Research Paper

An overview of geological originated materials as a trend for adsorption in wastewater treatment

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A B S T R A C T

Adsorption is a unit operation widely used for the tertiary treatment of the most diverse effluents, whose mechanism is based on removing recalcitrant compounds from the organic and inorganic origin. In this process, choosing a suitable adsorbent is a fundamental point. This review article focuses on the adsorbents with natural geological origin: minerals, clays, geopolymers, and even wastes resulted from mining activity. Therefore, over 450 articles and research papers were explored. These materials’ main sources are described, and their characteristics, composition, and intrinsic properties are related to adsorption. Herein, we discuss the effects of several process parameters, such as pH, temperature, pollutant, and adsorbent concentration. Furthermore, equilibrium, kinetics, and thermodynamic aspects are also addressed, and relevant regeneration prospects and final disposal. Finally, some suggestions and perspectives on applying these adsorbents in wastewater treatment are presented as future trends.

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1. Introduction

Around 95% of the Earth’s crust is constituted by rock and rock-based composts; therefore, geological materials are abundant and accessible (Banning, 2020; Ronov and Yaroshevsky, 1922; Taylor and McLennan, 1985) Meanwhile, due to our planet’s population’s growth and need for more significant development, more and more areas are explored, and more cities are built. Because of these anthropogenic actions, geological materials are dislocated and disposed of as residues, creating an environmental problem (Bettencourt et al., 2007; Folke et al., 2020; Ghernaout et al., 2020). After considering that these materials are mostly made up of silicon, oxygen, and other metal oxides (Folk, 1954), several studies have demonstrated interest in applying and investigating their natural properties towards adsorption, aiming the removal of environmental pollutants as a bright and elegant way of solving two growing problems (Atun et al., 2009; Bundschuh et al., 2011; Dong et al., 2020; Gu et al., 2019; Li and Arai, 2020; Roy and Krapac, 1994; Teymouri et al., 2020b; Tsai et al., 2006).

Adsorption is one of the most effective techniques in advanced wastewater treatment and can be employed to reduce or even remove hazardous organic and inorganic pollutants present in the effluent (Burakov et al., 2018; Crini, 2006; Dabrowski, 2001; De Gisi et al., 2016; Dotto et al., 2016; Dotto and McKay, 2020; Lütke et al., 2019). The process concerns the accumulation of a substance at the interface between two phases, liquid-solid or gas-solid (Liu and Jiang, 2010; Ţöth, 1995). The substance that accumulates at the interface is named adsorbate, while the solid on which adsorption occurs is the adsorbent (Fig. 1) (Dotto and McKay, 2020).

Adsorption can occur by chemical sorption and physical sorption (Di Toro, 1985; Hammond and Conner, 2013). Chemical adsorption, or chemisorption, consists of forming strong chemical associations – or even bonds – between molecules or ions of adsorbate to the adsorbent surface (Breeuwsma and Lyklema, 1973; Fan et al., 2020; Hong et al., 2020). Contrarily, physical adsorption, or physisorption, is described by intermolecular interactions between adsorbate and adsorbent. Nevertheless, the main physical forces controlling adsorption are van der Waals forces, hydrogen bonds, polarity, dipole-dipole, and π–π interactions (Chen et al., 2020; Halsey, 1948; Li et al., 2019a).

Overall, adsorption provides an attractive alternative for the treatment of polluted waters, especially if the sorbent is inexpensive, which geological originated materials can be (Asfaram et al., 2014;...
Ghaedi et al., 2015; Saif Ur Rehman et al., 2013; Shams et al., 2013a; Uddin, 2017). This review article presents how natural, geological originated materials, such as minerals, clays, geopolymers, and even waste resulting from mining activity, can be applied to water treatment and decontamination purposes. The geological materials characteristics, composition, and intrinsic properties related to adsorption are presented. The effects of several process parameters, such as pH, temperature, pollutant, and adsorbent concentration, are discussed. Furthermore, equilibrium, kinetics, and thermodynamic aspects are also addressed mainly, according to each application. Finally, some suggestions and perspectives on applying these adsorbents in wastewater treatment are presented as future trends.

