

# Advancement of Clay and Clay-based Materials in the Remediation of Aquatic Environments Contaminated with Heavy Metal Toxic Ions and Micro-pollutants

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## Abstract

Clay minerals are natural materials that show widespread applications in various branches of science, including environmental sciences, in particular the remediation of water contaminated with various water pollutants. Modified clays and minerals have attracted the attention of researchers in the recent past since the modified materials are seemingly more useful and efficient for removing emerging water contaminants. Therefore, modified engineered materials having multi-functionalities have received greater interest from researchers. The advanced clay-based materials are highly effective in the remediation of water contaminated with organic and inorganic contaminants, and these materials show enhanced selectivity towards the specific pollutants. The review inherently discusses various methods employed in the modification of clays and addresses the challenges in synthesizing the advanced engineered materials precursor to natural clay minerals. The changes in physical and chemical properties, as investigated by various characterization techniques before and after the modifications, are broadly explained. Further, the implications of these materials for the decontamination of waterbodies as contaminated with potential water pollutants are extensively discussed. Additionally, the insights involved in the removal of organic and inorganic pollutants are discussed in the review. Furthermore, the future perspectives and specific challenges in the scaling up of the treatment methods in technology development are included in this communication.

**Keywords:** *Advanced clay based materials, Sorption mechanism, Micro-pollutants, Heavy metals, Synthesis of advanced materials*

## 1. Introduction

Rapid industrialization and urbanization resulted in the deleterious quality of fresh water. The occurrence of toxic heavy metals and emerging micro-pollutants in water resources is increased tremendously with the advent of enhanced industrial and anthropogenic activities, including the mining industry, electroplating industry, pesticides, metal rinse processes, tanning industry, textile industry, batteries, metal smelting, paper industry, electrolysis applications etc.[1,2]. Many heavy metals, including mercury, lead, copper, cadmium, arsenic, chromium, and many other (toxic) metals, are excessively released, which causes serious environmental and public health issues[3,4]. The primary sources, permissible levels in drinking water, and health effects of heavy metals are given in Table 1. The heavy metals are persistent and non-biodegradable; hence, even at low concentrations posing serious environmental concerns. The presence of these contaminants in water-

bodies resulted in a slow accumulation in the biological systems, both in marine and human lives. Hence, eliminating these heavy metals is a viable and effective solution to safeguard the human and aquatic environment[5].

Similarly, excess release of harmful endocrine-disrupting chemicals (EDCs), pharmaceuticals, dyes, personal care products etc. are entering the aquatic environment through various anthropogenic activities[6,7]. Micro-pollutants are usually detected at trace quantities ranging from  $\mu\text{g/L}$  to  $\text{ng/L}$  in waterbodies, including river and lake waters. Since the traditional wastewater treatment plants are not specifically designed to eliminate these emerging pollutants at low levels. Moreover, their potential persistency and bioactivity caused an additional pollutant load to the water bodies, which needs efficient removal of these emerging contaminants from the aquatic environment. Different types of micro-pollutants and their effects on human health are summarized in Table 2. Due to extensive and continuous usage of these pollutants with unmanaged disposal in the water bodies, they are detected in the aquatic environment. Therefore, these micro-pollutants pose several health issues in humans and living organisms and received a global concern [8,9].

Removing of toxic heavy metals and micro-pollutants from water bodies is of great environmental concern. A literature survey reveals that several methods, including chemical precipitation, evaporation, re-

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**Table 1. The Major Sources, Permissible Level in Drinking Water and Health Effects of Heavy Metals**

Heavy metals	Sources	Health effects	Permissible level in drinking water	Ref.
Mercury	Effluents from mining, power generation, chloralkali wastewater, rubber processing and batteries industry.	Blockage of the enzyme sites and inhibition of protein synthesis.	2 µg/L	[10-12]
Lead	Battery industries, metal plating, lead-acid batteries industries, paint, oil, metal, phosphate fertilizer industries, electronic, and wood processing.	General metabolic poisoning, inhibiting enzyme active sites and affecting the blood, liver, kidney and brains of human beings; stroke and even death.	0.01 mg/L	[13-15]
Copper	Copper mining and smelting, brass industry, electroplating industries and extreme usage of Cu-based agro-chemicals.	Diarrhea, abdominal pain, jaundice, gastrointestinal distress and nausea.	1.5 mg/L	[16-18]
Arsenic	Natural sources including volcanic eruption, rock fragmentation, mineral deposits, brackish water, hot spring, and anthropogenic sources including industrial processes, metal smelting, pesticide manufacturing and wood preservers.	Neurological, dermatological, gastro-intestinal and cardio renal diseases.	10 µg/l	[19,20]
Cadmium	Mining, painting, alloying, electrolyzing, electroplating, smelting, textile and printing industries.	Acute abdominal pain, diarrhea, nausea and a choking sensation.	0.005 mg/L	[13,21,22]

**Table 2. Different Micro-Pollutants and its Effects on Human Health**

Micro-pollutants	Class	Application	Health effects	Ref.
17 α Ethinyl-estradiol (EE2)	Synthetic estrogen	Human	Cancer risk especially in female.	[23,24]
Triclosan	Antibiotic	Commercial disinfectant	Antibiotic resistance, skin irritation, endocrine disruption, allergies, and carcinogenic by-products formation.	[25,26]
Diclofenac	Arthritis	Human and veterinary	Inhibits the activity of cyclooxygenases and DNA synthesis through multiple, interferes with the biochemical functions of fish mechanisms.	[27,28]
Sulfamethoxazole	Antibiotic	Human and veterinary	Development of bacterial resistance genes, resulting in emergence of multi drug resistant.	[29]
Ibuprofen	Analgesic	Human and veterinary	Dyspeptic symptoms and gastrointestinal (GI) ulcers.	[30]
Tetracycline	Antibiotic	Human and veterinary	Gastrointestinal distress, discoloration of teeth, kidney and liver.	[31]
Bisphenol A	Plasticizer	Production of plastics and resins	Reduced sperm quality, fertility, male sexual function etc.	[32,33]
Amoxicillin	Antibiotic	Human and veterinary	Extreme allergy to species that are sensitive which includes human beings.	[34]

verse osmosis, solvent extraction, ion exchange, biological, photocatalysis, electrochemical treatment, membrane filtration, etc. are employed for the decontamination of water polluted with toxic metal ions, including micro-pollutants[35,36]. Nevertheless, these methods have several disadvantages, for example, expensive, the requirement of skilled personnel for operation, incomplete removal, generation of by-products, and high energy requirement[37,38]. Moreover, these processes are not efficient for low-level metal pre-concentration. Adsorption is one of the most common methods used to remove of these pollutants from the aquatic environment due to its low cost, simplicity of operation, effectiveness, and high efficiency compared to other traditional removal methods[39-43]. Moreover, adsorbents could be reutilized by following an appropriate desorption procedure[44,45].

Clays are the most common adsorbents used in adsorption methods due to their abundance, low cost, eco-friendly, high specific surface area, etc.[46]. Researchers around the globe are focusing on the use of

natural and modified clays as adsorbents for treating wastewater since it contains exchangeable cations along with the surface functional groups, which facilitate the sorption of various water contaminants[47]. Clay minerals consist of aluminosilicate sheets, of which the structural layers are firmly arranged, and each sheet is made up of two, three, or four layers. This constitutes tetrahedral silicate  $[SiO_4]^{4-}(T)$  and octahedral aluminate  $[AlO_3(OH)_3]^{6-}(O)$ . The smaller metal cations occupy the interiors of tetrahedrons and octahedrons, and the oxygen atom occupies the apices from which some are connected with protons (as OH). Thus, fundamental structural elements form the hexagonal network with each sheet. The charges of the layers depend upon the ratio and number of sheets in the fundamental structural units[48,49].

