepsilon^2 \tag{4}$$

$$\varepsilon=\mathrm{RT}\ln\left(1+\frac{1}{\mathrm{Ce}}\right) \tag{5}$$

$$E=\frac{1}{\sqrt{(-2\beta)}} \tag{6}$$

where ε is the Polyani potential, q_m is the monolayer capacity (mol/g), C_e is the equilibrium concentration (mol/L), K is a constant related to adsorption energy $\mathrm{mol}^2\ (\mathrm{KT}^2)^{-1}$. The Polyani potential (ε) and mean free energy of adsorption (E, kJ/mol) can be calculated from the equations. β is the D– R model constant ($\mathrm{mol}^2/\mathrm{kJ}$) or the porosity factor which can be obtained from the slope of the plot of ln q_e verses ε^2.

Kinetic and thermodynamic studies

Thermodynamic parameters such as standard free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) were estimated using the following relations.

$$\mathrm{Kc}=\frac{C_{\mathrm{Ad}}}{C_e} \tag{7}$$

where Kc is the distribution constant, C_{Ad} and C_e are equilibrium concentrations of target pollutant on the adsorbent and in the solution, respectively. The Gibbs energy change (ΔG°) indicates the degree of spontaneity of an adsorption process, and a higher negative value reflects a more energetically favorable adsorption. According to thermodynamic law, ΔG° of adsorption is calculated as follows:

$$\Delta G^0=-\mathrm{RT}\log\mathrm{Kc} \tag{8}$$

where ΔG^0 is the Gibbs free energy, K_c is the thermodynamic equilibrium constant without units, T is the temperature in Kelvin and R is the gas constant. The values of ΔH^0 and ΔS^0 were calculated from the following Van't Hoff equation

$$\log \mathrm{Kc} = -\frac{\Delta H^0}{\mathrm{RT}} + \frac{\Delta S^0}{R} \quad (9)$$

These thermodynamic parameters estimates can offer insight into the type and mechanism of an adsorption process.

In order to understand mechanism of the adsorption process and to analyze the adsorption rate, the kinetic data was modelled to test experimental data using Lagergren pseudo-first-order[94] and pseudo-second–order equations[95]. The pseudo-first-order expression is given by the following equation (10).

$$\log\left(q_e - q_t\right) = -\left(\frac{K_1}{2.323}\right) \times t + \log q_e \quad (10)$$

where qe is the amount of adsorbate adsorbed per unit weight of adsorbent at equilibrium (mg/g), q_t is the amount of pollutant adsorbed per unit weight of adsorbent at any given time t, K_1 is the rate constant for pseudo first order model. The values of K_1 and qe (cal) was calculated from slope and intercept of the linear plots of log (qe-qt) versus t at various concentrations.

The pseudo-second-order rate expression is used to describe chemisorption involving valency forces through the sharing or exchange of electrons between the adsorbent and adsorbate as covalent forces, and ion exchange [96]. The pseudo-second-order adsorption kinetics rate equation is given as

$$\frac{t}{q_t} = \frac{1}{K_2 \times q_{e^2}} + \frac{1}{q_e} \times t \quad (11)$$

where h is the initial adsorption rate (mg/g/min), which is given as h = $K_2 \times q_e^2$. K_2 (g/mg min) is the adsorption rate constant for pseudo-second-order reaction.

Kinetics of the adsorption of metal oxides (MO) by MWCNTs as studied by Hosseini et al. [97] followed the pseudo-second order kinetic equation. Similarly, the adsorption of MB from aqueous solution by a novel carbon based hybrid, G-CNT also followed pseudo-second-order kinetic model[98]. The MWCNTs for the removal of Cd(II), Pb(II), and Cu(II) ions from aqueous solutions have also been reported[99]. The adsorption data obeyed the Langmuir model, and adsorption capacities were found to be 97.08, 24.49, and 10.86 mg/g for Pb(II), Cu(II), and Cd(II), respectively. Determination of atrazine, methidathion and propoxur (toxic pesticides) in tap and reservoir waters using MWCNT as solid phase extractant was developed by Al-Degs et al.[100]. MWCNT adsorbent showed excellent extraction/pre-concentration of pesticides present at trace levels. The atrazine, methidathion and propoxur were reproducibly detected with a detection limit of 3, 2 and 3 µg/L, respectively. There are only few reports which are published until now on the application of CNTs as adsorbent for dye removal from aqueous solution[101-104]. Magnetite loaded MWCNTs (M-MWCNTs) have received particular attention, with many studies demonstrating their promise[105]. M-MWCNTs was successfully used for the removal of MB dye from aqueous solution in a pH-dependent fashion with a maximum monolayer adsorption capacity of 48.06–48.1 $\mathrm{mg.g^{-1}}$ [106]. Novel core–shell nanostructured estrone-imprinted MWCNT-Est-MIP composites were applied for the removal of low concentrations of estrone from water samples with removal efficiencies ranging from 96.14 to 98.03% [107]. Methyl methacrylate (MMA) or chitosan (CS) grafted MWCNT composites have also demonstrated excellent removal efficiency for 4,4′-dichlorinated biphenyl (4,4′-DCB) [108].

Conclusions

The present review highlights the application of nanocomposite material in the removal of pollutants that have a great impact on the ecosystem. Trace amounts of any of these pollutants lead to an enormous pollution problem and consequently, the removal of these pollutants from aqueous solutions is a subject of paramount importance. Nanocomposite is one of the efficacious ways to improve the property of the catalyst. Photocatalytic system is also known to be a desirable method for degradation of environmental pollutants among various methods for wastewater treatment.

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