2. Mineral adsorbents

More than 4000 naturally occurring minerals have been found on Earth (Haldar and Tišlar, 2013). To be classified as a mineral, the solid must be inorganic with characteristic chemical composition and specific crystal structure (Haldar and Tišlar, 2013; Mitchell et al., 1994). Due to the abundant presence of oxygen, silicon, and aluminum, silicates and aluminosilicates are quantitatively the most relevant class of minerals. Furthermore, the following classes are recognized: native elements; sulfide, telluride, arsenide, and selenide minerals including sulfosalts of antimony and bismuth; halides; oxides; hydroxides; carbonates; nitrates; borates; chromates; tungstates; molybdates; phosphates; arsenates; vanadates; silicates and aluminosilicates (Mitchell et al., 1994). For adsorption application purposes, the most relevant minerals are silicates, hydrous silicates, oxides, and carbonates (Cornell, 1993; Pehlivan et al., 2009; Rao et al., 1991; Zhang et al., 2019b).

In general, there are several critical parameters for a material to be considered a potentially promising adsorbent, such as its surface area, and porosity, surface charge, mechanical strength, and the surface chemistry of the adsorbent (Dotto et al., 2016; Lütke et al., 2019). In Table 1, it is presented the classifications and the average surface area, connecting geological materials and adsorption (Brantley and Mellott, 2000; Giménez et al., 2007; Hodson, 1998; Meier et al., 1994; Nandi et al., 2009; Reddy and Claassen, 1994; Sorwat et al., 2020; Walker et al., 2003; Wang et al., 2020a; Wang and Zhang, 2020; Yan et al., 2020). Several examples of the application of minerals in adsorption have been reported for various types of contaminants. Talc, chalcopyrite, and barite were tested against the removal of lead ions from liquid wastes (Rashed, 2001), while bisphenol-A adsorption onto andesite, diatomaceous earth, titanium dioxide, and activated bleaching earth were studied. Their results were compared to those of different carbon-based materials (Tsai et al., 2006). Bituminous coal, pumice stone, coconut coal, and volcanic zeolite were evaluated to remove nitrogen, phosphorus, aluminum, iron, cyanobacteria, and saxitoxins (Guimarães Neto and Aguiar, 2020). Furthermore, mineral adsorbents’ addition to porous concrete was also investigated to reduce groundwater pollution (Teymour et al., 2020a,b).

2.1. Silicates

2.1.1. Feldspar

Feldspar is, up to now, little explored when compared to other minerals. In a thorough search, very few related studies were found on its adsorption capacity towards environmental pollutants. However, feldspar is estimated to be the greatest rock-forming mineral in the earth crust (Branlund and Hofmeister, 2012; Horai, 1971; Janecke and Evans, 1988); hence, it is a potentially low-cost industrial material that can be employed in environmental, economic processes (Yazdani et al., 2012). They can also undergo thermal treatment operations to improve its sorption capacity (Petit et al., 2000).

<table>
<thead>
<tr>
<th>Group</th>
<th>Mineral</th>
<th>Molecular formula</th>
<th>Average surface area (m² g⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicates</td>
<td>Feldspars</td>
<td>KAlSi₃O₈</td>
<td>0.8</td>
<td>Hodson (1998)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NaAl₂Si₃O₈</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CaAl₂Si₂O₆</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Micas</td>
<td></td>
<td>KAl₂(Si₂Al)·O₁₀(OH)₂</td>
<td>100</td>
<td>Meier et al. (1994)</td>
</tr>
<tr>
<td>Amphiboles</td>
<td></td>
<td>Na, Ca, Mg, Fe, Al silicate</td>
<td>3.1</td>
<td>Brantley and Mellott (2000)</td>
</tr>
<tr>
<td>Pyroxenes</td>
<td></td>
<td>Ca, Mg, Fe, Al silicate</td>
<td>2.3</td>
<td>Reddy and Claassen (1994)</td>
</tr>
<tr>
<td>Olivine</td>
<td></td>
<td>(MgFe)₁SiO₄</td>
<td>1.5</td>
<td>Brantley and Mellott (2000)</td>
</tr>
<tr>
<td>Hydrous silicate</td>
<td>Kaolinite</td>
<td>Al₂Si₂O₅(OH)₄</td>
<td>13.69</td>
<td>Meier et al. (1994)</td>
</tr>
<tr>
<td>Oxide</td>
<td>Quartz</td>
<td>SiO₂</td>
<td>0.17</td>
<td>Sorwat et al. (2020)</td>
</tr>
<tr>
<td></td>
<td>Aluminum</td>
<td>Al₂O₃</td>
<td>122</td>
<td>Wang et al. (2020a)</td>
</tr>
<tr>
<td></td>
<td>Iron oxides</td>
<td>Fe₂O₃</td>
<td>0.381</td>
<td>Giménez et al. (2007)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Fe₃O₄)₂(Fe₂O₃)₂</td>
<td>10.26</td>
<td>Yan et al. (2020)</td>
</tr>
<tr>
<td></td>
<td>Carbonates</td>
<td>calcite</td>
<td>37.21</td>
<td>Sorwat et al. (2020)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dolomite</td>
<td>0.5</td>
<td>Wang and Zhang et al. (2020)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.7</td>
<td>Yan et al. (2020)</td>
</tr>
</tbody>
</table>
The adsorption isotherms, kinetics, and thermodynamics of the cationic dyes Basic red 18 and Basic Blue 41 on feldspar were investigated, considering both single and binary systems. The optimal adsorbent dosage was 2.5 g L\(^{-1}\), with the dye’s concentration ranging from 12.5 to 50 mg L\(^{-1}\) (Yazdani et al., 2012). The dye uptake capacity increased as pH increased from 2.5 to 8. This behavior is an exciting point because most effluents’ final pH is around 5–8; therefore, no pH adjustment would be necessary (Bozczak and Fernandes, 2017). Their adsorption behavior followed Langmuir for single and extended Langmuir isotherms for binary systems, respectively. The adsorption kinetics was found to conform to pseudo-second-order kinetic for both systems. Meanwhile, the thermodynamic data showed that dye adsorption onto feldspar was spontaneous, endothermic, and physisorption was the dominant mechanism (Yazdani et al., 2012).