Clay minerals are efficient in removing several heavy metal toxic ions effectively, however; the organic pollutants having non- or low-polarity and anionic impurities such as As(V), As(III), Cr(VI) etc., are

less attracted by these pristine clay minerals[48,50,51]. Anionic contaminants and hydrophobic or non-polar organic pollutants, are feebly adsorbed by these clays, which possess enhanced hydrophilic character and charges on the surface[52,53]. Moreover, the pristine clay particles are difficult to recover and regenerate after the adsorption process and usually lose a significant quantity of their adsorption capacities during the regeneration process[54]. Therefore, the raw clay minerals require suitable modifications to remove these water pollutants efficiently these water pollutants. The suitable modification of clay minerals results in useful and engineered material in environmental engineering[55,56] and material sciences[57,58]. Organic cations with short and long-chain compounds are introduced within the interlayer spaces with the available exchangeable cations and the permanent negative charge of clay minerals. Thus, these modifications considerably change the hydrophilic nature of clay to hydrophobic nature, which in turn is employed to remove efficiently several organic compounds or even anionic water pollutants[59]. The synthesis of nanocomposites and incorporation into clay minerals has become of great interest recently because of their physical and chemical properties and distinctive applications in the diverse area of research[60,61]. Modification of clay minerals mainly involved two processes, i.e., chemical and physical processes. Modifying natural clay minerals with surfactants has shown their efficient adsorption process but their combined surface and thermal potential still need to be studied. Removal of several contaminants could be achieved using hybrid materials having inorganic/organic moieties[62]. Clay minerals physically modified by thermal activation remove intercrystallite water molecules and increases porosity and surface area[63]. Therefore, this review focussed on the applicability of natural clay and its modified form for removing toxic heavy metals and micro-pollutants from aqueous solutions.

## 2. Use of natural clay in the removal of heavy metals and micro-pollutants

Kaolinite[64], montmorillonite[65], vermiculite[66], sepiolite[67], bentonite[68], and laterite soil[69] in their pristine form are used for the removal of toxic heavy metals from aqueous solutions. The sorption of diatrizoic acid (DAT), iopamidol (IOP), metformin (MTF), and carbamazepine (CBZ) was conducted using montmorillonite. It was reported that montmorillonite could remove 70% of MTF and CBZ, 30% of DAT, and no removal of IOP without generation of by-products. Further, it was observed that the adsorption rates depend on the pollutant concentrations[70]. Palygorskite-montmorillonite (PM) is used to treat the effluent filter material for carbamazepine. The sorption of carbamazepine onto PM mainly occurred through the hydrogen bonding between the hydrogen donor group of carbamazepine and the hydrogen acceptor group of the PM[71]. Montmorillonite and kaolinite are used for the sorption of antibiotic nalidixic acid (NA). The adsorption of NA on kaolinite and montmorillonite was higher at lower pH. The adsorption of NA on montmorillonite is promoted by a coordination bond between the keto oxygen or C=N group in the pyridine ring and the exchangeable cations in the interlayer of montmorillonite according as

**Table 3. Adsorption Capacities of Raw Clays for the Removal of Various Heavy Metals and Micro-Pollutants**

Raw clays	Pollutant	pH	Maximum adsorption capacity (mg/g)	Ref.
Montmorillonite	Pb(II)		3.71	[73]
	Cd(II)	2~7	2.45	
	Ni(II)		1.76	
Bentonite	Cd(II)	5	13.17	[74]
	Cr(VI)	6	12.61	
Sepiolite	Cr(III)	3	14.1	[67]
	Cd(II)	3	32	
	Ni(II)	7	7.56	
	Cu(II)	4	13.8	
	Zn(II)	7	8.67	
Kaolinite	Ag(I)	7	12.6	[75]
	Pb(II)	5.7	5.3	
	Cd(II)	5.5	4.0	
Beidelite	Ni(II)	5.7	5.2	[76]
	Pb(II)	6	83.33	
Montmorillonite (SAz-1)	Cd(II)	6	45.66	[76]
	Ciprofloxacin	4.5	395	
Illite (IMt-2)	Ciprofloxacin	4.5	135	[77]
Rectorite	Ciprofloxacin	4.5	33	[77]
Montmorillonite	Tetracycline	1.5	468	[78]
Montmorillonite	Tetracycline	8.7	375	[78]
Illite	Tetracycline	5~6	32	[79]
Kaolinite	Triclosan	3	22	[80]
Montmorillonite	Triclosan	3	3.3	[80]
Natural bentonite	Diclofenac	2	62.50	[81]
Sodium bentonite	Diclofenac	2	40	[81]
Montmorillonite	Diclofenac	-	680	[82]
Bentonite	Amoxicillin	2.31	53.93	[83]
Natural Bentonite	17a-Ethinylestradiol	7	5.16 ± 0.29	[84]

revealed by the FT-IR analyses[72]. The adsorption capacity of various natural clay for heavy metals and micro-pollutants is summarized in Table 3.

## 3. Thermal modification of clay

Thermal modification of clay minerals is termed calcination[85]. Clay minerals are usually heated up to 200~1000°C for 2~4 hrs. The thermal activation of clay minerals causes the activation of clay's active sites, which promote the sorption of pollutants[86,87]. During calcination, dehydration and then dihydroxylation occurred, which resulted in the reduction of mass while the porosity was increased significantly; the clay surface became more exposed to the ion exchange process[88]. It was reported that the surface properties of bentonite and kaolinite

were changed substantially on heat treatment. The volatile impurities and physico-adsorbed water molecules were removed at 100 °C, increasing the specific surface area of clay[89]. However, the specific surface area was reduced if the temperature was increased up to 500 °C, mainly due to the collapse of clay layers and the dihydroxylation process[85]. A similar decrease in surface area was observed in kaolinite and montmorillonite after the heat treatment at 750 °C[90]. Further, calcination of montmorillonite at 600 °C results in a decrease in surface area but increases with sorption capacity[91,92]. This showed that the sorption potential was also affected by other factors[93]. The cation exchange capacity (CEC) of clay is likely to be reduced once clays are treated at a very high temperature; however, the temperature must be maintained carefully during thermal treatment[85]. The adsorption capacity of bentonite and kaolinite was decreased by calcining the solids from 500 to 900 °C[94]. The maximum sorption capacity of various heavy metals and micro-pollutants using thermally treated clays is included in Table 4.

X-ray diffraction analysis of thermally treated bentonite at 400 °C showed a significant decrease in the basal spacings from 1.48 nm to 0.97 nm[95]. A similar observation was also reported on the thermal treatment of bentonite clay[96]. The FT-IR spectra of thermally treated bentonite clay decrease in the intensity of H-O-H deformation band at 1600 to 1700  $\text{cm}^{-1}$  and O-H stretching vibrations at 3100 to 3700  $\text{cm}^{-1}$  [97].

#### 4. Activation of Clay

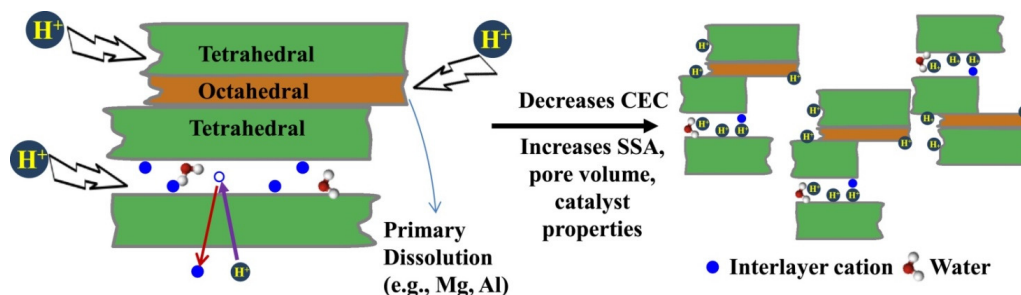
Clay minerals are often treated with acids to modify their surface and remove impurities[104]. Activation of clay minerals with acids, caused by the opening of pores and exposure of clay edges, leads to an enhanced sorption capacity for several pollutants[105]. Activation of clay minerals with acid is found to be an effective method of modification[106]. Calcium, potassium, magnesium, iron, and metal oxides are also removed from clay minerals during acid treatment, increasing surface area and further providing open spaces for heavy metal adsorption[87,107,108]. Sulphuric, phosphoric, nitric, and hydrochloric acids are the most common acids used to activate clay minerals[109,110]. The structural changes on the surface and interlayer spaces of montmorillonite clay due to acid treatment are shown in Figure 1. Generally, the activation of clay minerals involves the treatment of clay with acid for the selected time at constant stirring and

