

Review

Advancements in Clay Materials for Trace Level Determination and Remediation of Phenols from Wastewater: A Review

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Abstract: The wide spread of phenols and their toxicity in the environment pose a severe threat to the existence and sustainability of living organisms. Rapid detection of these pollutants in wastewaters has attracted the attention of researchers from various fields of environmental science and engineering. Discoveries regarding materials and method developments are deemed necessary for the effective detection and remediation of wastewater. Although various advanced materials such as organic and inorganic materials have been developed, secondary pollution due to material leaching has become a major concern. Therefore, a natural-based material is preferable. Clay is one of the potential natural-based sorbents for the detection and remediation of phenols. It has a high porosity and polarity, good mechanical strength, moisture resistance, chemical and thermal stability, and cation exchange capacity, which will benefit the detection and adsorptive removal of phenols. Several attempts have been made to improve the capabilities of natural clay as sorbent. This manuscript will discuss the potential of clays as sorbents for the remediation of phenols. The activation, modification, and application of clays have been discussed. The achievements, challenges, and concluding remarks were provided.

Keywords: clays; environment; extraction; remediation; recovery; reusability; wastewater

1. Introduction

Water is essential for the continuing survival of all organisms. However, constant disturbance of water bodies due to pollution from chemical substances have been observed over the last five decades. Water contamination is due to the industrial demands of chemicals and energy [1], urbanization [2], agricultural mechanization [3], transportation, mining, and crude oil extractions [4,5]. To a smaller extent, natural phenomena such as bush burning, decay of organic matter, earthquakes, petroleum seep, volcanic eruptions, and wildfires contribute to water contamination [6,7]. However, major sources of pollutants are chemical processing industries [8,9], mining, and exploration sites [10,11]. Ground and surface waters serve as the major reservoir of these pollutants which, in turn, pose serious threat to waters and disharmony to the existence of living organisms [12,13].

Phenols are among the most frequently detected organic species in environmental waters. They are a class of aromatic compounds with hydroxyl group(s) directly bonded to aromatic ring(s). They mostly result from industrial effluents from petroleum refining [14], petrochemical [15], pharmaceuticals [16], textile, cosmetics, wood, and leather processing industries [17,18]. Although small quantities of phenols are produced from the decomposition of plants and animals [19,20], the majority results from anthropogenic sources. Different research findings have shown the presence of phenols and their derivatives at both higher and lower concentrations in wastewater, reaching up to thousands of mg/L [21,22]. These compounds are primarily insoluble, hydrophobic, and non-biodegradable, thus persist in the environment for a long period of time [23,24]. They bioaccumulate in living organisms and enter the human body through the food chain [25,26]. They are known to pose serious threats to the human system, associated with carcinogenicity, skin diseases, respiratory ailments, diarrhea, irritations of the eyes, and urine coloration [27,28]. Consequently, environmental regulatory agencies marked them as priority pollutants (POPs) in wastewater [29,30]. The chemical structure and physicochemical properties of phenols is highlighted in Table S1 of the Supplementary Material.

Despite the established fact that phenols represent a large group of organic pollutants frequently detected in wastewater, and the fact that numerous articles were presented on their trace determination and adsorptive remediation using clays due to their potential properties such as good porosity, mechanical strength, cationic exchange capacity, as well as their relative abundance, no review on the subject was published. Thus, in this work, an attempt was made to discuss and analyze, past and present, the application of raw and modified clays for microextraction and adsorptive removal of phenols from wastewaters. The major rationale behind the use of clays for the remediation of phenols was due to their availability and low cost, as well as higher adsorption capacities. Furthermore, this review also aimed at addressing the shortcomings of the findings on the application of clay materials towards phenols detection and remediation. The modification of the clays, methods optimization, reusability, isotherms, and kinetics of the process for improving the remediation efficiency has been extensively discussed. Lastly, recommendations have been proposed, and the future direction of the research has been highlighted towards better understanding of the subject matter. Figure 1 shows the graph on the trends of publication on microextraction and adsorptive removal of phenols from wastewater from 2010–2022, as obtained from ScienceDirect data. It can be observed that the trend is increasing each year for the past 12 years, indicating the significant progress in the field.

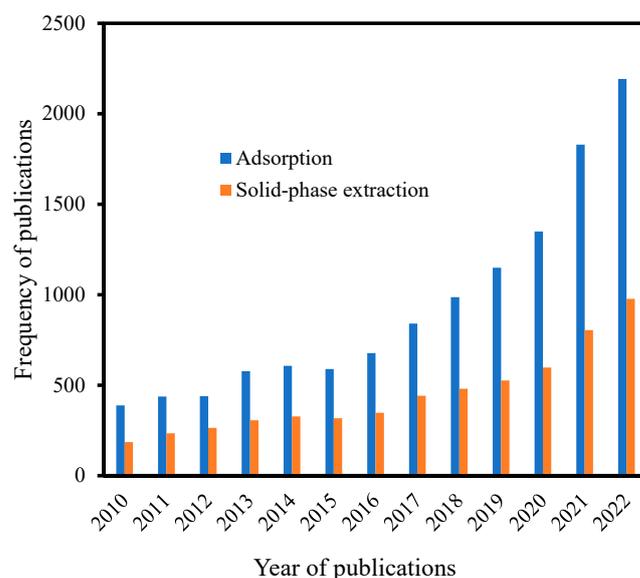


Figure 1. Trends in article publications from 2010–2021 on the adsorption and solid-phase extraction of phenols. The data were extracted from ScienceDirect repository on 7 January 2023.

1.1. Sources of Phenols

Various routes by which phenols enter the environment have been studied. There are several industries that have contributed to the mass production of phenols as wastes. Examples include crude oil refining [31] petroleum tankers and ships [32]. Crude oil refining refers to the production of fuel components such as gasoline, diesel, kerosine etc. This process is usually associated generation of by-products such as phenols, which are often discharged into the water bodies. Moreover, oil spillage has also been widely recognized as a major source of phenols. Every year, about 5–30 million tons of crude oil are estimated to spill into the oceans due to either accidents or leakage of containers from the shipping industry and oil tankers [33,34]. Recent spills include the Ambarnaya River, Russia [35], and the Mauritius coast [36]. It caused devastating effects and resulted in surface water obstruction and widespread of pollutants (particularly phenols and PAHs) into the water bodies. Phenols are also deposited in petroleum sludge, which is usually transferred into the soils, causing the pollutants to enter the surface and ground waters [14,37]. Similarly, the significance of petrochemical industries in the economic development of every country is vital. The major products include olefins and essential oils, cosmetics, personal care, and dyes [38,39]. These industries consume large quantities of water during production, which are subsequently discharged as effluents into the water bodies [40]. The wastewater usually contains phenols as the major organic components and other inorganic species such as dyes and heavy metals [29,41,42]. Additionally, coal processing also contributed to the presence of phenols in the water bodies. The coal is used as an alternative source of for power generation which is cheap for industrial and domestic consumption. In the coal plants, a water circulation system is created for cooling engines which is when discharged established direct contact with the surface water, causing detrimental pollution. According to EPA, coal processing plants immensely contributed to the persistent global warming and water pollution problem. Phenols have been identified as major pollutants and can be found at high and lower concentrations in the coal-processed wastewater [43,44].

Apart from industry, natural disasters also could cause the unintentional distribution of phenols to the environment. Flood water contains suspensions of organic and inorganic particles from roads, warehouses, petrol stations, tanks, and waste disposal [45,46]. This catastrophe is more pronounced in tropical areas with high amounts of rainfall. According to some studies, phenols have been detected in flood-consumed regions [47,48]. This could cause the pollutants to enter the water bodies and easily disseminate to plants, aquatic organisms, and humans [49,50].

1.2. Toxicities of Phenols to Humans

The toxicities of phenols to humans have been well investigated. The primary source of human exposure is associated with consumption of contaminated foods and water, or inhalation of polluted air [51,52]. The pollution is more intense in petroleum exploration and refinery sites as well as coastal areas, where discharged wastes are directly transported to the water bodies [53]. Thus, people living around these areas are at potential risk from these toxic chemicals and their detrimental effects. Due to their toxicities, they are classified as endocrine disruptors, and long-term exposure to phenols may result in carcinogenic, mutagenic, and other sublethal effects [54,55]. The toxicity increases due to biochemical alterations in the human body, leading to hematological and physiological effects associated with breast, lungs, kidney, and bladder cancer [56,57]. Moreover, it was reported that phenols may lead to immune suppression [58], causing protein coagulation, denaturation of cells, skin damage, affecting the central nervous system and respiratory tract [16,59].

1.3. Environmental Regulations on Phenols

Due to their environmental impact and apparent human toxicities of phenols, regulatory agencies such as the United States Environmental Protection Agency (USE PA) and World Health Organization (WHO) have set some restrictions on their usage. The aim is

to limit their environmental impact from higher level in parts per million (ppm) to much lower levels, in parts per billion (ppb). The US EPA has determined the content of phenol in potable and mineral waters to 0.5 ppb and in wastewater discharges between 0.5 and 1.0 ppm [60], while the allowable level of phenols in drinking water regulated by WHO was identified as 0.001 ppm [61].

1.4. Trace Level Extraction and Adsorptive Removal of Phenols from Waters

In recognition of the toxicities and mobility of phenols in environmental waters, prompt action has been desired for their mitigation and possible elimination. Researchers and environmental regulatory agencies have focused on developing suitable means for effective extraction and identification. Moreover, investigations on the detection and remediation of phenols using various techniques have been employed. These include conventional techniques of coagulation and flocculation [62,63], solvent extraction [64], reverse and forward osmosis [65,66], membrane technologies [67,68], photocatalytic degradation [69,70] and electrochemical oxidations [71,72]. However, most of these methods suffer from major drawbacks, partly due to the lower solubility of the compounds. They have shown strong resistance to biodegradation [73,74], while chemical remediation causes secondary pollution due to the generation of oxygenated species that are equally hazardous [75,76]. Additionally, some of these techniques are not economical. Thus, the quest to explore other means remained endless.

Solid-phase extraction (SPE) technologies have been recognized as way forward for effective determination of phenols from environmental waters. In solid phase extraction, the pollutant (phenol molecules) is adsorbed from the sample matrix by an extractant material (which is solid materials known as sorbents) and is widely used for the removal of a wide range of organic and inorganic pollutants from the aqueous media due to their prospects to effectively remove the pollutants, even in trace amounts, from the environmental waters [77,78]. Thus, numerous sorbents of natural and synthetic originality have been proposed and employed for SPE determination of phenols from the wastewaters. The method is more straightforward, low-cost, and effective than most extraction technologies [32,79].

1.5. Clay Minerals

Clays are naturally occurring deposits of hydro aluminum silicates found in the Earth's crust. They contain cations of alkali and alkaline earth metals [80], that can be found abundantly in different parts of the world, each constituting different compositions with varying sizes and textures [81]. They have been utilized for various applications ranging from commercial to academic purposes. For example, clays are widely used as building materials due to their textual and mechanical properties in making bricks, tiles, replacement in cement, mortars, and concrete reinforcement [82,83]. They are also used as geopolymer materials as an alternative to cement or other conventional binders for construction and protection barriers towards sea water, and coating of materials [84]. Owing to their porous nature, they are employed in environmental remediation for toxic pollutant adsorption from water [85,86]. Natural clays are classified into nine groups according to their chemical compositions and atomic structures, including kaolinite (halloysites, lizardite and chrysotile), pyrophyllite (Illite, glauconite and celadonite), vermiculite, mica, smectite (montmorillonite, nontronite and saponite), chlorite (sудоite, clinochlore and chamosite), sepiolite, palygorskite, interstratified (rectorite, corrensite and tosudite), and allophane-imogolite clays [87]. Figure 2 shows the molecular structure and chemical compositions of some clays.