Besides organic molecules, the adsorption of potentially harmful ions has also been studied in natural and modified feldspar. Ferric ions, uranium (U(VI)), and arsenic (As(V)) are some examples (Al-心血管，2015; Ding et al., 2014; Yazdani et al., 2016). Natural feldspar was spontaneous, endothermic, and physisorption was the dominant mechanism (Yazdani et al., 2012). The dye uptake capacity increased as pH increased from 2.5 to 8. This behavior is an exciting point because most effluents’ final pH is around 5–8; therefore, no pH adjustment would be necessary (Bozczak and Fernandes, 2017). Their adsorption behavior followed Langmuir for single and extended Langmuir isotherms for binary systems, respectively. The adsorption kinetics was found to conform to pseudo-second-order kinetic for both systems. Meanwhile, the thermodynamic data showed that dye adsorption onto feldspar was spontaneous, endothermic, and physisorption was the dominant mechanism (Yazdani et al., 2012).

### 2.1.2. Micas

Micas are monoclinic pseudohexagonal crystals, similar in chemical composition, with the general molecular formula of \(X_2Y_4Z_8O_{20}(OH, F, F)\) – where \(X\) is K, Na, or Ca, \(Y\) is Al, Mg, or Fe, and \(Z\) is Si or Al but also may include \(Fe^{3+}\) or Ti (Frye, 2006). Some examples are biotite, muscovite, lepidolite, phlogopite, zinnwaldite, and margarite (Deer et al., 2013). This mineral was employed in few studies, mostly for the adsorption of metal ions, surfactants, and pharmaceuticals (Alexandre-Franco et al., 2011; Gier and Johns, 2000; Klapyta et al., 2001; Li et al., 2019b, 2019c; Martín et al., 2018, 2019; Orta et al., 2018; Osuna et al., 2019; Pazos et al., 2017).

### 2.2. Oxides

The oxides include about 40 cationic elements in their composition, such as Si, Ti, Nb, Ta, Mn, Al, Mg, Sn, and Zr combined with oxygen or hydroxyl (Frye, 2006; Marfunin, 1994). The most commonly known and occurring are cuprite (Cu\(_2\)O), corundum (Al\(_2\)O\(_3\)), hematite (Fe\(_2\)O\(_3\)), cassiterite (SnO\(_2\)), magnetite (Fe\(_3\)O\(_4\)), ilmenite (FeTiO\(_3\)), perovskite (CaTiO\(_3\)), brucite (Mg(OH)\(_2\)) and gibbsite (Al(OH)\(_3\)) (Frye, 2006; Marfunin, 1994). Among the above-cited minerals, magnetite, hematite, and ilmenite stand out. Because iron is present in their structure, simultaneous degradation reactions can occur, a process known and well-established as Fenton reactions (Ghernaout et al., 2020). Moreover, the naturally occurring oxide of titanium, TiO\(_2\), is typically obtained from the minerals ilmenite, rutile, and anatase (Lahiri and Jha, 2007). It is widely used as a pigment in paints and personal care products, and its activity as a photocatalyst is well-established (Diebold, 2003; Weir et al., 2012). Still, these light-interacting properties are mostly used to degrade pollutants, not adsorption per se (Shiraishi et al., 2005).