**Table 4. Removal of Heavy Metals and Micro-Pollutants Using Thermally Treated Clays**

Thermoactivated clay	Target heavy metals/ Micro-pollutants	pH	Maximum adsorption capacity (mg/g)	Ref.
Calcinated Bofe Bentonite (500 °C)	Ni(II)	5.3	1.91	[98]
Calcined and vibratory ball milled bentonite (500 °C)	Cr(VI)	$\geq 5$	62.5	[99]
Turkish montmorillonite (100~800 °C)	Cr(VI)	1~7	0.5~4.20	[100]
Verde-lodo (CVL) bentonite 500 °C	Ciprofloxacin	-	114.4	[101]
Natural Bentonite Clay 500 °C	Tetracycline	5	388.1	[102]
Kerolite 200 °C Sepiolite 200 °C	Atrazine Cholirdazon	-	0.468 0.041	[103]

temperature. The excess free ions, such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  etc., are detached from the clay once it is activated and then washed with distilled water, dried, and employed for its applications[104].

Acid activation of bentonite clay was performed using a clay concentration of 6 % (w/v) under mild conditions. The XRD results of activated bentonite significantly affected the crystallinity of bentonite, leading to a decrease in the peak intensity, and the width of the '001' peak was increased. FT-IR results showed that the vibrations bands at 3417, 1640, and 3617  $\text{cm}^{-1}$  are significantly changed after activation. Nevertheless, the layered structure of bentonite was not changed, which was affirmed by the presence of a weak vibrational band at 1039  $\text{cm}^{-1}$ . The increased intensity of band at 793  $\text{cm}^{-1}$  and the band's widening at 1041  $\text{cm}^{-1}$  showed that amorphous silica is formed after activation. The specific surface area and pore volume were increased by 3.3 and 2.75 times, respectively. The SEM images showed that activated bentonite appeared highly compact and showed large pores than raw bentonite[14]. Further, the XRD results of two clays: raw green clay (RGC) and raw red clay (RRC), after treating with acid, showed an increase in silica due to its poor solubility in acid solutions, while the octahedral and exchangeable ions are significantly removed. Moreover, the textual analysis showed that the internal porosity, pore volume, specific surface area, and pore sizes were increased after activation



**Figure 1. Structural changes of montmorillonite by acid attack on the surface and interlayer spaces[111].**

**Table 5. Removal Efficiency of Heavy Metals by Various Activated Clays under Batch Reactor**

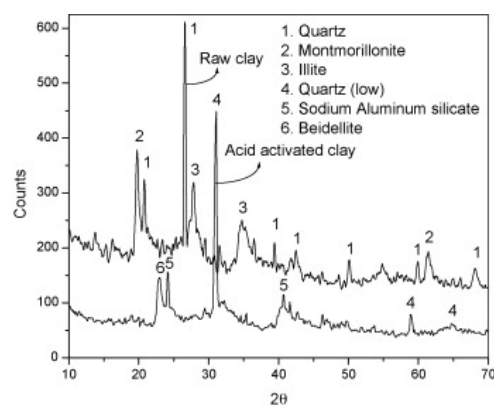
Type of clay	Activating agent (Acid used)	Target pollutants	pH	Adsorption capacity (mg/g)	Ref.
Palygorskite	4 M HCl	Cu(II)	2-7	29.70	[115]
Montmorillonite	H <sub>2</sub> SO <sub>4</sub>	Zn(II)	6.5	76.92	[105]
		Cu (II)		2.76	
		Mn(II)		2.21	
		Cd(II)		0.62	
		Pb(II)		1.62	
Shaltishkiai clay	HCl	Ni (II)		80.9	[110]
		Cu (II)		83.3	
		Zn (II)		63.2	
Bentonite	H <sub>2</sub> SO <sub>4</sub>	Cr(VI)	5	91.7	[116]
Tunisian Bentonite	HCl	Cr (VI)	5	83	[117]
Attapulgite clay (magnesium silicate)	HCl	Propranol hydrochloride	-	159.2	[118]
Montmorillonite	H <sub>2</sub> SO <sub>4</sub>	2,4,5-trichlorophenol	4	33	[119]

with acid[112]. A similar result was also reported using bentonite activated with 0.35, 0.70, 1.0, 1.5, 2.0, 3.5, 7.0, and 10 N hydrochloric acid in the liquid-to-solid ratio 4 : 1 for 45 minutes[113]. Montmorillonite-illite type of clay was activated with sulphuric acid. The mineral phase analysis of montmorillonite-illite clay (MIC) and montmorillonite-illite activated clay MIC (AA) from XRD analyses showed that some magnesium and potassium, were activated during activation, and calcium was removed, and as a result, montmorillonite and illite phases disappeared in the clay sample. Moreover, quartz to quartz inversion was also observed. The XRD image is given in Figure 2[114].

Further, it was observed that the adsorption of heavy metals by activated clay is also influenced by the strength of the acid used during activation. For example, the adsorption of Cu(II) on activated palygorskite clay activated by HCl showed substantial improvement with increasing the concentration of the acids[115]. The efficiency of various activated clays in removing toxic heavy metals is highlighted in Table 5.

## 5. Clay modification using surfactants

Clay minerals are often modified with organic compounds[120]. Over the past few decades, organoclays have drawn attention in many areas like medicine, engineering, environmental sciences, etc.[121,122]. Due to the presence of chelating functional groups in the organoclay, heavy metals are bonded onto its surface with a stronger bond than the pristine clay[123]. Quaternary ammonium organo-clays are classified into two groups. Firstly, quaternary ammonium cations (QACs) having short-chain alkyl groups such as tetramethylammonium (TMA)/trimethylphenylammonium (TMPA) or benzyltriethylammonium (BTEA), the groups of organo-clays is called adsorptive clay. Secondly, the QACs containing long-chain alkyl groups, for example, didodecyltrimethylammonium (DDDMA) and hexadecyltrimethylammonium (HDTMA) -clays, are called organophilic clay[124]. The presence of benzyl groups, long and short chain aliphatic, and often hydroxyl groups



**Figure 2. XRD image of montmorillonite-illite clay(MIC) and montmorillonite-illite activated clay MIC (AA)[114].**

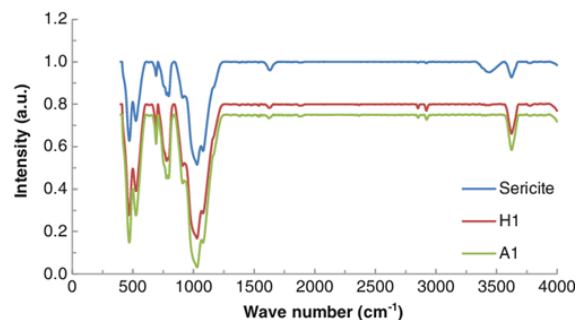
caused to increase in the basal spacing of clay along with their adsorption capability[125]. Clay with higher charge density and the surfactant molecules' length increases the interlayer spacings of clay structure[126]. The aqueous and ethanolic solutions of hexadecyltrimethylammonium (HDTMA) bromide reacts with the different charge of layer silicates, the intercalated HDTMA formed flat-lying molecules (monolayers), and the charges on the layer are  $< 0.5 e^-$  (per unit cell basis); flat-lying molecules (bilayers) for layer charges between 0.5 and  $1.0 e^-$  and bent paraffin-like arrangements for layer charges  $< 1.0 e^-$ . For smectites and vermiculites with layer charges  $> 0.5 e^-$ , greater layer spacing is achieved by intercalating of salt molecules from an aqueous medium rather than an ethanol medium[127]. Organoclays are synthesized depending on the mechanisms of reactions that organic compounds are introduced into clay minerals. Polar molecules displace water molecules in the interlayer space of vermiculites and smectites. Several organic cations exchange interlayer cations. Cation exchange and solid-state reactions are mainly used to prepare organoclays[128]. Organoclays are mostly prepared by cation exchange reactions[129]. Quaternary alkylammonium cations (QAC) exchange the interlayer cations of clay minerals in aqueous solutions. Different physicochemical conditions are

demonstrated in the preparation of organophilic clays[130-132]. The reaction of clay minerals and ammonium cations using a solid-state reaction was first reported by Ogawa *et al.*[133]. In a solid-state reaction, organic molecules are intercalated within the interlayer spaces of clay minerals in the absence of solvent since, without solvent, it is a more eco-friendly and reliable process for industrialization. Cation movement between silicate layers is not always taking part in the intercalation of neutral molecules[128]. Aniline salts are intercalated using the mechanochemical process with several counter ions in montmorillonite[134]. Ion-dipole interaction plays a key role in many solid-state reactions. The interlayer cations and organic molecules with polar groups are attached during ion-dipole interaction. Cations on the surface interact with the negative part of the molecule, thereby displacing water molecules from the interlayer cations[129,135].