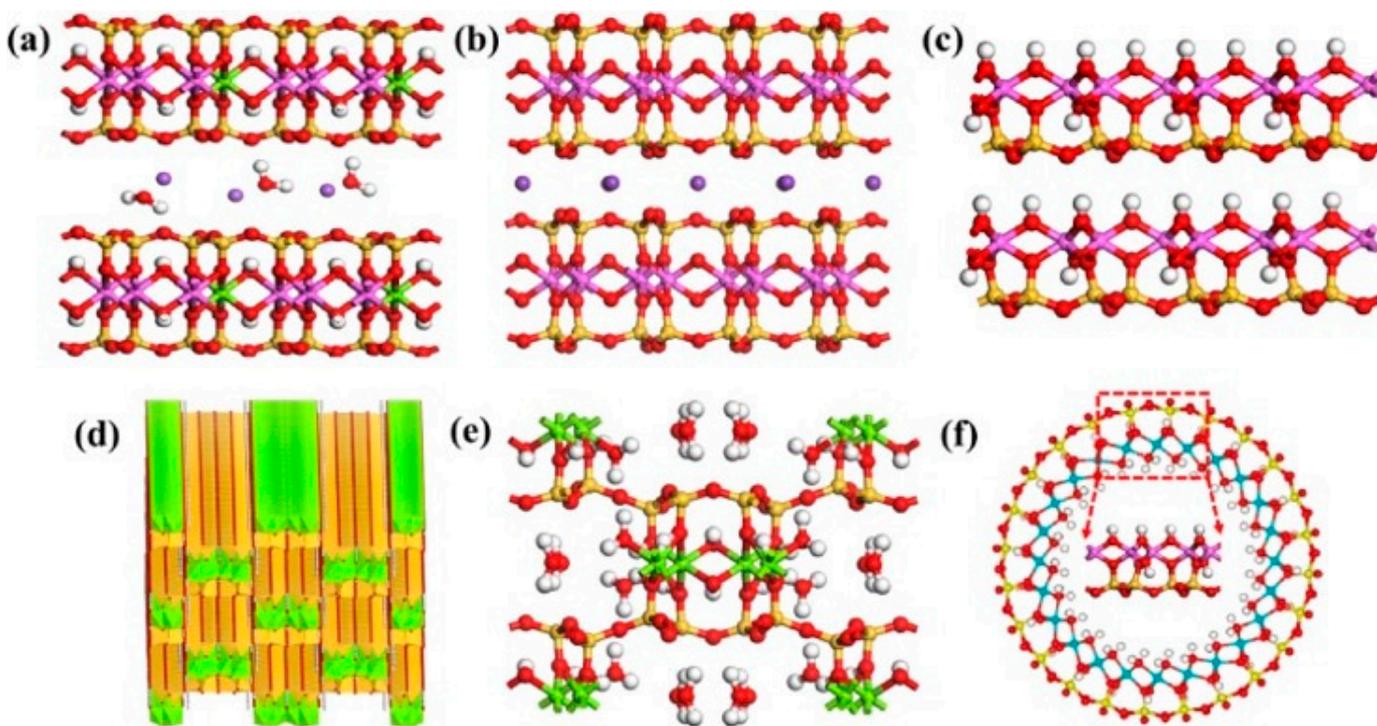


Figure 2. Schematic diagram showing various clay minerals: (a) montmorillonite, 2:1 layer type clay mineral with interlayer cations and water molecules; (b) illite, 2:1 layer type clay mineral and potassium ions locked up in the interlayers; (c) kaolinite, 1:1 layer type clay mineral with no substitution; (d) schematic of palygorskite, 2:1 type layer-chain type clay mineral with zeolitic water and (e) partially enlarged structural details of (d); (f) halloysite, 1:1 layer type clay mineral with a tubular structure [88].

For water remediation applications, clays have been well explored for pollutants adsorption. Some researchers compiled findings reporting on the employment of various clays for the adsorption applications. The work of Awad et al. (2019) discussed the application of clays for organic pollutants adsorption. Although various clays have been reported and have demonstrated good adsorptive performances, micro-level extraction of the pollutants was not considered, and the findings were limited only to the synthetic wastewater [89]. Han et al. (2019)’s review was mainly focused on natural and composites clays for heavy metals and dyes adsorption [90] and did not consider the adsorbents’ reusability and their application for trace detection of the pollutants. Similarly, Chari et al. (2019) and Uddin. (2017) reported mainly on pristine clays for dyes and heavy metals adsorption, respectively [91,92]. Del et al. (2020) addressed the application of biopolymer-clay nanocomposites towards organic pollutants adsorption [8]. In all cases, trace extraction and regeneration of the clays and the real wastewater applications were not considered.

1.5.1. Activation of Clays

Often, raw clays require activation prior to the intended application. Clay activation is a process to increase the clay character to obtain the desired properties in accordance with its use. Physical treatments such as acid [93], thermal [94], and alkaline [95] activations have been explored. Thermal treatment is costly and often disrupts the clay’s interlayered structure and the alkaline treatment. The most widely used chemicals are sulfuric acid and sodium hydroxide. Alkaline activation enhanced mechanical and physical properties of the clay and improved its water-resistant ability. However, it lowered its capillarity [95]. Thus, acid activation has been identified as the simplest approach to improve the characteristic features of the clays for effective performance. Clay surface area and pore volume can be increased through treatment with mineral acids [87]. Researchers have investigated

the acid activation using various inorganic acids. For instance, bentonite activated with HCl has shown improvement in the surface porosity. The Brunner–Emmett–Teller (BET) surface area was $65.89 \text{ m}^2/\text{g}$ and $50.93 \text{ m}^2/\text{g}$ for the modified and pristine bentonites, respectively [96]. Furthermore, the activation of Moroccan clay with sulfuric acid at $110 \text{ }^\circ\text{C}$ for 12 h has resulted in higher BET specific surface area of $74.43 \text{ m}^2/\text{g}$ and $51.42 \text{ m}^2/\text{g}$ for the activated and pristine clays, respectively [97].

1.5.2. Modifications of Clays

Alternatively, surface modification and functionalization have been proposed as the best approach to improve the performance of the clays. Polymer incorporation [98], grafting with organic compounds [99,100], surface charged modification with cations [101], etc., have shown positive improvement in the performance of the clays. They not only alter the surface structure of the materials, but also improve the physicochemical properties such as surface porosity, polarity, texture, and cation-exchange capacity [102,103].

Of the techniques, surfactant modification has been considered the most effective method to improve the clays' intrinsic properties and performance. Usually, it resulted in organoclays with improved surface porosity, mechanical stability, and polarity for more efficient applications [96,104]. Richards and Bouazza (2007) explored the use of hexadecyltrimethylammonium (HDTMA) and Phenyltrimethylammonium (TPMA) for the surfactant modification of basaltic and bentonite clays. The BET specific surface area of the pristine bentonite and basaltic clays was 370 and $170 \text{ m}^2/\text{g}$, and the ion exchange capacity was 63 and 50 meq/g , respectively. The BET surface slightly reduced to 327 and $153 \text{ m}^2/\text{g}$, while the cationic exchange capacity significantly improved to 81 and $84 \text{ meq}/100 \text{ g}$ for the HDTMA-bentonite and HDTMA-basaltic clays, respectively [105]. Similarly, the carbon content of the composites was much higher than the pristine, related to the increased in the level of organic matter and the number of active sites on the surface of the modified clay [105]. The surface modification of montmorillonite with hexamethylene bis-pyridinium dibromides (HMBP) formed reduced-charge montmorillonites (RCMs) with smooth surfaces and uniformly sized particles [100]. For the first time, modification of Na-montmorillonite with surfactant, bis-hexadecyldimethyl-p-phenylenediammonium dibromide (BHPD) was reported [106]. The composite has demonstrated fascinating properties such as good mechanical strength, higher chemical and moisture stability and improved surface porosity compared to the unmodified. The higher adsorption capacity of the former was attributed to its stronger hydrophobicity and the number of delocalized π -electrons [106].

Charged ions (such as Na^+ , Cs^+ , Ca^{2+} , NH_3^+) and metal oxide nanoparticles (such as Fe_2O_3 , CuO , ZnO , etc.), have also been reported to improve the surface properties of the pristine clays [107]. Physical properties and crystal structures improved upon modification with weakly hydrated cations (such as K^+), hence improved their adsorption efficiency [108]. The effect of sodium ion (Na^+) on the surface property enhancement of montmorillonite was reported. Based on the result, the Na-montmorillonite have a well-defined crystalline structure, good thermal stability and dispersibility in water and organic solvent [109]. Another study on Ghanaian Muscovite clay functionalized with Ca^{2+} , Mg^{2+} , Na^{2+} , and K^{2+} has also shown that this has better porosity and cation exchange capacity [110].

Polymer incorporation and grafting with other functionalized organic functional materials have also been described as alternative approaches to enhance the properties and efficiency of the clays. Composites of the clays with activated carbon [111], biochar [112], graphene [113], chitosan [114], geopolymers [84], etc., have demonstrated improved performance of the minerals. The composites are often considered low-cost and possess good BET specific surface area and pore volumes [115,116]. They also possess superior chemical properties, good thermal stability, and mechanical resistance to the pristine clays [9,90]. In addition, they are characterized by higher adsorption efficiency and cationic exchange capacity [117]. However, despite the advantages of improved surface properties, mechani-

cal strength, and thermal stability, the high costs of the modifications served as the major shortcomings of the materials.

2. Clays for Environmental Water Remediation

2.1. Clays in Trace-Level Determination of Phenols from Environmental Water

Analytical determination of phenols in environmental samples involves multiple steps, starting from sample preparation, extraction until detection. The sample preparation step helps to isolate the analyte(s) of interest, and to clean-up and preconcentrate the analyte(s) for better detection. Moreover, sample preparation is important for enhancing the selectivity and sensitivity of the analytical method [118]. Sample extraction is a technique in which sorbent is used to extract analyte(s) from the sample. Depending on the extraction mode, the extractant could be in a solid (sorbent) or liquid (solvent) phase [119]. In solid-phase techniques, the sorbent plays a crucial role in determining the success of the process. Several criteria need to be considered in determining good sorbents, such as their large surface area, sorbent–analyte interaction, and sorbent–solvent interaction. The unique features demonstrated by both raw and modified clays allow for their utilization as good sorbents for extracting phenols from the wastewaters. Different extraction modes (Figure 3) such as solid phase extraction (SPE), solid phase microextraction (SPME), dispersive solid phase extraction (DSPE), magnetic solid phase extraction (MSPE), rotating disk adsorption extraction (RDSE), and stir bar sorptive extraction (SBSE) have been explored as discussed below.

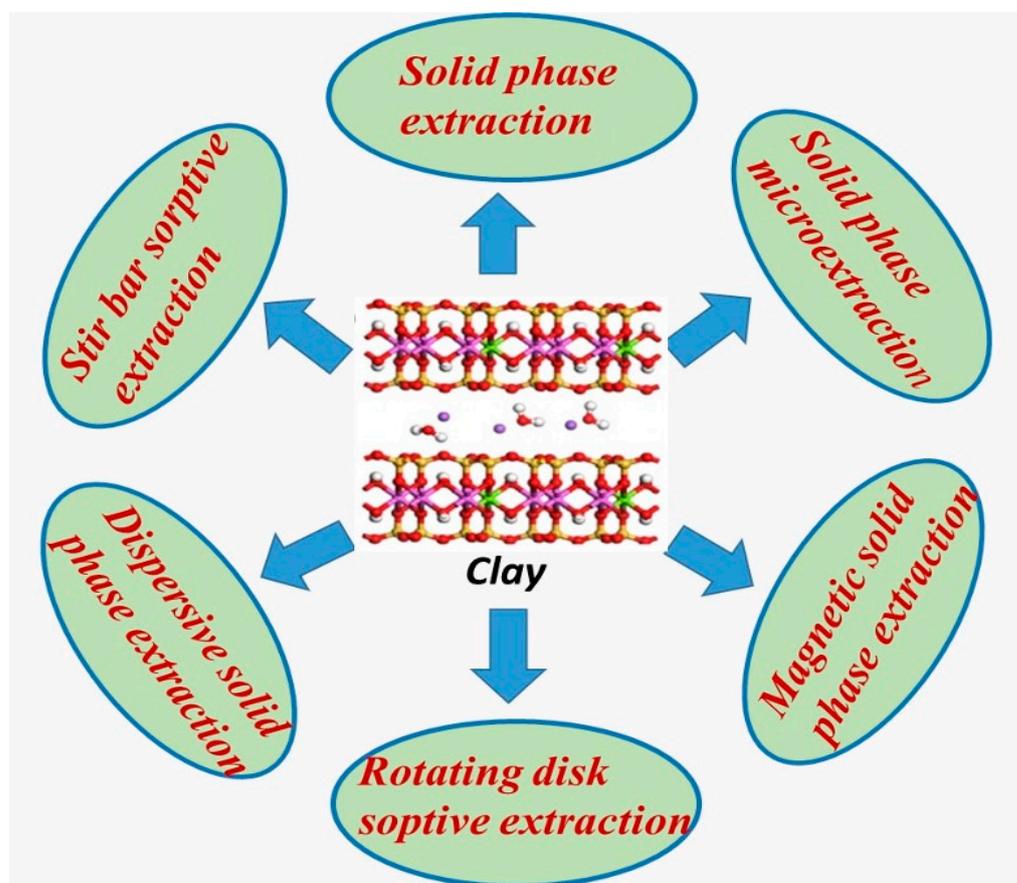


Figure 3. Solid-phase technologies for the extraction of phenols by clay and modified clay materials.