Inorgano-organo-clay minerals are developed for the treatment of industrial wastewater [136,137]. Both organic surfactant and hydroxide pillaring agents are intercalated for the modification of clay minerals with inorgano-organo compounds[138-141]. Hence hydrophobic and hydrophilic compounds are removed simultaneously. Polycations of iron (III), aluminium (III), or titanium (IV) are intercalated into the interlamellar spaces of montmorillonite and further modified with cetyl trimethylammonium bromide. The material showed enhanced removal efficiency for diuron and its three degradation products: 3-(3,4-dichlorophenyl)-1-methylurea, 1-(3,4-dichlorophenyl) urea, and 2,4-dichloroanilin. It was reported that hydrophobic interaction was the main mechanism for the adsorption of these pesticides by the organo-inorgano-clays[138].

Several organic cationic surfactants (Dodecyltrimethylammonium bromide, Hexadecyltrimethylammonium bromide, Tetradecyltrimethylammonium bromide, Tetraphenylphosphonium bromide, Zinc Stearate) were used for the modification of montmorillonite.

Sericite was modified with hexadecyltrimethyl ammonium bromide (HDTMA) and alkyldimethylbenzyl ammonium chloride (AMBA). FT-IR results show that the vibrational band at  $3443\text{ cm}^{-1}$  almost vanished for the modified sericite, indicating the replacement of organic molecules with the hydroxyl group. The two new bands at  $2920\text{ cm}^{-1}$  and  $2856\text{ cm}^{-1}$  were attributed to the C-H stretching and C-H scissoring vibrations, respectively, which infer that the hexadecyltrimethyl ammonium bromide and alkyldimethylbenzyl ammonium chloride are introduced within the sericite clay (*Cf* Figure 3)[142]. A similar observation was also observed when kaolinite was modified with HDTMA[143]. In other studies, montmorillonite was modified with cetyltrimethylammonium bromide (CTMAB); XRD results showed basal spacing of montmorillonite was increased from 1.52 to 1.81 nm, which confirmed that (CTMAB) was intercalated within the interlayer space. The insertion of Fe polycation, on the other hand, did not intercalate into the interlayer of montmorillonite[144]. The SEM image of bentonite modified with octadecyl benzyl dimethyl ammonium (SMB3) displayed a smoother surface than unmodified bentonite. Moreover, the SMB3 showed small size fragments and layers alike contexture, indicating that bentonite is evenly distributed while the modification was carried out using these surfactant molecules[145]. The kaolinite modi-



**Figure 3.** FT-IR spectra of sericite, HDTMA-sericite (H1) and AMBA-sericite (A1)[142].

fied with HDTMA (SMK) showed a significant decrease in specific surface area from  $8.61$  to  $3.39\text{ m}^2/\text{g}$ , pore volume and diameter were increased from  $0.04$  to  $0.07\text{ cc/g}$  and  $9.53\sim 20.41\text{ nm}$ , respectively[146]. These results indicated that HDTMA was successfully intercalated within the interspace of kaolinite. Similar findings were reported in the literature in which bentonite was modified with cetyltrimethyl ammonium bromide (CTMAB)/ hexadecylammonium bromide (HDTMA) or pillared with aluminium and then modified with CTMAB/ HDTMA [147,148].

Montmorillonite was modified by polyamine Gemini surfactant and employed in the removal of Cu(II) with a maximum removal capacity of  $29.30\text{ mg/g}$  at  $75\text{ mg/L}$  of Cu(II) initial concentration[149]. In another study, modification of rectorite with stearyl trimethylammonium chloride removes Cr(VI) with approximately  $400\text{ mmol/kg}$  via electrostatic interactions in acidic pH conditions[150]. A comparative study for the sorption of bentonite (BT), bentonite modified with hexadecyltrimethylammonium (BT-HDTMA), and phenyl fatty hydroxamic acid (BT-PFHA) showed that the monolayer adsorption capacities of BT, BT-HDTMA and BT-PFHA for Pb(II) were found to be  $149.3$ ,  $227.3$  and  $256.4\text{ mg/g}$ , respectively. Further, the sorption data were fitted well to the Langmuir, Dubinin-Radushkevich, and Temkin models. The kinetic data is fitted well with the pseudo-second-order kinetic model, and the thermodynamic studies revealed that the adsorption was feasible, spontaneous, and exothermic[151]. Single and complex modified bentonite was synthesized using iron (hydr)oxides ( $\text{Fe}_x(\text{OH})_y$ ), manganese oxides ( $\text{Mn}_x\text{O}_y$ ) and cationic surfactants, cetyltrimethylammonium bromide (CTMAB), and poly(dimethyldiallylammonium chloride) (PDMDAAC) and employed in the sorptive removal of arsenic. Results showed that arsenic removal greatly depends upon the combination, type, and amount of modifiers used in clay modification. The removal of arsenic in single modified bentonite was in the order  $\text{Fe}_x(\text{OH})_y\text{-Bent} > \text{Mn}_x\text{O}_y\text{-Bent} > \text{CTMAB-Bent} > \text{PDMDAAC-Bent}$ . Moreover, the complex modified bentonite, manganese oxide, and PDMDAAC showed the best arsenic removal due to the presence of several manganese oxide particles and the change in the surface properties of bentonite. The decrease in the removal of arsenic was observed with CTMAB- $\text{Mn}_x\text{O}_y\text{-Bent}$ , CTMAB-, or PDMDAAC $\text{Fe}_x(\text{OH})_y\text{-Bent}$ [152]. The removal efficiency of heavy metals and micro-pollutants using organo- and organo-inorgano clays are summarized in Table 6.

**Table 6. Removal of Heavy Metals and Micro-Pollutants using Organo- and Organo-Inorgano Clays**

Clay	Type of modification	Target pollutants	pH	Adsorption Capacity (mg/g)	Ref.
Kaolinite	Hexadecyl trimethyl ammonium bromide	Cr (VI)	3	27.8	[143]
Kaolinite	HDTMA	As (III)	4~8	2.33	[146]
		As (V)		2.88	
Bentonite	BH	As (III)	4.5	2.792	[147]
	BAH			2.247	
	LCH			1.824	
	LCAH			2.184	
Bentonite	BH	As (V)	4.5	3.449	[147]
	BAH			8.937	
	LCH			2.287	
	LCAH			4.255	
Bentonite	HDPy-Bn	Cr(VI)	4.5	27	[153]
	HDTMA-Bn			43	
Vermiculite	BE-Bnechanism			17.5	
	HDPy-Ver			3.7	
	HDTMA-Ver			0.5	
Bentonite	Hexadecyl trimethyl ammonium bromide	Cr(VI)	6	19.01	[143]
Montmorillonite	CTMAB-FeIII	As (III)	-	16.13	[154]
		As (V)		15.5	
Bentonite	Bencylhexadecyldimethyl ammonium chloride	Cu (II)	5	50.76	[155]
		Zn (II)		35.21	
Bentonite	Hexadecyl trimethyl ammonium bromide	Amoxicillin Cu(II)	-	33.51	[156]
Montmorillonite	Didodecyldimethyl ammonium bromide (DDDMA)	Bisphenol A	4~5	20	[157]
Montmorillonite	1,10-didodecyl-4,40-trimethylene bispyridinium bromide	Bisphenol A	6	222.22	[157]
	1,10-dihexadecyl-4,40-trimethylene bispyridinium bromide			208.3	
Vermiculites	(1,1'-didodecyl-4,4'-trimethylene bispyridinium bromide	Sulfamethoxazole	-	63.14	[158]
Montmorillonite	cetyltrimethylammonium cation (CTA <sup>+</sup> )	Ehynyl estradiol (EE2)	-	4.38	[159]
Montmorillonite	Octadecyltrimethylammonium bromide (ODTMA) + hydroxy aluminium (Al)	Bisphenol A	-	109.89	[160]
Bentonite Magadiite	Diocadecyldimethylammonium	Triclosan	-	422	[161]
Magadiite	Diocadecyldimethylammonium	Triclosan	-	543	[161]

HDTMA: hexadecyltrimethylammonium, BH: bentonite modified with hexadecyltrimethylammonium, BAH: bentonite pillaring with aluminium and modified with hexadecyltrimethylammonium, LCH: local clay modified with hexadecyltrimethylammonium, LCAH: local clay pillaring with aluminium and modified with hexadecyltrimethylammonium, HDPy-Bn: bentonite modified with hexadecylpyridinium, HDTMA-Bn: bentonite modified with hexadecyltrimethylammonium, BE-Bn: bentonite modified with benzethonium, HDPy-Ver: vermiculite modified with hexadecylpyridinium, HDTMA-Ver: vermiculite modified with hexadecyltrimethylammonium, BE-Ver: vermiculite modified with benzethonium, CTMAB: cetyltrimethylammonium bromide.

## 6. Grafting or silylation of clay

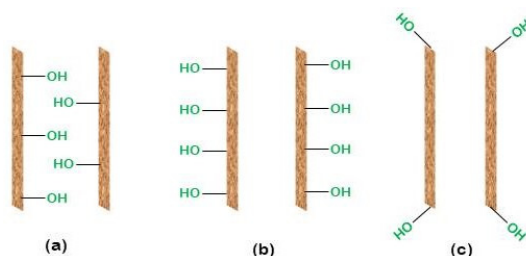
Grafting or silylating the surface of clay minerals has drawn greater attention because the grafted materials showed varied applications in environmental and chemical engineering[162]. Various types of clay functionalized with different silanes are given in Table 7. In general, there are three possible sites for silylation/grafting of silane at the surface of the clay, i.e., the external surface, internal surface, and broken edges of clay minerals, as shown in Figure 4[163,164].

The reactive sites of montmorillonite were increased on acid treatment, leading to greater silane molecules loading[56,165]. The interactions of clay minerals with silane molecules were facilitated by increasing the concentration of silane and the temperature of the

**Table 7. Characterization of Different Clay Functionalized with Different Silanes**

Functionalized clay	FTIR		XRD	BET surface area			Ref.
	Assignment	Wavenumber (cm <sup>-1</sup> )		Specific Surface area (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Pore size	
K10/MPTS	C-H	2929	-	-	-	-	[173]
	C-H	1402					
	C-S	682					
	Si-O	465					
	OH	3500					
BN-SH	-OCH <sub>3</sub>	2931	No change in d-spacing	93	0.24	131.26 Å	[174]
	-CH <sub>2</sub>	2843					
	-SH	2559					
	Si-OR	1000-1100					
	Si-OH	950					
BN-APTES	N-H	3300	2.01 nm	-	-	-	[167]
	C-H	700					
	Si-C	1340					
	Si-O-Si	1200-1100					
MSEP-GF	MgOH	3688.62, 691.07, 647.44	No change in d-spacing	84.78	-	-	[175]
	H <sub>2</sub> O <sub>Cordinated</sub>	3563.90					
	H <sub>2</sub> O <sub>Zeolite</sub>	3415.93, 1663.81					
	C-H-O-CH <sub>3</sub>	2932.59					
	SH	2562.66					
	Si-O	1210.59, 1078.54, 980.17					
	Si-O-Si	1019.45					
	Si-O-Mg	470.72, 441.31					
AS-APTES	CH <sub>2</sub> <sub>asym</sub>	2920	2θ=8.63	59	0.110	7.66 nm	[176]
	CH <sub>2</sub> <sub>symm</sub>	2850					
	Si-O-Si	1060					
	O-Si-O	560 and 480					
MPTS/BENT	CH <sub>3</sub>	2,914	No change in d-spacing	4.42	0.071	20.15 nm	[177]
	CH <sub>2</sub>	2,831					
	SH	2555					
BNAPTES	CH <sub>2</sub>	1485	No change in d-spacing	12.50	0.051	165.13 Å	[178]
	C-N	1319					

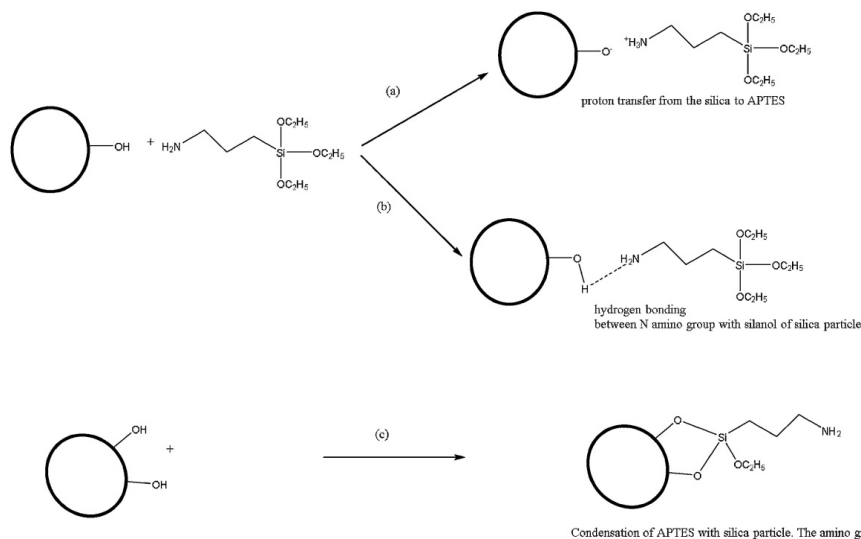
Abbreviations: AS-activated sericite, BN-Bentonite, K10- Montmorillonite, MPTS-3-mercaptopropyletrimethoxy silane, APTES-3-aminopropyltriethoxy silane, MSEP-GF- 3-mercaptopropyletrimethoxy silane functionalized sepiolite.


**Figure 4. Probable sites for grafting or silylation, i.e. (a) internal clay surface, (b) external surface of clay, (c) broken edges of clay.**

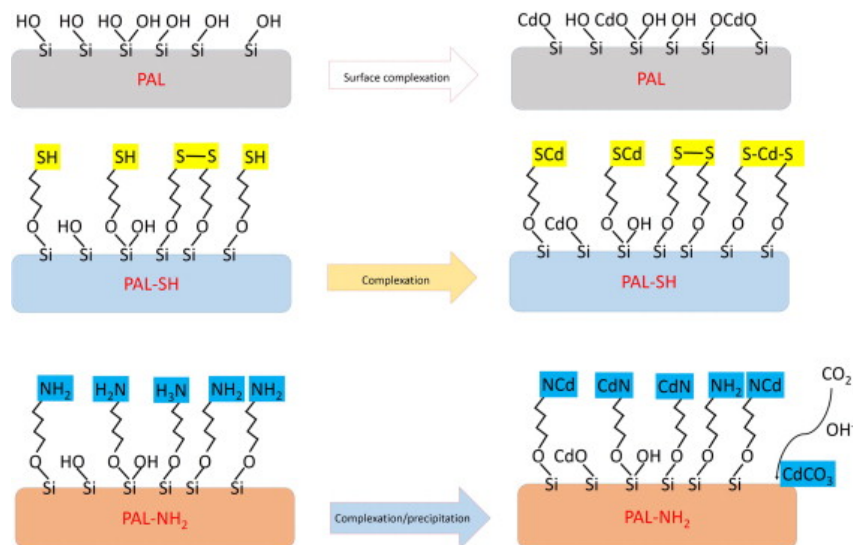
reaction[166]. The surface of bentonite was grafted with 3-aminopropyltriethoxysilane (APTES), allowing its nano-space to be utilized for intercalation of cations, bio-molecules, polymeric materials, drug delivery, and several commercial uses[167]. “Flip mechanism” de-

scribes the mechanism of amine grafted onto silica minerals. Firstly, amine forms a hydrogen bond with the hydroxyl group on the surface of silica particles, or proton is transferred from the silica particles to amine forming an ionic bond. On the silicon side of silane molecules,





**Figure 5.** Interaction types between silicate surface material and APTES in absence of water (a) proton transfer, (b) Hydrogen bonding, (c) Condensation of APTES with silica particle[169].