2.1.1. Solid-Phase Extraction (SPE)

SPE is one of the most widely used techniques for analyte(s) isolation and preconcentration in waters [120], food [121], and pharmaceutical analysis [122]. In SPE, a sample solution is loaded into a cartridge containing sorbent that retains the targeted analyte(s) and removes the undesired components. The target analyte(s) is then eluted using solvent and transferred to a collection tube [123]. It has been widely used due to its simplicity, high enrichment factor advantage, and lower solvent consumption [122]. However, one of the major drawbacks in SPE is the selection of sorbent that can extract the pollutants in trace level. The sorbent C₁₈ (a form of silica sorbent) is the commonly used material in SPE. Nevertheless, it is incapable of extracting a polar analyte, which limits its application. Thus, various materials have been developed and applied as an alternative to replace the conventional C₁₈. Examples are multiwalled carbon nanotubes [124,125], Oasis HLB 6cc, MAX 6cc 150 [126], graphene [127] and molecularly imprinted polymer [128,129]. Moreover, the potential of natural and modified clays as sorbents in SPE has also been investigated.

Chu et al. (2015) prepared a natural clay composite 4-butylaniline-modified attapulgite to determine bisphenol A (BPA) in water. Attapulgite comprises silica tetrahedral chains linked by octahedral species of oxygen and hydroxyl groups of aluminum (Al) and magnesium (Mg) ions with a chain-like inverted structure. The large surface area and porous structure are capable of the cation exchange of the material, which makes it suitable to be utilized as a sorbent in SPE. The composite was used to extract BPA from river water samples by spiking the sample at concentration levels of 22.8, 45.6, and 68.4 µg/L, respectively, determined by HPLC. The recoveries for the three spiked samples obtained from the river water samples were in the range of 93.0–96.6%, with a root-mean-square deviation (RMSD) of less than 2% [122]. Chai et al. (2018) also utilized polyethyleneimine (PEI) modified with attapulgite as a sorbent for SPE for the determination of chlorophenols (CPs) in environmental water [130]. The PEI has the capability to donate electrons due to the presence of numerous amine groups in its structure, which can be utilized for the adsorption of polar analytes [131]. The result of its analytical performances on three targeted chlorophenols, 4-chlorophenol (4-CP), 2,6-dichlorophenol (2,6-DCP), and 2,4,6-trichlorophenol (2,4,6-TCP), have shown that the coefficient of determination (R^2) obtained was larger than 0.99, with limit of detection (LOD) and quantification (LOQ) obtained ranging from 0.26 to 0.08 µg/L and 0.27 to 1.88 µg/L, respectively. Moreover, the method also shows good accuracy and precision within 84.4–96.8% for all the target analytes when applied in river water samples with analyte concentrations of 10, 100, and 200 µg/L. The RMSDs obtained were less than 4.56 and 6.30% for inter- and intraday, respectively [130]. This result indicates that PEI-attapulgite has greater potential to be utilized as an adsorbent in SPE with good accuracy and precision.

2.1.2. Dispersive and Magnetic Solid-Phase Extraction (DSPE and MSPE)

DSPE is another mode of solid-phase extraction. The major difference between DSPE compared to conventional SPE is that, in DSPE, the solid sorbent is introduced directly to the sample solution without any conditioning process. The extraction procedure relies only on agitation such as sonication, vortex, shaking and centrifugation [132]. The target analytes retained on the adsorbent will then be separated through filtration or centrifugation with an organic solvent prior to instrumental analysis.

MSPE is an extraction technique where the target analyte's preconcentration is carried out using magnetizable sorbents [133]. MSPE employs the same principle as DSPE, where the sorbent will be introduced directly to the sample followed by an agitation process to disperse it throughout the sample solution (Figure 4). The employment of magnetic sorbent simplifies the recovery of the extractant from the sample without requiring centrifugation, as is necessary for DSPE [134].

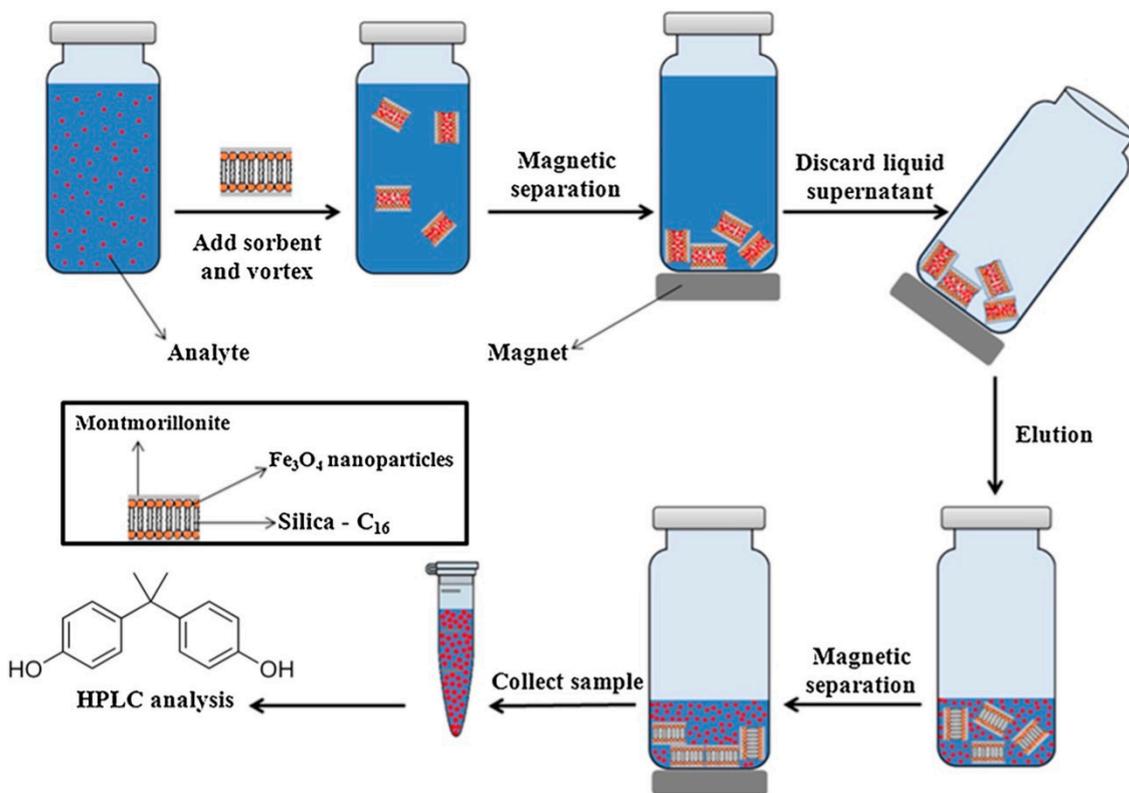


Figure 4. Schematic set-up for magnetic solid-phase extraction BPA from water using C₁₆-silica/magnetic montmorillonite [135].

Liu et al. (2011) reported the utilization of polysulfone microcapsule organic montmorillonite magnetic nanoparticles (montmorillonite/Fe₃O₄@PSF) for the determination of 2-CP and 4-CP in river and wastewater samples. Several parameters have been optimized and validated prior to application to real samples. The result showed that the reported method has a good enrichment factor of 58 and 251 for 2-CP and 4-CP, respectively. The technique was also applied to two types of matrices (river and wastewater) to determine the method’s accuracy. Before the extraction step, two different concentrations (0.99 and 1.73 µg/L) were spiked into the sample. Good recovery was obtained, ranging between 90.9–115.0%, which shows the method has good accuracy with an RMSD of less than 7% [136]. Similarly, Salehinia et al. (2016) reported on hydrophobic magnetic montmorillonite composite to extract BPA in water samples. Under the optimum condition, hydrophobic magnetic montmorillonite can remove the BPA from water samples with a LOD and LOQ of 0.15 and 0.35 µg/L, respectively. The precision was investigated by carrying out extraction in a spiked sample at two different concentrations (50 and 200 mg/L). The result indicated that the reported method had a good precision with RMSD less than 2.5%, and an enrichment factor of 34. Additionally, to investigate its capability in real samples, the authors applied the method to several water samples (well, wastewater, river, and leachates) by spiking the sample at three concentration levels (10, 20 and 50 µg/L). Relative recoveries of >95% were obtained, with RMSD 2.7% and 3.8% for inter- and intra-day, respectively. This indicates that the reported method has a good sensitivity with no significant effect on the matrices from the samples [135].

Another MSPE technique was reported by Peng et al. (2020), where the application is slightly different compared to other reported methods. In this technique, magnetic montmorillonite was used to remove the interferences present in the sample prior to the extraction of the BPA. A negatively charged Fe₃O₄/montmorillonite surface at the entire extraction pH condition made it suitable to remove the interferences from the sample without affecting the target analyte. The BPA was extracted by ultrasound-assisted methanol–water

mixture (1:1, *v/v*). The reported method has shown good LOD and LOQ ranging from 5.1–8.6 and 16.9–29.2 $\mu\text{g/L}$, respectively. Furthermore, the method's precision by conducting five parallel experiments for the analyte at a concentration of 100 and 300 $\mu\text{g/L}$ has indicated that the method has good precision with RMSD lower than 7%. Furthermore, the accuracy of the method was investigated by assessing the relative recoveries of the BPA at three different concentrations (200, 400 and 800 ng/g, respectively). The relative recoveries obtained ranged from 84.3–98.2%, with an RMSD of less than 7% [137].

2.1.3. Stir Bar Sorptive Extraction (SBSE)

Generally, SBSE is a solid based extraction technique where sorbent is coated onto a glass-coated magnetic bar. The bar will be introduced into the sample solution and stirred for extraction process. The bar will then be removed from the sample, dried, and desorbed using solvent [118]. Thus, in the technique, montmorillonite was coated onto the glass magnetic bar by using an epoxy resin, which exhibited robust support with excellent mechanical stability. Under the optimum SBSE condition, the technique demonstrated good linearity and R^2 of 0.9922. The LOD and LOQ were 0.02–0.34 $\mu\text{g/L}$, and 0.06–0.92 $\mu\text{g/L}$, respectively with good RMSD within the range of 2.8–4.3% for all the analytes. The bar-to-bar RSDs obtained were in the range of 4.6–5.1% ($n = 6$). The method has been successfully applied in different types of environmental waters (well, leachates, and wastewater) and good relative recoveries higher than 88.0% were achieved [138]. These results indicate that the developed techniques have good sensitivity and ability to determine chlorophenols at trace levels. Furthermore, the employment of montmorillonite is also capable of enhancing the extraction efficiency and enrichment factor of the technique.