**Figure 6.** Schematic of sorption mechanisms of Cd(II) on PAL, PAL-SH and PAL-NH<sub>2</sub>[179].

self-catalyzation of hydrogen-bonded molecules occurred, forming a covalent bond with siloxane. Due to this condensation, the interaction of the amine group at the surface is lost, and the amine is far apart from the surface. Fast stabilization occurs when a higher amount of ethoxy group on the APTES is present. Therefore, the original amine-down position of the silane molecule is changed to the amine-up-position resulting in a ‘flip mechanism’(Figure 5)[168,169].

The grafting of silane was not favored using the nonpolar solvents (e.g., toluene)[50,161,162], while intercalation of silane was observed when polar solvents (e.g., water/ethanol mixture and ethanol) was used as a dispersing medium[172].

Nano-texturization method was employed for the functionalization of palgorskite clay with mercapto and amino silane to efficiently remove cadmium from polluted soils and water. Results show that functionalized materials significantly increased the adsorption capacity compared

to the unmodified palgorskite clay. The enthalpy change was positive, and the endothermic sorption process(Figure 6)[179].

The interlayer spaces of vermiculite were incorporated with CYS and CTA and utilized for the adsorption of Hg(II). The intraparticle diffusion, controls the adsorption kinetics of Hg(II). Batch adsorption of Hg(II) using modified 3-MPS is similar to Na-VT and follows pseudo-second-order kinetics. Higher breakthrough volume was achieved using vermiculite modified with 3-MPS in column studies. The adsorption is irreversible[180]. As shown in Table 8, the adsorption capacities of various functionalized clay possessed relatively high adsorption capacity for heavy metals and micro-pollutants in the aqueous medium.

## 7. Clay based composites

Clay and clay-based composites materials are found to be promising

**Table 8. Removal of Heavy Metals and Micro-Pollutants using Functionalized Clay**

Clay	Type of modification	Target heavy metals/ Micro-pollutants	pH	Adsorption Capacity (mg/g)	Ref.
K10	MPTS	Ni(II)	-	5.3	[173]
Attapulgite	APTES	Hg(II)	3~11	90	[181]
Activated Sepiolite	MPTS	Cr (VI)	2	60	[182]
Monmorillonite	MPTS	Cd (II)	7.44	30.10	[183]
Bentonite	MPTS	Cd (II)	6.40	27.54	[184]
Palygorskite (PAL)	MPTS	Cu (II)	< 5.83	30	[185]
Activated Sericite	APTES	Cd (II)	5	5.747	[176]
Bentonite	APTES	Pb(II)	5~6	110.0	[186]
		Hg(II)		102.7	
		Cu(II)		45.8	
Montmorillonite	AEPE	Hg(II)	4	46.1	[187]
Hectorite	AEPE	Hg(II)	4	54.7	[187]
Sepiolite	APTES	Atenolol	-	2.66	[188]
		Ranitidine		3.14	
		Carbamazepine		0.06	
Sepiolite	OTES	Atenolol	-	13.32	[188]
		Ranitidine		16.66	
		Carbamazepine		0.40	
Sepiolite	CPTES	Atenolol	-	12.78	[188]
		Ranitidine		20.12	
		Carbamazepine		0.35	
Sepiolite	TFS	Atenolol	-	9.99	[188]
		Ranitidine		8.17	
		Carbamazepine		0.65	
Sericite	MPTS	Diclofenac	6	1.868	[189]
		clofibrac acid	7	1.749	
Bentonite	MPTS	Tetracycline	4	16.64	[177]
		Triclosan		18.87	
Bentonite	APTES	Tetracycline	4	15.70	[178]
		Triclosan		16.91	
Bentonite	MPTS	17 $\alpha$ -ethinylestradiol	4	8.1	[190]
Bentonite	APTES	17 $\alpha$ -ethinylestradiol	4	4.28	[190]

K10: Montmorillonite, MPTS: 3-mercaptopropyletrimethoxy silane, APTES: 3-aminopropyltriethoxy silane, AEPE: 2-(3-(2-aminoethylthio) propylthio)ethanamine, OTES: Triethoxy(octyl)silane, CPTES: 3-(chloropropyl)- triethoxysilane, TFS: Triphenylsilane

in the remediation of toxic heavy metals from an aqueous environment due to their large surface area, low-cost, stability, high cation exchange capacity, high porosity, and the ability to swell to a large extent, which overcomes with the conventional methods. One or more components of composites are functionalized to increase the sorption efficiency [191-194]. Cellulose -montmorillonite[195], poly (acrylic acid)/organo-montmorillonite[196], bentonite/NZVI[197]; Kaolinite/ZrO and kaolinite/TBA[198]; chitosan-clay nanocomposite[199] are some clay-based composites employed in the removal of heavy metal ions. The adsorption capacity of various clay-based nanocomposites in the removal of heavy metal ions are summarized in Table 9.

Liquid phase reduction was employed for the synthesis of benton-

ite-supported nanoscale zero-valent iron (B-nZVI) and utilized in the removal of Cu(II), Pb(II), and Cr(VI) from electroplating wastewater. More than 90% removal efficiency was achieved using the composite material. Further, ethylenediaminetetraacetic acid (EDTA) solution was used to desorb the heavy metals, but the removal capacity of Cr(VI) was decreased by approx. 70% using the reutilized material[200]. Single and mixed pillared clays (Zr-Bent, Al-Bent, Al-Zr-Bent, Ce-Zr-Bent, Ce-Al-Zr-Bent, Ce-Al-Bent) were utilized for the adsorption of Cu(II), Co(II) and Cd(II). The adsorption of heavy metals was higher for pillared clays rich in cerium. The experimental data is well fitted to the second-order-kinetic model and Langmuir adsorption isotherm[201]. 4-aminoantipyrine was immobilized onto bentonite and

**Table 9. Clay Based Nanocomposites for the Removal of Toxic Heavy Metal Ions and Some Micro-Pollutants**

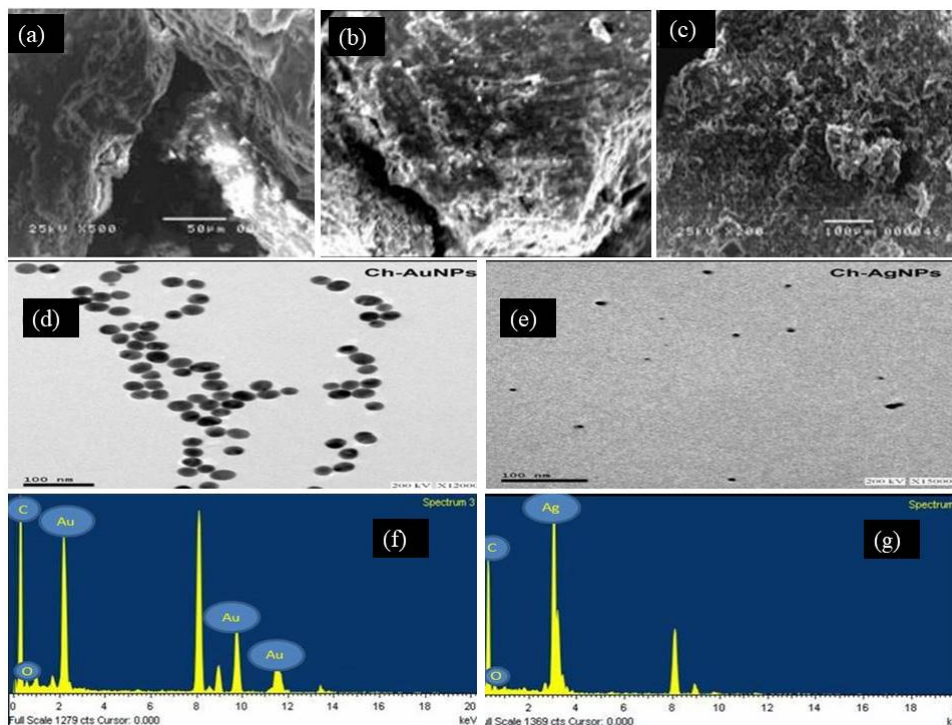
Clay	Type of modification	Target heavy metals/ Micro-pollutants	pH	Adsorption Capacity (mg/g)	Ref.
Sepiolite	Activated with 4 M HCl + nZVI	Cr (VI)	6.0	43.86	[210]
		Pb (II)		44.05	
Montmorillonite	nZVI	As (III)	7.0	59.9	[211]
		As (V)		45.5	
Bentonite	Chitosan	Ni (II)	4.0	12.35	[212]
		Cu (II)		20.9	
		Pb (II)		28.77	
Bentonite	nZVI	Cr (VI)	5.0	60.5	[197]
Montmorillonite + Kaolinite	TiO <sub>2</sub>	Cu (II)	2.0-6.4	42.9	[213]
		Cd (II)		13.8	
		Zn (II)		15.4	
		Pb (II)		71.9	
Bentonite	Polymeric Al/Fe	As(III)	7.0-9.0	21.233	[214]
		As (V)	3.0-6.0	19.11	
Montmorillonite	ZnO-NP	Cu(II)	4.0	54.06	[215]
		Pb(II)		88.50	
Vermiculite	Chitosan	Cd(II)	4	58.5	[216]
		Pb(II)		166.7	
Sepiolite	Chitosan	Cu(II)	-	75	[217]
		Pb(II)		100	
Montmorillonite	CTAB/cellulose	Cr(VI)	3.8-5.5	22.2	[195]
Montmorillonite	PANI/Starch	Cr(VI)	2	208.6	[218]
Clay	PANI	Pb(II)	5	7.4	[219]
Bentonite	Chitosan/Polyninyl alcohol	Hg(II)	-	360.74	[220]
Laterite	Polyanion, polystyrene sulfonate	Tetracycline	4	2.85	[221]
Montmorillonite	Titanium pillaring	Amoxicillin	-	4.48	[222]
		Imipramine		91.51	
		Diclofenac		23.83	
		Paracetamol		22.08	
Montmorillonite	$\beta$ -cyclodextrin	Bisphenol A	-	0.1	[223]
Bentonite	Humic acid	2,4- dichlorophenol	6.5	14.23	[224]
Na-Montmorillonite	Alginate	4-nitrophenol	5-6	27.1	[225]
Kaolin	Aluminum-Pillared + Sodium Alginate	Ciprofloxacin	4	68.36	[226]
Zeolites	Fe <sub>3</sub> O <sub>4</sub>	Diclofenac	7	0.0996	[227]
		Naproxen		0.098	
		Gemfibrozil		0.0978	
		Ibuprofen		0.0974	

OMMT: Organically modified montmorillonite (C20A), ZnO-NP-Zinc oxide nanoparticle, TiO<sub>2</sub>-Titanium dioxide, nZVI- nano zerovalent iron, CTAB: Cetyltrimethylammonium bromide, PANI: polyaniline, Fe<sub>3</sub>O<sub>4</sub>

employed in the elimination of Hg(II), Cr(III), and Pb(II) from an aqueous solution. The maximum adsorption capacity of the solid material was found to be 52.9, 52.9, and 55.5 mg/g for Hg(II), Cr(III), and Pb(II), respectively[202]. *E-coli*-kaolinite nanocomposite was used in the adsorption of Cr(VI), Cd(II), Fe(III), and Ni(II) from water with adsorption capacity of 4.6, 10.3, 16.5, and 6.9 mg/g, respectively[203].

Synthesis of polymer-layered silicate nanocomposite includes solution blending, *in-situ* polymerization, and melt blending. In the sol-

ution blending method, prepolymer and polymer are soluble in a solvent such as toluene, chloroform, or water resulting in exfoliation of layered clay. After mixing the layered clay and polymer/prepolymer, intercalation of polymer chains and solvent displacement occurs within the clay's interlayer[204,205]. Desorption of solvent molecules results in the gaining of entropy, which is responsible for intercalation in the solution blending[206]. Chitosan gold clay nanoparticles (Ch/AuNPs/clay) and chitosan silver clay nanoparticles (Ch/AgNPs/clay) were synthe-



**Figure 7.** SEM images of Ch/Clay (a), Ch/Clay/AuNPs (b), Ch/Clay/AgNPs (c); TEM images of Ch/Clay/AuNPs (d), Ch/Clay/AgNPs (e); EDX image of Ch/Clay/AuNPs (f), Ch/Clay/AgNPs (g)[207].

sized by solution blending method. From the SEM image [Figure 7(a), (b), (c)], the (Ch)/Clay composite comprised several layered structures with bulky flakes and interlayer spaces. While in the case of (Ch)/AuNPs/Clay and (Ch)/AgNPs/Clay nanocomposites, there was a significant decrease in the interlayer spaces of clay, which reaffirmed the impregnation of the chitosan assembled on nanoparticles between the clay layers. It was also observed that (Ch)/AgNPs and (Ch)/AuNPs were primarily circular in shape and poly-dispersed from the transmission electron microscope (TEM) analysis. Moreover, the TEM images showed that the prepared nanoparticles are well stabilized due to the interaction with the free amino groups of chitosan [Cf Figure 7(d) and (e)]. Further, in the EDX spectra, the intense and distinctive optical absorption peaks were observed around 3 keV and 2.1 keV due to the surface plasmon resonance (SPR) of metallic silver (Ag) and gold (Au) nanocrystals, respectively [Figure 7(f) and (g)] [207].

*In situ* polymerization method involves swelling of layered silicate inside the monomer solution resulting in polymer formation between intercalated sheets. Before swelling of layered silicate by monomer, heat, or radiation, organic initiator or diffusion of appropriate initiator or by fixing catalyst through cationic exchange inside the interlayer is employed for the initiation of polymerization [204]. Montmorillonite clay nanocomposite (PPy-OMMT NC) was prepared via *in situ* polymerization of pyrrole monomer. From the FT-IR spectrum of the Ppy-OMMT NC3, the C-H deformation, C-H stretching vibration, conjugated C-N stretching, and pyrrole ring stretching are observed at 824–958  $\text{cm}^{-1}$ , 1081  $\text{cm}^{-1}$ , 1423  $\text{cm}^{-1}$ , and 1513  $\text{cm}^{-1}$ , which confirmed the presence of PPy moieties in the nanocomposite [Fig. 8(c)]. The

XRD data of Ppy-OMMT NC3 could not show any distinct peak, which suggests that almost all the clay sheets in the polymer matrix are exfoliated. The small angle X-rays (SAXS) pattern also revealed that no low angle diffraction occurred with the nanocomposite prepared by *in situ* polymerization. The studies show that the insertion of polypyrrole has successfully exfoliated the OMMT clay sheets [Fig. 8(b)]. High-resolution transmission electron microscopic images (HR-TEM) of OMMT show sheets as black strips, while in Ppy-OMMT NC3 these strips are well distributed [Fig. 8]. The SEM image of OMMT show flaky structure, after modification with PPy, the OMMT clay structure was covered by polypyrrole [Fig. 8] [208].