2.1.4. Rotating Disk Sorptive Extraction (RDSE)

RDSE is an improvised SBSE extraction technique where a Teflon disk coated with polydimethylsiloxane (PDMS) film on one of its surfaces is used instead of a stir bar. The PDMS surface will act as the extraction phase to extract the target analyte from the samples. The main advantage of RDSE is the utilization of a Teflon disk which has a larger surface area than the stir bar and will improve the contact area of the extraction phase. Apart from that, since the extraction phase and the container are separated, it allows high velocity stirring to be carried out (facilitating the mass transfer of analyte) without damaging the extraction phase [139]. Thus, Fiscal-Ladino et al. (2017) employed the RDSE method using montmorillonite 1-hexadecyl-3-methylimidazolium bromide montmorillonite (montmorillonite-HDMIM-Br) for the determination of phenols in water. The technique has good accuracy and precision with low LOD and LOQ of 0.003–0.043 $\mu\text{g/L}$ and 0.007–0.100 $\mu\text{g/L}$, respectively. Furthermore, the method achieved good reproducibility and high recovery of the analytes at different extraction disks ($n = 6$) with analytes concentration of 1.0 $\mu\text{g/L}$ in a water sample. The recovery ranged between 35.8–55.5%, with an RMSD of less than 25%. The developed method has revealed that the montmorillonite-HDMIM-Br composite can retain most polar PCBs compared to other non-polar sorbents [140]. The finding demonstrated the capability of the modified clay to be employed for phenols determination in environmental waters.

2.1.5. Solid Phase Microextraction (SPME)

Numerous modifications of montmorillonite have been carried out to improve the sensitivity and extraction efficiency. As an example, in the SPME technique, a montmorillonite-based composite was synthesized and utilized as fiber as an alternative to PDMS fiber. SPME technique is another example of SPE in which a coated fiber will be inserted into the samples and the analytes are transported from the sample matrix to the vicinity of the fiber (extracting phase) through the agitation process [141]. Abolghasemi et al. (2015) reported on the SPME technique for phenol determination in water. In the method, montmorillonite was directly intercalated with polyaniline, a long chain cationic surfactant. The polyaniline was chosen due to its promising properties such as high surface area, and capability to

establish π - π and hydrophobic interaction. Addition of polyaniline to the montmorillonite caused a change in polarity of the material from hydrophilic to hydrophobic and was able to extract phenols from the water. Moreover, the reported technique has a good LOD in the range of 0.005–0.014 $\mu\text{g}/\text{L}$ with corresponding R^2 between 0.993–0.998. The technique also has good precision (4.6–9.1%) and reproducibility (14.3–7.9%). The result has indicated that polyaniline–montmorillonite fiber was able to improve the chromatographic responses to 2.5–3.5 times higher than the results acquired using conventional PDMS fibers [142]. Abolghasemi et al. (2014) also synthesized montmorillonite composite by adding polypyrrole polymer for modification of interlayer surface of montmorillonite. This composite was able to improve the adsorption of the phenols by increasing surface area, thermal and mechanical properties of the SPME fiber. The LOD obtained for the study was between 0.05–1.3 $\mu\text{g}/\text{L}$ with R^2 ranging between 0.996–0.998. The method was also compared with other reported SPME fibers such as 3-(trimethoxysilyl) propyl amine/PDMS, polyacrylate, dodecylsulfate-doped polypyrrole, and oxidized multiwalled carbon nanotubes and it has shown that montmorillonite–polypyrrole composite has comparable LOD [143].

Apart from montmorillonite, other natural clays have also been used as SPME fiber such as halloysite nanotubes and hydroxyapatite. Abolghasemi et al. (2016) reported another approach by using halloysite coated with polyaniline polymer for determination of CPs in water. The presence of hollow tubular structure in the halloysite-coated polyaniline resulted in high surface area and improved the phenols extraction. The analytical performance of the newly developed SPME fiber was evaluated and, based on the result, the method has good LOD ranging from 0.01–100 $\mu\text{g}/\text{L}$ with a precision lower than 10%. The reproducibility of the fiber was also investigated and RSD less than 13% was recorded. Moreover, the reported SPME fiber achieved a lower LOD, with better precision compared to commercial fibers [144]. Additionally, Abolghasemi et al. (2016) have utilized hydroxyapatite coated onto nanoporous anodized alumina wire for SPME fiber extraction of phenols. It possessed good mechanical strength, high adsorption capacity, and exceptional biocompatibility for the extraction process. It shows good LOD of 0.5–1.2 $\mu\text{g}/\text{L}$, and R^2 of 0.995–0.997 with good precision of <8.3%. Furthermore, the study also revealed that the nanocomposite fiber has a better mechanical strength, flexible thermally stability, and robustness for reusability, compared to the conventional SPME fiber [145].

In summary, the pristine and modified clays have shown a good capacity for trace level extraction and determination of phenols from the environmental waters. Table S2 in the supplementary material highlighted more studies reported on clays for the extraction of phenols from environmental waters. Among the various clays, montmorillonite is widely used, owing to its promising properties, particularly its large surface area and cation exchange capacity [137]. Apart from that, the ease of its surface modification from hydrophilic to hydrophobic makes it a versatile sorbent for such applications [140].

2.2. Clays for Adsorptive Removal of Phenols

2.2.1. Natural Clays Phenols Adsorption

The application of natural clays such as quartz, montmorillonite, halloysite, dickite, nacrite, and bentonite has been widely explored for the adsorption of various pollutants from environmental waters [71,146]. They are characterized as nanostructured porous materials with large surface areas and uniform surface conformations [147,148]. Furthermore, they are also known to possess interlayer microstructures with good mechanical strength, which enable them to retain large and small molecules from an aqueous medium [149,150]. Thus, both natural and modified clays have been widely applied for wastewater treatment applications due to their availability, cost effectiveness, and ease of application.

Researchers have investigated the adsorption of phenols onto various natural clays. Liu et al. (2015) studied the adsorption of phenols onto montmorillonite clay. The strong adsorption of the pollutants onto the adsorbent is attributed to the affinity of the homoionic Na, K, and Cs ions from the clay towards the pollutants [151]. Ben-Moshe et al. (2018) studied the phenol adsorption onto montmorillonite, hectorite, sepiolite, and halloysites

with improved efficiency [152]. The binding of aromatic cations to both charged and neutral sites of the adsorbents elucidated the porous nature of the clays and the formation of multilayer surface adsorption [153]. Previously we have reported on the adsorption of 2,4,6-TCP onto halloysite nanotube with BET specific surface area of 30 m²/g. The adsorbent achieved maximum adsorption capacity of 139 mg/g with the adsorbate concentration of 200 mg/L within 4 h [101]. The adsorption of organic pollutants onto the halloysite nanotubes occurs via multiple surfaces; the external surface, the interlayer surface, and the internal lumen of the adsorbent [154,155]. Calcination of the raw clays at higher temperature improved their adsorption capacity, which was attributed to the increased in surface porosity of the clays. This was proven by the work of Ouallal et al. (2019) on the adsorption of phenol onto calcined Moroccan clay. The porosity of the calcined clay (at 1000 °C) was higher compared to the uncalcined clay with BET specific surface area of 62.20 m²/g (calcined clay) and 25.35 m²/g (uncalcined clay). Thus, the calcined clay has achieved higher adsorption capacity (2.93 mg/g) than the uncalcined (1.64 mg/g) [156].

Usually, the activated clays offer a better retaining capacity of the pollutants from the aqueous medium [105]. Thus, researchers have investigated the activation of clays using acidic reagents. For instance, acid activation of bentonite with HCl resulted in the improved porosity of the material, with a BET specific surface area of 65.89 m²/g and 50.93 m²/g for the modified and pristine bentonite, respectively. Consequently, the modified bentonite achieved higher phenol adsorption of 55 mg/g within 30 min [96]. Furthermore, the activation of Moroccan clay with sulfuric acid at 110 °C for 12 h resulted in the materials with BET specific surface area of 74.43 m²/g (activated) and 51.42 m²/g (pristine), while the adsorption capacity of the activated clay was 6.80 mg/g, compared to 2.71 mg/g for the pristine [97]. Table 1 highlighted more on the adsorption of phenols onto the natural clays. In addition, the adsorption capacities and equilibrium time were discussed comprehensively to understand the adsorbent’s performance.

Table 1. Adsorption of phenols onto natural clays.

Adsorbent	Pollutant	Concentration (mg/L)	Adsorption Capacity (mg/g)	Equilibrium Time (min)	Ref.
Natural clay	phenol	5	11.1	15	[157]
Na-Montmorillonite			18.9		
Natural clay	phenol	400	37.6	120	[158]
Bentonite	phenol	500	1.8	360	[159]
Raw clay	phenol	50	2.7	180	[97]
Activated clay			6.8		
Stevensite	phenol	100	8.9	180	[160]
Clay	Phenol	100	14.5	720	[161]
	3,4-DCP		48.7		
	2,5-DCP		45.5		
Montmorillonite clay	4-CP phenol	10	0.5 0.4	555	[98]
Kaolinite clay	phenol	100	25.5	40	[94]
Metakaolinite			24.0		
Natural clay	phenol	98	10.6	1440	[162]
Calcined clay			59.1		
Natural clay	2-CP	100	27.5	60	[163]
Calcined clay	phenol	40	12.0	840	[164]
Muscovite clay	phenol	5	-	600	[110]
Magadiite	phenol	50	52.1	60	[165]
Palygorskite	BPA	50	30.0	120	[166]
Montmorillonite	BPA	100	1.3	240	[167]

2.2.2. Modified Clays for Phenols Adsorption

Notwithstanding the application of various clays in adsorption studies, some researchers argued on the lack of selectivity of the pristine clay towards pollutants adsorption, particularly those pollutants containing cationic and ionic functional groups [26,168]. Thus, surface modification has been proposed as the best approach to improve their adsorption properties. Various modifications using surfactants [169], polymer incorporation [98], organic compounds [99], metal oxide nanoparticles and surface charged ions [101], have been shown to effectively increase the surface porosity and cation exchange capacity of the clays for the adsorption performance [102,170]. Moreover, the modifications also improved the physicochemical properties of the pristine clay, such as the polarity of the clay, which is vital for the adsorption process [103,171].

Cationic surfactants have demonstrated effective performance of the clays for adsorption application. They were shown to improve the porosity, stability, and polarity of the clays [104]. For instance, Richards and Bouazza (2007) explored the physical features of HDTMA surfactant in the modification of bentonite and basaltic clays, forming composites with good cationic exchange capacity and enhanced adsorption efficiency for phenols adsorption [105]. Furthermore, potential properties of octadecyl trimethyl ammonium chloride (OTMAC)-modified attapulgite was also investigated for phenol adsorption and the material was capable to completely removed the pollutant within 60 min of the batch adsorption experiment [172]. The surfactant modification of montmorillonite with HMBP resulted in montmorillonite with effective adsorption of phenol in the aqueous solutions, achieving the highest adsorption capacity of 30.6 mg/g [100]. Another report has shown that surfactant modification of montmorillonite using HDTMA resulted in composites with improved adsorption efficiency towards elimination of phenol and 4-CP at room temperature and shorter equilibrium time of 25 °C and 15 min, respectively [98].

Similarly, adsorption of phenols was reportedly investigated using charged-ions-modified and metal-oxide-nanoparticles-modified clays. These materials were shown to significantly improve the clays' surface properties and adsorption performance. Comparison studies were reported by Berraouan et al. (2020) for the adsorption of carvacrol onto bentonite and Na-modified bentonite. The cation exchange capacity of the Na-bentonite increased compared to the pristine bentonite, 83.33 meq/g (Na-bentonite) and 61.84 meq/g (pristine bentonite). Similarly, the BET specific surface area and pore volume of the composite was 94.25 m²/g and 0.166 cm³/g respectively, which was much higher than the pristine bentonite, with BET surface area and pore volume of 3.89 m²/g and 0.006 cm³/g, respectively. Thus, the Na-bentonite offers higher adsorption sites for the adsorbate molecules, achieving an adsorption capacity of 110 mg/g at equilibrium [104]. The effect of Na⁺ for the enhancement of montmorillonite adsorption capacity towards phenol was reported and the adsorbent possessed good thermal stability and dispersibility in both water and organic solvent, thus, showing good efficiency in phenols adsorption [109]. Previously, our group has also demonstrated the adsorption performance of halloysite nanotubes for the 2,4,6-TCP adsorption upon introduction of Cu²⁺ ions on the surface of the clay. The monolayer adsorption capacities were 196 and 217 mg/g for the pristine and functionalized material, respectively [101]. Higher adsorption efficiency of dual-cation montmorillonite for phenol adsorption was also reported [173]. The BET surface area of the adsorbent was 46 and 50 m²/g for the pristine and modified clays, respectively. Thus, the latter attained equilibrium within 10 min. The adsorption of phenols and CPs were reported with Ghanaian Muscovite clay functionalized with Ca²⁺, Mg²⁺, Na²⁺, and K²⁺, achieving better adsorption efficiency than the pristine clay [110]. On the application of metal-oxide nanoparticles, the materials have also shown improved in the clays' adsorption performance [107]. The composites possessed superior chemical properties, good thermal stability, and mechanical resistance than the pristine clays. The adsorbent can also be regenerated with a magnetic bar, such as in the case of magnetic oxide nanoparticles [9,90].

Composites of clays with activated carbon [111], biochar [112], graphene [113], chitosan [114], geopolymers [84], and transition metal complexes [174], were investigated for

the phenol’s adsorption. They were mostly characterized by higher adsorption efficiency and good mechanical stability. Table 2 represents the previously reported studies on the adsorption of phenols onto various modified clays. Higher adsorption capacity and shorter equilibrium time have been emphasized as their major advantages. Despite the significance of the composites, the high cost of the modification served as their major shortcoming.

Table 2. Adsorptions of phenols onto modified clay minerals.

Adsorbent	Pollutant	Concentration (mg/L)	Adsorption Capacity (mg/g)	Equilibrium Time (min)	Ref.
Na-Montmorillonite	Phenol	5	18.9	15	[157]
Chitosan-coated montmorillonite	Phenol	100	28.4	240	[175]
Modified montmorillonite	Phenol	250	10.0	240	[176]
HDTMA-stevensite	Phenol	100	13.2	180	[160]
C ₁₄ -4-C ₁₄ im-Vt organo-clay	BP	200	400.2	180	[177]
C ₁₄ -4-C ₁₄ im-SiNSs organo-clay			230.8	20	
C ₁₄ -4-C ₁₄ im-Mt organo-clay			220.3	120	
HDTMA-bentonite	Phenol	200	50.0	30	[96]
OTMAC-modified attapulgite	Phenol	0.05	0.8	60	[172]
HMBP-montmorillonite	Phenol	47	8.3	120	[100]
Surfactant-bentonite	Phenol	60	8.4	30	[147]
Surfactant-kaolinite			3.5	50	
DDTMA-montmorillonite	p-CP	100	4.1	80	[178]
DDDMA-montmorillonite	p-NP		11.5		
	p-CP		12.9		
	p-NP		14.3		
CTAB-modified clay	phenol	1.0	28.0	720	[179]
	<i>m</i> -NP	0.7	31.0		
BHPD-montmorillonite	2-napthol	160	124.0	40	[106]
	phenol	100	34.0		
CHS-STAC-montmorillonite	phenol	40	2.6	120	[173]
Surfactant-aluminum-pillared montmorillonite	4-NP	20	14.0	70	[180]
	2-NP		17.0		
FTMA-montmorillonite	Phenol	200	18.5	420	[181]
HDTMA-bentonite	phenol	30	22.4	60	[182]
Na exchanged bentonite			2.6		
HDTMAB-Modified Palygorskite	BPA	50	108.2	120	[166]
Ca-montmorillonite	BPA	100	34.2	240	[167]

2.3. Parameters Optimization for Phenols Adsorption

Adsorption study is usually accompanied by stoichiometric factors and represented as the rate of the removal of pollutants. Studying these factors enables researchers to ascertain the performance of a given adsorbent and correlate the mechanism of the process. It enables the researchers to ascertain best experimental design of the process according to the effects of the individual parameters. Various factors such as the stirring rate, volume of the sample used, contact time, dosage of adsorbent, concentration of the analyte, pH of the medium, temperature, desorption time, etc., are the most widely employed methods to describe adsorption processes. Evaluation of these factors is usually conducted at predefined range of values by a trial-and-error approach or based on the literature studies. The most widely used approach is one factor at a time. However, it is time consuming and involves multiple steps. Alternatively, multi-variable optimization tools, such as response surface methodology (RSM) and Taguchi optimizations, can be used to overcome these shortcomings. For phenols adsorption onto clays, the parameters widely employed include

contact time, clay loading, concentration, pH, and temperature (Figure 5). Findings on the effects of these individual parameters are illustrated and analyzed below.

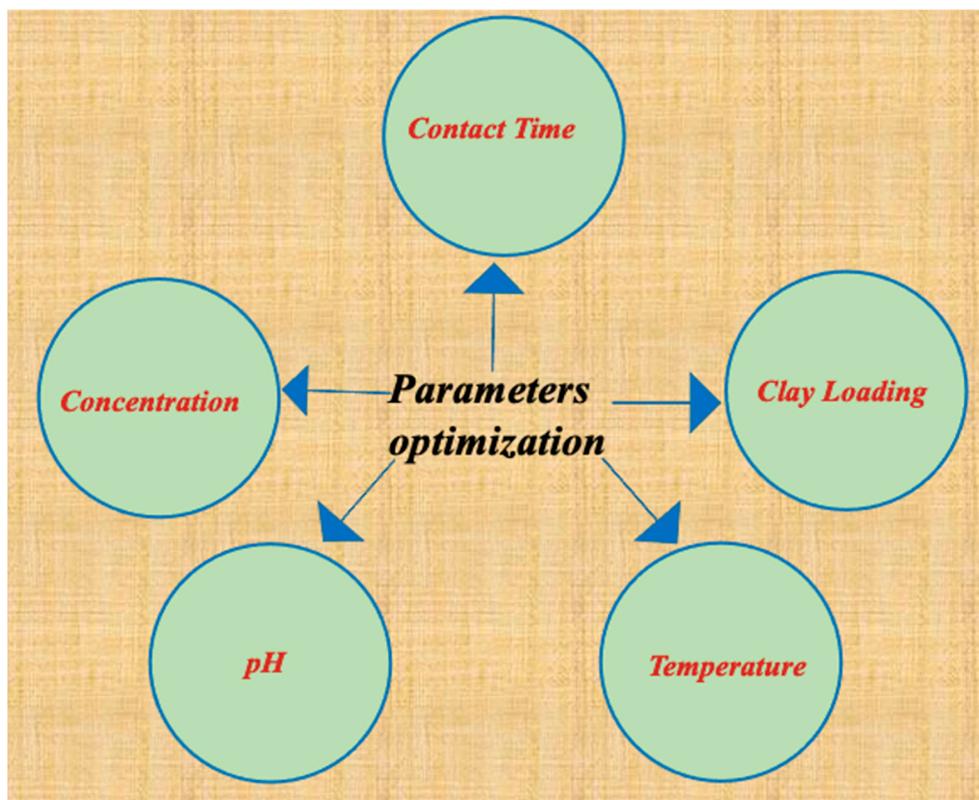


Figure 5. Parameters optimization for the phenol adsorption by clay and modified clay materials.

2.3.1. Contact Time

The effect of contact time on trace level extraction and adsorptive removals of phenols using various clays was widely studied. It is a vital parameter used to estimate the efficiency of the materials. Typically, a clay is rated based on its uptake of pollutant molecules from the aqueous medium within the shortest possible time. The time for the completion of adsorption has been explored. Salehinia et al. (2019) discussed the performance of C₁₆-silica/magnetic montmorillonite for BPA microextraction. About 90% of the analyte was extracted within 5 min at sorbent dosage and BPA concentration of 5 mg and 5 mg/L, respectively. The adsorption capacity achieved at the equilibrium was 4.36 mg/g [135]. Dehmani et al. (2020) reported on the rapid extraction of phenol onto raw and activated Moroccan clays. The equilibrium was achieved within 180 min with 3 times the magnitude of the raw clay, attributed to its higher BET specific surface area [97]. The superior performance of the composite was attributed to the enhanced affinity of the BPA to the hydroxyl alkyl chain functional groups of the composite. Abolghasemi et al. (2015) also reported on headspace SPME extraction of 4-CP, 2,4-DCP, 2,6-DCP, 2,4,6-TCP, 3-NP, and 4-NP from water onto a fiber coated with a polyaniline-montmorillonite nanocomposite. The extraction profile indicated the affinity and efficiency of the fiber to adsorb analyte until equilibrium was attained within 50 min [142].

For adsorption application, surfactant-modified montmorillonite composite was used for adsorption of 4-NP and 2-NP. The equilibrium was attained within 70 min for both single and multi-component adsorption systems. Additionally, the process was characterized by two adsorption steps: the rapid adsorption of the molecules to the surface of the composite and the steady state associated with the adsorption of the molecules onto the internal pores of the composite [180]. Phenol removal onto surfactant-modified bentonite has also been reported, with optimum contact time achieved within 60 min [182]. The Moroccan

stevensite and its corresponding surfactant-modified form adsorbed phenol molecules gradually until equilibrium was established at 180 min [160]. The complete adsorption of 2-naphthol and phenol was achieved within 40 min by surfactant-modified montmorillonite. The adsorption capacity of 2-naphthol and phenol using surfactant-modified stevensite were 107 mg/g and 21 mg/g, respectively. (Figure S1 in Supplementary Material). The reason for the higher adsorption capacity of phenol and 2-naphthol resulted from extra phenyl in the structure, which caused delocalization of π -electron density and stronger π - π interactions between the pollutant and the clay adsorbent [106]. Thus, a clay mineral or composite is classified as efficient because it achieves complete uptake of pollutant molecules within the shortest possible time.

2.3.2. Clay Loading

The amount of clay used strongly influences the recovery and adsorptive removal of the phenols from the medium. In most cases, higher dosage resulted in higher adsorption capacity and shorter equilibrium time due to more available adsorption sites [123]. Therefore, Liu et al. (2011) have investigated the effect of sorbent dosage on the MSPE extraction of CPs by montmorillonite/ Fe_3O_4 @PSF composites. The amount of sorbent used was studied in a range of 20 to 150 mg with a sample volume of 25 mL, containing 10 $\mu\text{g}/\text{mL}$ of the analytes. The findings indicated that a high amount of sorbent was required to sufficiently recover the analytes. Thus 80 mg was maintained as the dosage for the process optimization [136]. Peng et al. (2020) reported on the use of DSPE for BPA microextraction using magnetic montmorillonite. The sorbent dosage significantly impacted the extraction efficiency and ease of recovery. The amount of Fe_3O_4 /montmorillonite was varied from 10 to 50 mg, and the extraction efficiency is presented in a chromatogram presented in Figure S2 in supplementary material. It indicated that higher recovery of the analytes was achieved at 50 mg of adsorbent [137].

The amount of kaolinite and metakaolinite for phenol uptake was investigated by Ghogomu et al. (2015). Varying the dosage from 0.1 to 0.7 g increased the removal efficiency [94]. Tabana et al. (2020) have shown that adsorption of phenol onto calcined clay increased as the amount of sorbent loading increases from 5 to 10 g, achieving the adsorption efficiency of 68–83%. However, no significant removal efficiency was observed when the clay dosage was increase from 15 to 20 g. This is due to the saturation of active site of the clays by the phenol molecules in a sequential manner. Increasing the dosage above the optimum limit decreased the dispersion efficiency of the clay, leading to agglomeration and blocking of adsorption sites [164]. The sorbent dispersion in an aqueous solution occurs uniformly up to a certain point at which all the active sites become exposed and fully occupied by adsorbates [183]. Thus, optimum adsorption was achieved at a moderate dosage of the sorbents.