In the melt blending method, the molten form of polymer matrix was mixed with layered silicate. If the selected polymer and layer surfaces were appropriately suited, the polymer crept into the interlayer gallery, resulted from the formation of exfoliated or intercalated nanocomposite [204]. Al-pillared-montmorillonite (AIPMt)/poly(methyl methacrylate) (PMMA) nanocomposites were synthesized via melt blending method (MBM) and solution blending method (SBM). The FT-IR spectra of AIPMt/PMMA nanocomposite showed that the interaction of AIPMt and PMMA proceeded via C=O and C-O groups [Fig. 9(a)]. The XRD patterns of AIPMt/PMMA nanocomposite displayed an increased amorphous nature. The characteristic reflection of AIPMt was not found in XRD patterns since AIPMt was homogeneously dispersed within PMMA matrix [Fig. 9(b)]. The TEM image of AIPMt/PMMA (2.5 wt%) nanocomposite for MBM is shown in Fig. 9(c). Clay platelet (dark zone) was observed using this method. In the polymer matrix, the pillared clay layers were distributed evenly and homogeneously,

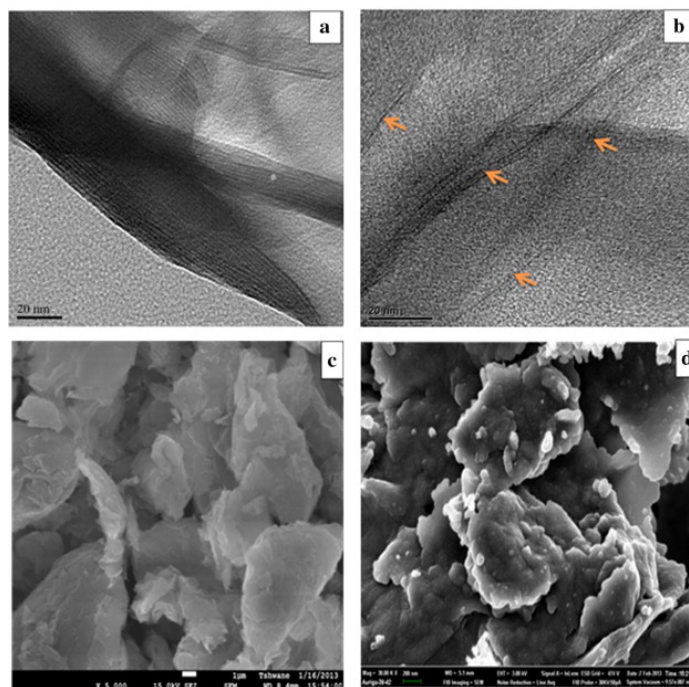


Fig. 8. Transmission electron microscopic images of (a) OMMT and (b) Ppy-OMMT NC3, and scanning electron microscope of (c) OMMT and (d) Ppy-OMMT NC3[208].

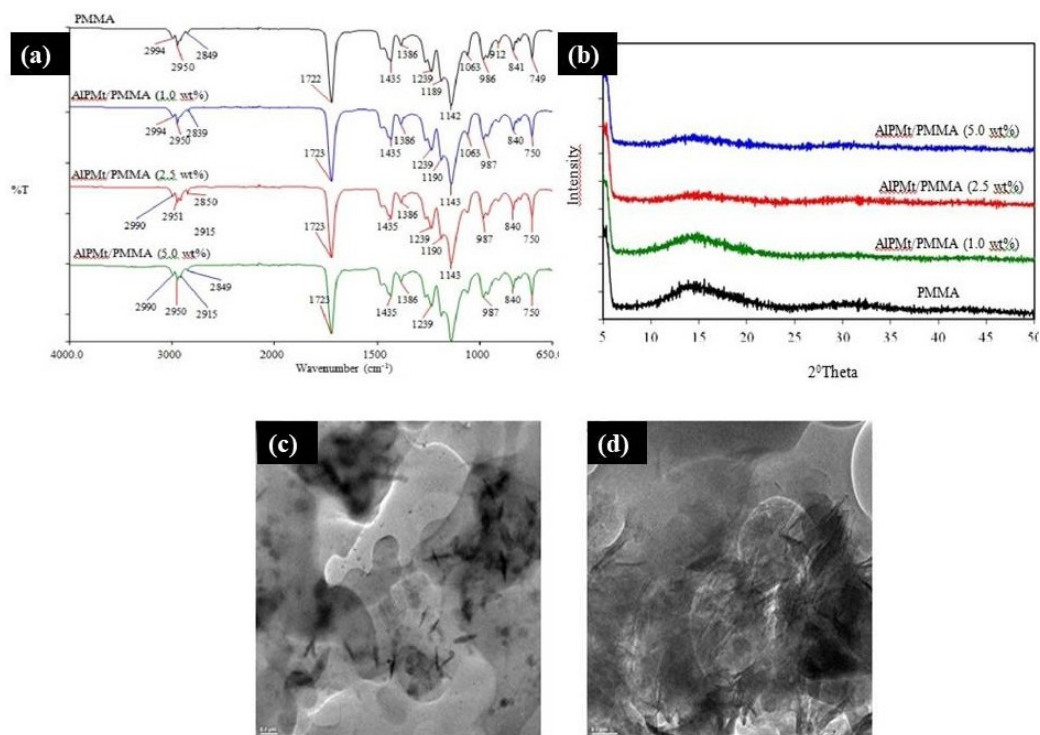


Fig. 9. (a) FTIR-ATR spectra of AIPM/PMMA nanocomposites with MBM, (b) XRD patterns of AIPM/PMMA nanocomposites with MBM and (c) TEM images of AIPM/PMMA (2.5 wt.%) nanocomposites synthesized via MBM[209].

which was evidence of the intercalated morphology. The homogeneity of dispersions from the image is on a nanometer scale, which agrees with the XRD results[209].

It is observed that the mechanistic pathway in removing pollutants

involved surface complexation[187,202-205,207,210]. The electrostatic interaction[212,213,218] and the hydrophobic interactions[130,181] significantly remove micro-pollutants using clay-based composites. Moreover, the ion exchange[214] and surface complexation[217] were

found to occur in removing micropollutants' toxic heavy metal ions from the aquatic environment by clay-based composite using clay-based materials.

## 8. Conclusion and future perspective

This review broadly discussed various techniques employed for modifying different types of clays. Also, different types of clay-based materials were comprehensively reviewed for their efficiency in the remediation of aqueous waste contaminated with toxic heavy metals and emerging micro-pollutants. The surface complexation is the prominent mechanism involved in removing toxic heavy metal ions by clay-based composite, whereas the electrostatic interaction plays a significant role in micro-pollutants removal using these types of composite. Thermal and acid-activated clay is simple, easy to prepare, and has an enhanced adsorption capacity. The modifications of clay minerals with surfactants are promising adsorbents for decontaminating different pollutants from wastewater. However, the intercalated surfactant might leach into the surrounding solutions, which leads to secondary contamination of water. Silylation of clay minerals is a promising method since the organosilanes are immobilized through strong covalent bonding into the clay network, which further prevents the leaching of the organic moieties into the surrounding environment. Moreover, the silylated materials exhibit more enhanced adsorption selectivity and efficiency for removing pollutants from aqueous solutions.

Even though enormous work is carried out and much literatures has reported the removal of heavy metals and micro-pollutants using clay-based advanced materials from the aquatic environment, the perspective of scaling up the laboratory trials to the technology development for real application is still a challenge for researchers. The adsorbent is designed in such a way that the clay-based materials are eco-friendly, have no hazardous by-products, and have a high sorption capacity towards these pollutants. Moreover, simultaneous removal of anionic, cationic, and non-ionic pollutants is a real challenge using these advanced materials to simulate the complex matrix. Further, there is a challenge associated with the disposal of utilized materials and recovery of the pollutants, especially the toxic metal ions, for the potential future implications.

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