2.3.3. Concentration

Phenol concentration has significant effect on the adsorption efficiency of the clay materials. Higher concentrations resulted in the increase of the adsorption capacity due to mass transfer of the pollutants from the aqueous phase to the vacant sites of the sorbent's surface. According to Liu et al. (2011), increases in both extraction time and initial concentrations of the 2-CP and 4-CP resulted in the enrichment of an SPE for CPs microextraction using montmorillonite and montmorillonite/ Fe_3O_4 @PSF composite. Thus, better recovery, of 90–109%, was achieved for all the real water samples studied at the higher concentration of the analytes [136]. Banat et al. (2000) reported that phenol adsorption onto bentonite increased with increasing pollutant concentration from 50 to 500 mg/L. Due to the abundant adsorption sites on the surface of the clays, the phenol molecules were completely adsorbed even at the higher concentrations. [159]. According to Maarof et al. (2002), the adsorption of phenol, 3-CP and o-cresol onto montmorillonite increases, as the concentration of the pollutants increases from 25 to 200 mg/L. Phenol has higher solubility compared to the other pollutants; resulting in lower adsorption efficiency (70%)

compared to *o*-cresol (88%) and 3-CP (97%) [176]. Ghogomu et al. (2015) emphasized that the uptake of phenol by kaolinite and metakaolinite increases as the initial concentrations increase from 20 to 160 mg/L. This is related to the collision of phenol molecules with the active sites of the adsorbent's surface. At higher concentration, the maximum adsorption capacity achieved was 24.48 mg/g for kaolinite and 31.1 mg/g for metakaolinite [94]. Yang et al. (2015) also studied the adsorption of phenol and 2-naphthol onto gemini surfactant organo-montmorillonite at different concentrations of 0.4 to 2.0 mg/L (Figure S3 in Supplementary Material). The adsorption capacity increased with the concentrations and the findings indicated that 2-naphthol has higher adsorption capacity compared to phenol at similar conditions, attributed to the stronger hydrophobicity of 2-naphthol and delocalized π -electron density [106]. Chidi et al. (2018), reported that the adsorption of phenol onto surfactant-modified bentonite at 298K increased steadily with concentrations from 30 to 120 mg/L. The equilibrium was achieved within 60 min even at the highest concentration, attributed to the available adsorption sites on the surface of the composite [182].

2.3.4. pH of the Solution

The pH of the medium at which the extraction occurs is an important factor in microextraction study. In phenol microextraction, the pH affects the extraction efficiency and recovery of the sorbent. It influences the chemical form and solubility of phenols existing in the solution. Generally, phenols exist in ionic form at pH higher than their pKa [26]. Liu et al. (2011) studied the influence of pH on the extraction of 4-CP and 2-CP onto montmorillonite/Fe₃O₄@PSF composite. The extraction was favored by the acidic pH of 2–6, attributed to the hydrophobicity of the analytes and the cation-exchange interaction existing between the composite and the analytes. When the sample pH is adjusted to pH higher than 8.0, the extraction efficiency decreases, attributed to the deprotonation of phenols [136]. Ghani et al. (2016) stated that extraction of CPs onto montmorillonite/epoxy occurred at acidic pH. The highest extraction efficiency of 2,4,6-TCP and penta-CP was achieved at sample pH 5.0, which is due to the retention of analytes onto the montmorillonite through electrostatic interaction between the analytes and the functional group on the solid support. The pKa of the analytes were 6.59 and 4.90 for the 2,4,6-TPC and penta-CP, respectively [138].

Investigations have been made on the effect of pH toward the adsorptive removal of the phenols. Park et al. (2013) have shown that an acidic condition was better for *p*-chlorophenol and *p*-NP adsorption onto surfactant modified-montmorillonite. This can be explained by the presence of a siloxane (Si-O) group in the form of tetrahedral sheets on the external surface of the montmorillonite that becomes weaker and leads to the formation of Si-O⁻, a bond that eventually converts to Si-OH depending on the variation of the pH. Upon increasing the pH, the surface functional group of the montmorillonite became fully or partially deprotonated, thus forming a negatively charged surface. The surfactant molecules in the interlayer space of the organoclays acted as an efficient partition medium, and the predominant hydrophobic interaction and van der Waals interaction resulted in the better adsorption of the pollutants [178]. Similar observation was made by Li et al. (2018) using FTMA-montmorillonite. The adsorption capacity decreased when the sample pH exceeded 9 (Figure S4 in supplementary material). The reason was due to electrostatic repulsion between the adsorbent and the phenol solution [181]. A recent finding from Ouallal et al. (2019) has also reported on the decreased of the adsorption capacity of phenol onto calcined clay when the sample pH increases. The q_e values were 2.88 and 2.54 mg/g at pH 4 and 11, respectively. This was attributed to the predominance of negative charges on the surface of the adsorbent at the alkaline pH, which coincided with the negative charge on the phenol at pH above 9, forming phenolates (C₆H₅O⁻) with a pKa value of 9.95. Thus, repulsion has resulted between the two surfaces [156].

2.3.5. Temperature

The effect of temperature on the phenol adsorption onto clay materials have been extensively explored. Increase in temperature will increase the adsorption performance, due to swelling effect of the clays. Investigation carried out by Li et al. (2018) has shown an increase in the adsorption capacity from 17.60 to 19.30 mg/g at 25–35 °C for phenol adsorption onto FTMA-montmorillonite [181]. They have attributed the findings to the swelling of the adsorbent as the temperature increased. The extraction efficiency of phenols onto the polyaniline-montmorillonite nanocomposite using headspace SPME was also found to increase with temperature. As the temperature increased, the rate of transfer of the analytes onto the surface of the adsorbent increased [142]. Dehmani et al. (2020), pointed out that the adsorption of phenol onto the raw and activated Moroccan clay is affected by the increase in temperature. For activated clay, adsorption temperature was studied at 30–50 °C, achieving adsorption capacities of 5.84–6.84 mg/g, respectively. Similarly, for the raw clay, adsorption capacity was between 1.39–2.71 mg/g. The endothermic behavior observed was attributed to the increase in the mobility of the phenol molecules to the clay surfaces at the higher temperature due to the dissipation of energy to the system [97].

However, a significant decrease in the adsorption capacity was observed with an increase in temperature from 25–55 °C for the HMBP-montmorillonite (Figure S5 in Supplementary Material) [100]. This is due to the decrease in the interaction between phenol and the adsorbent as the temperature is increased (Luo et al. 2015). Li et al. (2018) reported that, at temperatures above 35 °C, the adsorption capacity of phenol onto the FTMA-montmorillonite drastically decreased, associated with the weakening of the adsorptive forces between the active site of the adsorbent and the phenol [181]. From the finding of Salehinia et al. (2016), an increase in temperature from 25 to 65 °C decreased the adsorption efficiency. The maximum adsorption capacity at 25 and 65 was 59.17 and 38.76 mg/g, respectively [135].

2.4. Modeling Kinetics

The kinetic study of adsorption describes the process's mechanism and rate-controlling steps [184]. Thus, the kinetics for the uptake of phenols by clay materials have been studied. Various adsorption models such as pseudo-first order, pseudo-second order, intra-particle, and Elovich models were employed. The aim was to determine the process's steady state and the rate-controlling steps by subjecting the experimental data to the models. Tai et al. (2014) studied various kinetic models for the adsorption of 2-naphthol onto organopolygorskite (Figure 6). It was found that the adsorption process of 2-naphthol onto organopolygorskite fit the pseudo-second-order model. According to the obtained results, its R^2 and calculated adsorption capacity (q_e cal) values were 0.9999 and 19.08 mg/g, respectively, which has shown good agreement with the experimental q_e value of 18.86 mg/g. Moreover, from the intra-particle model, the adsorption proceeds via two steps. The first step involved the adsorption of the 2-naphthol molecules onto the surface of the clay, while the second step represented a diffusion of the molecules onto the clay's pores [185]. Chidi et al. (2018) studied the adsorption of phenol onto Na-bentonite and surfactant-modified bentonite clays. The results also indicated that the adsorption process fit the pseudo-second-order model, indicating a chemisorption process. The adsorption was higher for the surfactant-modified bentonite than the Na-bentonite, attributed to the increased in the affinity of the adsorbent to the phenol molecule upon the surfactant modification [182]. Similarly, the characteristic parameters for the phenol's adsorption onto the pristine and thermally modified kaolinitic clays obeyed the pseudo-second-order model [94]. Hamdaoui et al. (2018) explained the adsorption of phenols onto the Moroccan stevensite, otherwise known as Rhassoul clay and the HDTMA surfactant modified clay. The adsorption was associated with the rapid phenol uptake at the initial stage of the process. The process was also described as pseudo-second order based on the result of linear regression fitting [160]. Xiang et al. (2019) also described the adsorption of bromophenol blue onto imidazolium-based gemini surfactant organoclays followed pseudo-second-order model,

indicating a chemisorption process between the clays and bromophenol. This is due to the present of abundance sites on their surfaces that allow the chemical interaction between bromophenol and imidazolium-based gemini surfactant organoclays to occur [177]. In conclusion, it can be observed that the adsorption kinetics of phenols onto clay material are mainly dominated by chemisorption process, which is reflected in the availability of adsorption sites and functional group on the surface of the clays.

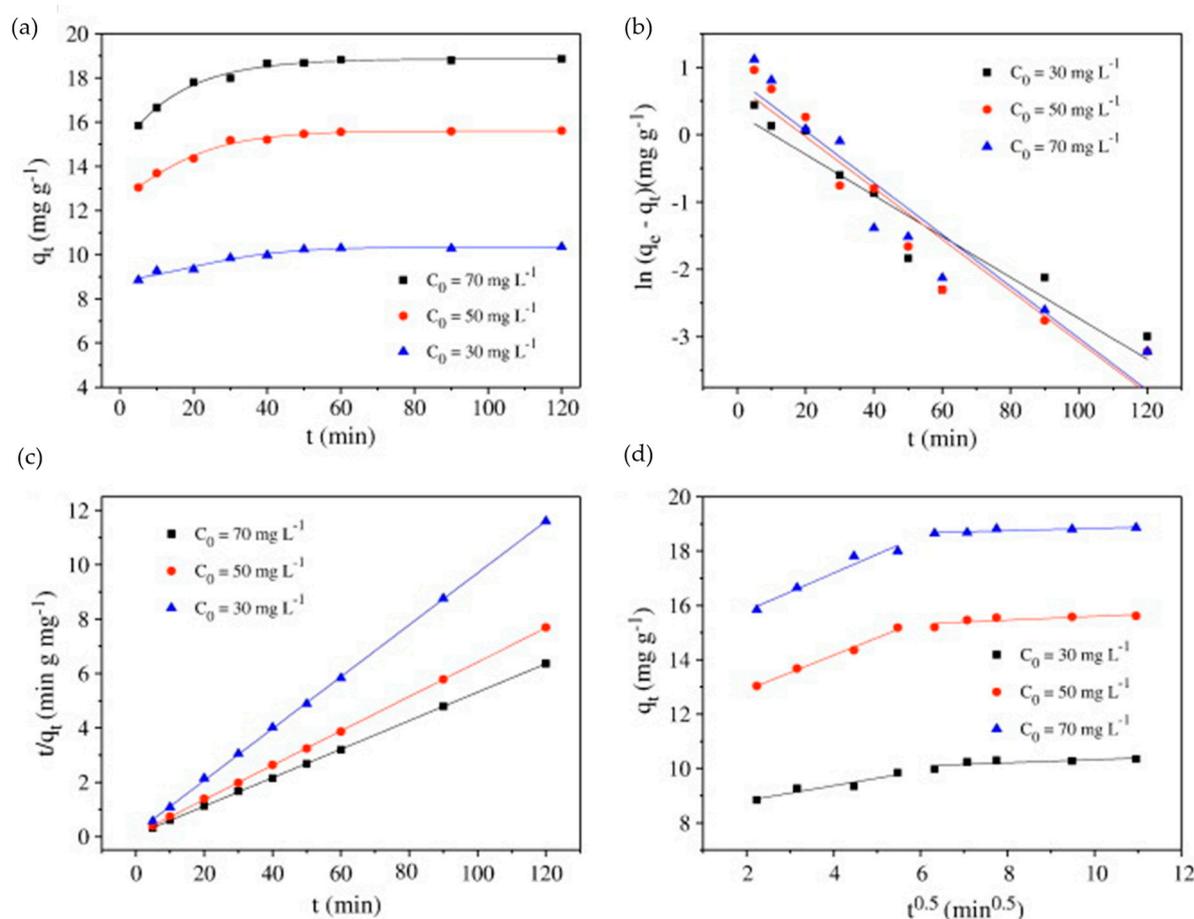


Figure 6. Kinetics for the 2-naphthol adsorption onto the anion-cation organopolygorskite (a) Contact time, (b) Pseudo-first order, (c) Pseudo-second order, and (d) intra-particle diffusion models [186].

2.5. Modeling Isotherms

The isotherm studies are conducted to describe the equilibrium process, the interaction between the adsorbent and adsorbate and the surface properties of the adsorbent. Adsorption isotherms were predicted using different models, e.g., Langmuir, Freundlich, Temkin, Dubinin–Radushkevich, Redlich–Peterson. An isotherm studies was conducted for the adsorption of 2,4,6-TCP onto raw and Cu²⁺-Halloysite clay. The finding revealed that, the adsorption isotherm was dominated by Langmuir model, implying a monolayer coverage. The Cu²⁺-Halloysite clay also exhibited higher monolayer adsorption capacity (q_{max}) value of 217 mg/g as compared to the raw clay with q_{max} value of 196 mg/g. The observed difference was attributed to the presence of Cu²⁺ ions on the surface of the halloysite clay [101].

In contrast, Cardenas et al. (2008) described the adsorption of 3,4-DCP and 2,5-DCP onto natural clay as multilayer adsorption process according to the Freundlich model. The adsorption capacity increased exponentially with concentration of the pollutants in the aqueous phase. The q_e experimental values were 45.5 and 14.5 mg/g for the 3,4-DCP and 2,5-DCP, respectively. However, at higher concentrations the adsorption process

avored the Langmuir model, signifying a monolayer coverage. This phenomenon is due to the saturation of active sites at higher concentration of 3,4-DCP and 2,5-DCP. [161]. Park et. (2013) also reported the adsorption of p-CP and p-NP onto surfactant modified montmorillonite via multilayer adsorption rather than the monolayer process. The binding of the pollutants onto the adsorbent surface implied its higher number of adsorption sites, and hence the higher adsorption capacity [178]. Luo et al. (2015) explored several isotherm models for the phenol adsorption onto HMBP-montmorillonite at various temperatures (Figure 7). Based on the linear regression analysis, Langmuir, and Redlich–Peterson models best described the isotherms of the adsorption process, according to R^2 values of the two models. Additionally, the monolayer formation and the separation factor (R_L) value lies between 0–1, which signifies the dominance of Langmuir model for the adsorption process [100].

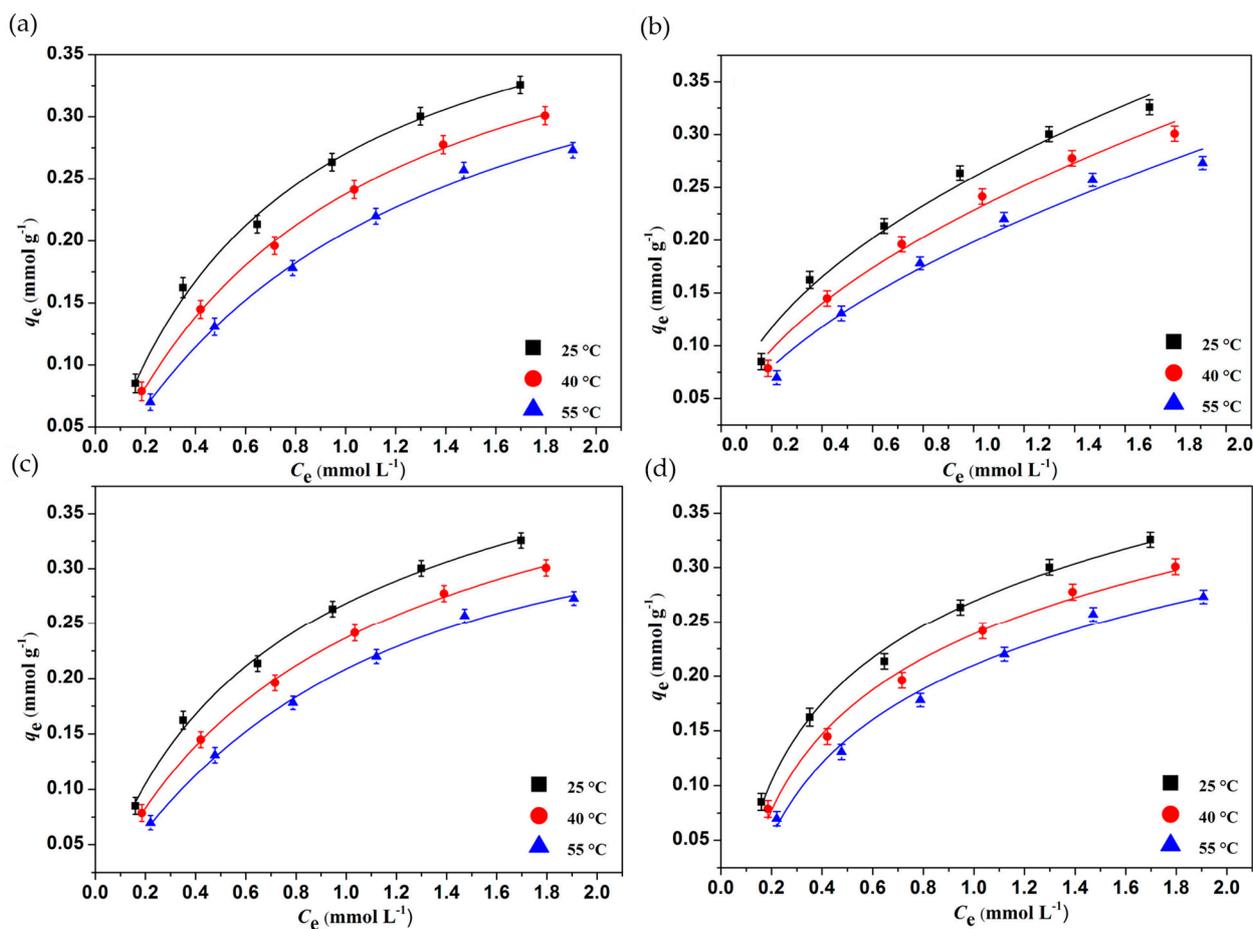


Figure 7. Isotherms studies for the adsorption of phenols onto modified montmorillonite clay. (a) Langmuir, (b) Freundlich, (c) Redlich–Peterson and (d) Temkin models [100].

2.6. Regeneration and Reusability of the Clay Minerals

The economic aspect of microextractions and adsorption processes is the ability of the adsorbent to be reused continuously without decrease in its efficiency over considerable number of cycles [186]. An ideal adsorbent can remove pollutants from water continuously without posing additional risk to the water or causing harm to the environment [187,188]. The regeneration and reusability of clays is important for economic practicability, ease of operation, environmental sustainability, and viability of the microextraction and adsorption techniques. Clays are considered essential and not known to pose potential harm to the environment and toxicity to living organisms. Thus, they demonstrated potential and promising application for environmental water remediation.

Tai et al. (2014) reported on the reusability of organopolygorskite for 2-naphthol adsorption. The adsorption mixture was subjected to rotary shaking at 150 rpm at 298 K for 4 h before separating the supernatants by centrifugation. The adsorption was then subjected to further adsorption cycles, i.e., each clay was regenerated for five consecutive cycles. Little or no reduction in the adsorbent dosage was observed. The obtained adsorption capacities were 27.0 and 23.8 mg/g, at 1st and 5th cycles, respectively [185]. Li et al. (2018) studied the recovery of surfactant-modified montmorillonite using a reduction method conducted at constant potential of +0.0 V for 21 h under N₂ atmosphere at 25 °C. The adsorption cycle was terminated at the 5th run due to the gradual decrease in the adsorption capacity and the loss of the clay during regeneration. The adsorption of 4-NP onto coconut shell–clay composite was investigated by Adebayo and Areo (2021). The adsorbent was regenerated using 90% acetone and subjected to reusability for five consecutive cycles as shown in Figure 8 [40]. The observed decrease in the adsorption capacity of the clay was attributed to the decrease in the adsorption sites due to incomplete electrochemical oxidation surfactant [181]. The reusability of thermally modified double-layered hydroxide clay via calcination at 500 °C for 4 h was also reported. The regenerated clay was able to achieve 86–60% adsorption efficiency at 1st, 2nd, 3rd, and 4th cycles, respectively [164]. Some researchers have stated that the calcination of regenerated clay could improve its adsorption performance [189,190]. However, others argued that higher temperature calcination usually leads to a decrease in the clay's adsorption capacity because of decreases in its crystallinity [162,191].

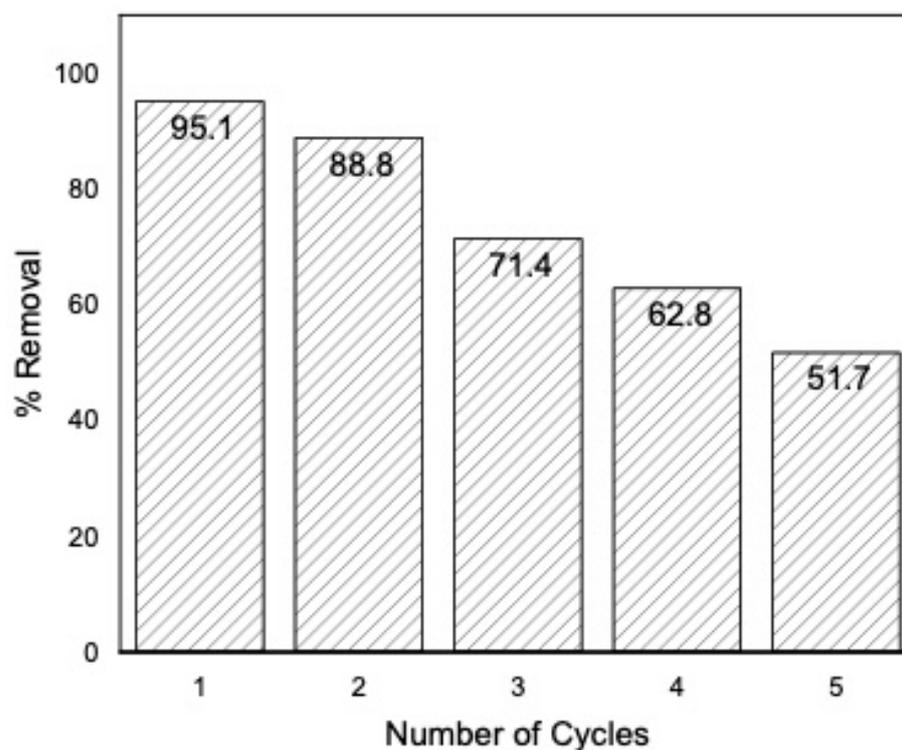


Figure 8. Reusability of Coconut shell–clay composite for phenol adsorption [40].

2.7. Mechanisms for the Phenol Adsorption onto Clays

Some research has attempted to propose a mechanism for the adsorption onto clays. The ways in which phenols interact with the clays include hydrophobic, electrostatic, and molecular interactions [192]. An investigation of the adsorption of phenol on Algerian clay was reported. The mechanism of the adsorption studied revealed that the phenol molecules interacted with the silanol group on the clay surface via hydrogen bonding. Ouallal et al. (2019) pointed out that hydrogen bonding was predominant for the adsorption of phenol onto raw and calcined Moroccan clay. This is because the kaolinite structure of the clay

contained sodium cation (Na⁺) with water of hydration on its surface. Thus, at higher concentrations, the phenol molecules could penetrate the intermediate layer of the kaolinite and form hydrogen bonding with the clay [156].

Apart from hydrogen bonding, electrostatic interaction, π - π interaction and van der Waals interaction are also involved in the adsorption process. Li et al. (2015) investigated various possibilities for 4-CP and 2,4-DCP adsorption onto dodecyltrimethylammonium bromide (DTAB) and cetyltrimethylammonium bromide (CTAB)-modified montmorillonites. The surface characteristics of the clay organophilic upon modification enhanced the composite's adsorption properties. The negatively charged CP molecules interact with the electrostatic bonding with positively charged surfaces of the DTAB-montmorillonite and CTAB-montmorillonite.

Additionally, π - π interaction existed between the benzene ring of the 4-CP and 2,4-DCP and the exterior and interior surface sites of organoclays [193]. Luo et al. (2015) explored possible pathways for the adsorption of phenol, PCP, PMP, and PNP onto HMBP-modified montmorillonite. HMBP formed a heteroatomic ring with the clay via monolayer in a direction parallel to the siloxane surface of the clay (Figure 9). As such, chances for the hydrophobic interaction between the phenols and the surface of the clay and the phenol molecules were limited. Similarly, the possibility of the formation of electrostatic attraction between the negatively charged HMBP-montmorillonite and the phenols was unfavorable due to the acidic pH of the solution. Thus, the possibility of π - π interaction was considered. Since HMBP contained a pyridine ring, the adsorption occurred via π - π bonding between the phenol and HMBP surface. For PCP, PMP, and PNP, the presence of an electron-withdrawing group on their surface weakened the interaction by decreasing the aromatic ring's π electron density. Hence the adsorption capacity for phenol was higher (30.6 mg/g) than the other pollutants [100]. These findings agreed with various studies reported elsewhere [193,194].

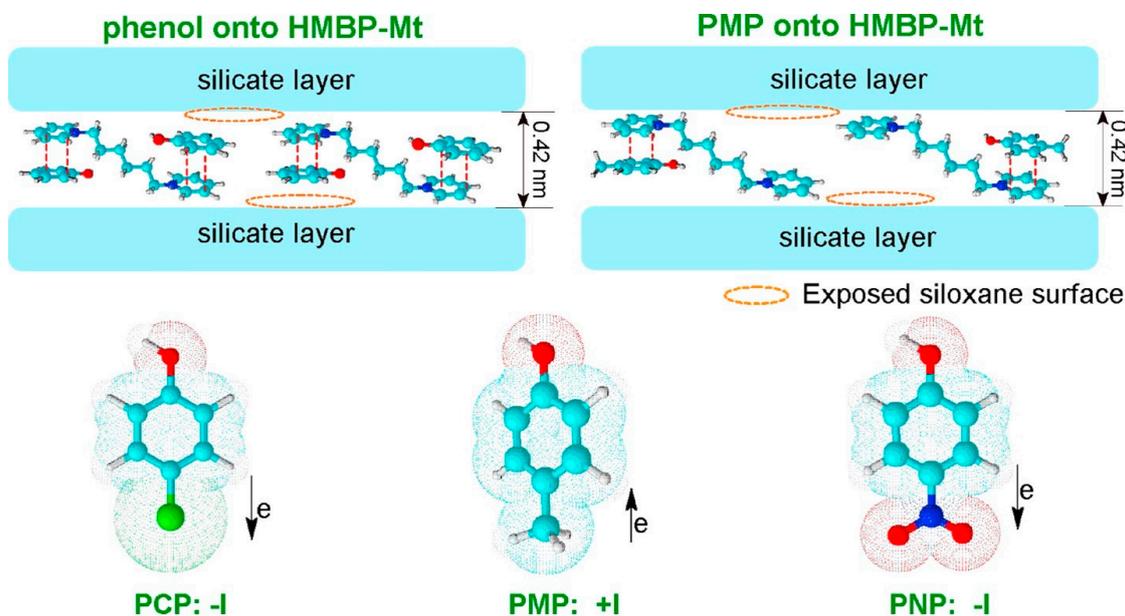


Figure 9. Mechanism for the adsorption of phenol and p-methyl phenol (PMP) onto HMBP-montmorillonite clay [100].

3. Application of Clays for Phenols Remediation in Real Water Samples

Clays have been extensively used as an ideal sorbent for environmental water remediation [195]. Its efficiency in various real water samples was examined and well reported. Researchers have extended the work to real samples' phenol microextractions and adsorptive removal. Peng et al. (2020) studied the extraction of five bisphenols using

DSPE with magnetic montmorillonite. Good recovery of the analytes was achieved in the range of 84.3–98.2 (Figure 10). Additionally, inter-day and intra-day RMSD of the method was in the range of 2.9–6.8% and 2.6–5.6%, respectively [137]. The applicability of montmorillonite/epoxy-coated stir bars for recovering CPs from different environmental water samples was studied. The relative recovery was obtained by measuring the ratio of the analyte concentration in the real samples to that in the pure water samples spiked. Thus, the recovered analytes reported were 88.5–98.5% for the studied CPs [138]. Liu et al. (2011) reported on the SPE extraction to determine 4-CP and 2-CP in environmental waters using montmorillonite/ Fe_3O_4 @PSF composite. The recoveries of the analytes were in the range of 97.1–105.1% in a river water sample, whereas 109–115% were recovered in the wastewater samples. The higher recovery achieved demonstrated the clay material's suitability for extracting the analytes [136]. Preconcentration of BPA in trace amount using attapulgite as SPE sorbent was also reported. The relative recovery of the analyte in real water samples achieved was 93–97%, indicating the effectiveness of the material for the BPA extraction [122]. Salehinia et al. (2016) demonstrated the efficiency of C_{16} -silica/magnetic-montmorillonite for the extraction of BPA from river water samples. The relative recovery of the analyte achieved was higher than 95% [135]. These findings emphasized the efficiency of the clays as adsorbent for sample preparation technique.

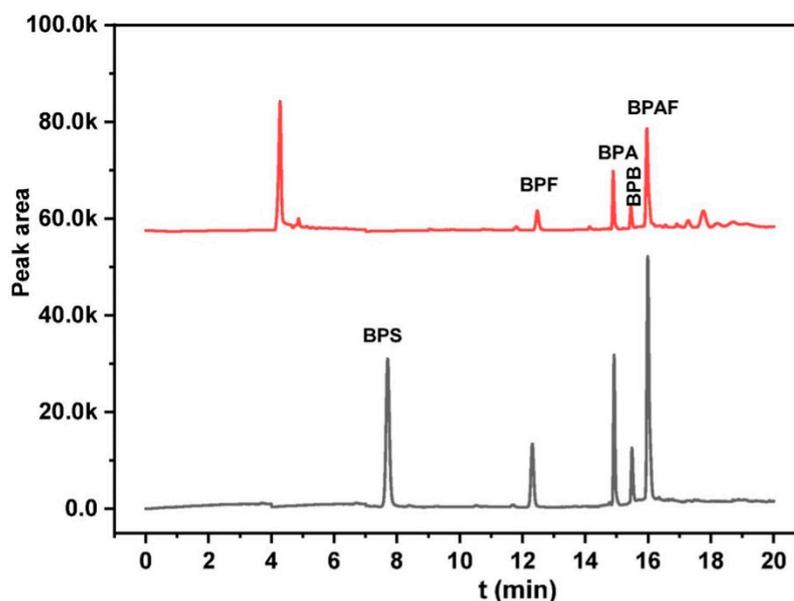


Figure 10. Recovery of bisphenols from real sludge samples using magnetic montmorillonite [137].

3.1. General and Concluding Remarks

3.1.1. Achievement

Based on the literature work covered by this research, it is sufficient to mention that tremendous achievements have been recorded on the application of raw clays and modified clays for phenols remediation from environmental waters. Over the last two decades, various attempts have been made to modify clays to suit the applications on microextraction and adsorptive removal of phenols. The materials served as good sources of natural and low-cost sorbents with good porosity and excellent mechanical strength, water, chemical, and thermal stability for environmental remediation applications. The mesoporous and heterogenous surface of the clays rendered them able to trap large and small molecules from the aqueous media. Thus, they have demonstrated good performance for microextraction and adsorptive removal of phenols from environmental waters. Montmorillonite, being the most widely explored clay, has shown excellent performance for phenol molecules extraction. Its hydrophilic and porous surface has been the dominant factor and tremendous success compared to the other clays. It also possessed cationic charge on its surface and

the silanol group. Thus, it interacted with the phenols through different mechanisms. The surface functionalization by various processes such as surfactant modification, grafting with organic compounds, and cations functionalization had been vital for the improvement of the properties and performance of the clays. Thus, both raw and modified clays have presented better adsorption efficiency for the remediation of phenols.

3.1.2. Challenges

Apart from the overwhelming success achieved, there are some gaps that require the attention of researchers. In accordance with the literature, the discoveries were mostly limited to batch processes at laboratory scale. As such, investigations on integrated adsorption process using continuous flow system, column, and membrane technologies need to be explored for both pilot and industrial scale applications. Moreover, for better understanding of the performance and prospects of the materials, design-of-experiment (DOE) models such as response surface methodology (RSM) and Taguchi, etc., should be studied. Additionally, use of computational techniques such as molecular docking, dynamics, density functional theory (DFT), *ab initio*, etc., should be applied to ascertain the actual bonding interactions taking place at molecular levels.

Another challenge is the issue of discharge of the spent clays after subsequent usage. Recovery studies served as an alternative to utilize the clays for large number of extraction or adsorption cycles. However, the issue of disposal remains a challenge. Sometimes, they are a secondary pollution to the environment, particularly when used as a composite in combination with other chemical substances. Thus, proper means of disposal are needed to mitigate these shortcomings and maintain a greener environment. Incineration is mostly considered. However, it has higher operation cost, poses environmental risk, and could lead to air pollutions. Researchers are therefore encouraged to discover more innovative technologies for the sustainable disposal of the spent clays.

3.1.3. Conclusions

The application of clays for trace determination and adsorptive removal of phenol from environmental waters recently gained more recognition. The natural source and relative abundance of the minerals was emphasized as one of their major advantages. They possessed high porosity, good mechanical strength, and cationic exchange capacity. Montmorillonite has been the most widely employed clay due to its higher BET specific surface area and cation exchange capacity. Acid and thermal activation has shown to improve the adsorptive performance of the natural clays. Thus, they interacted with the phenol via both hydrogen bond formation and van der Waals interactions. Activation processes via calcination, acid, and alkaline treatment have been shown to improve the promising features of the raw clays. Thus, the performance of the activated clays has exceeded that of raw clay in all ramifications.

Surface modifications and functionalization have also been shown to enhance the characteristic features of the clays. They have good impact on the adsorption efficiency of clays towards phenols extraction. Processes such as surfactant modification, grafting with organic molecules, polymer, and metal oxide nanoparticles incorporation, as well as charged ions functionalization, explicitly improved surface properties of clays, mechanical strength, polarity, cationic exchange capacity, water, moisture, and chemical stability for better performance in the microextraction and adsorptive removal of phenols from the environmental waters. The surfactant modifications proved the more positive of the various modification techniques. Similar metal oxide nanoparticles resulted in clay composites with improved characteristics of adsorption performance and ease of sorbent generation. The effective recovery and reusability of the materials for the microextraction and adsorptive removal of the phenols clearly indicate their potentialities and prospects for pilot and industrial scale application.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/separations10020125/s1>, Figure S1: Effect of contact time for the adsorption of 2-naphthanol and phenol onto montmorillonite surfactant modified organoclay; Figure S2: Effect of adsorbent dosage for the extraction of bisphenols onto Fe₃O₄/montmorillonite composite; Figure S3: Adsorption of (a) 2-naphthol and (b) phenol onto organo-montmorillonite at different concentrations of the adsorbate; Figure S4: Effect of pH on the removal of phenol using surfactant modified montmorillonite; Figure S5: Effect of temperature changes for adsorption of phenol onto HMBP-montmorillonite; Table S1: Chemical structures and physicochemical values of some phenols; Table S2: Various Solid-Phase Extraction Techniques Reported on Determination of Phenols. Refs. [100,106,122,130,135–138,142–145,181] are cited in Supplementary Materials.

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