Magnetic properties are of most interest, considering the difficulty of separating solid catalysts from aqueous solutions (Serpone et al., 2010). Therefore, Fe\(_3\)O\(_4\) is the most popular iron oxide: there are about 15 times more studies published on its regard than hematite and ilmenite. Magnetite properties as adsorbent are widely known and accepted (Milonjić et al., 1983; Udovic and Dumesic, 1984), mostly by the adsorption of ions as phosphate, arsenite, and arsenate (Dauo et al., 2007; Yean et al., 2005), but its use for adsorption of organic molecules has been reported only with hybrid materials (Cheng et al., 2012b; Qin et al., 2014; Vieira et al., 2020).

Overall, this class of natural geological materials is interesting for adsorption applications because, in their structure, they have metal atoms electrostatically charged or in different oxidation states, which enhances the attraction of the pollutant to the adsorbent surface and, consequently, increases the total removal efficiency (Khaleel et al., 1999; Velazquez-Jimenez et al., 2015; Wang et al., 2020a). Table 3 is presented a portrait of the most relevant studies on adsorption onto oxides.

### 2.3. Carbonates

In geology and mineralogy, minerals dominated by the carbonate ion, CO\(_3^{2-}\), are designated simply as carbonates, which are incredibly varied and omnipresent in chemically precipitated sedimentary rocks (Lippmann, 1973). The trivial are calcite, dolomite, and siderite (Curtis and Coleman, 1986; Pearce et al., 2013). Calcite, CaCO\(_3\), is the primary constituent of limestone and the main component of mollusk shells and coral skeletons (Lorenz, 1981; Somasundaran and Agar, 1967; Wray and Daniels, 1957). Dolomite, CaMg(CO\(_3\))\(_2\), is used as an ornamental stone, a concrete aggregate, and a source of magnesium oxide (Baker and Kastner, 1981; Sibley and Gregg, 1987; Warren, 2000). Siderite, FeCO\(_3\), is the essential iron ore and has been used for steel production (Matthiesen et al., 2003; Mozley, 1989; Zhu et al., 2020). Moreover, some other popular carbonates, such as sodium carbonate and potassium carbonate, have been used since antiquity for cleaning and preservation, as well as for the manufacture of glass (Freilich et al., 2014; Konkol and Rasmussen, 2015; Krumbine et al., 1991; Wood et al., 1984). Carbonates are widely used in industry, e.g., in iron smelting, as a raw material for Portland cement and lime manufacture, in the composition of ceramic glazes, and more (Al-Shalabi and Sepehrnoori, 2016; Boyjoo et al., 2014; Clements, 2003; Dhani et al., 2013).

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Main feldspar applications in adsorption.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbent</td>
<td>Dosage (g L(^{-1}))</td>
</tr>
<tr>
<td>Natural feldspar</td>
<td>2.5</td>
</tr>
<tr>
<td>Natural feldspar</td>
<td>2.5</td>
</tr>
<tr>
<td>Natural feldspar</td>
<td>0.5</td>
</tr>
<tr>
<td>Natural feldspar</td>
<td>4</td>
</tr>
<tr>
<td>Natural feldspar</td>
<td>100</td>
</tr>
<tr>
<td>Natural feldspar</td>
<td>125</td>
</tr>
</tbody>
</table>

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The removal of phosphate species from solution by adsorption onto natural-calcite was evaluated alongside the effect of pH, phosphate/mineral ratio, and contact time (Karageorgiou et al., 2007). The results indicated that pH plays an important role, and the adsorption process is more efficient in the basic pH region. The orthophosphate removal is almost complete for concentrations as high as 60 mg L$^{-1}$ of phosphate, which corresponds to 0.1 to 1 mM g$^{-1}$ pollutant to adsorbent ratio (Karageorgiou et al., 2007). Tannic acid, a calcite pack (Karageorgiou et al., 2007); L-malic, D-malic, and succinic acid adsorbed tannic acid (Karageorgiou et al., 2007). Moreover, other studies were conducted by chemical reaction. The maximum adsorption capacity of tannic acid increased with initial concentration in the optimal pH 8. Sips isotherm model best fit the Langmuir, Freundlich, or Triple-layer model the competitive As(III)/Cr(VI) was reinvestigated. As and Cr sorption isotherms fit the Langmuir model. Its competitive sorption responded to a sigmoidal Hill model. The maximum uptake for each pollutant was around 60 mg g$^{-1}$ (Hajji et al., 2019). Conversely, by submitting the wasted iron mud to hydrothermal treatment, a magnetic adsorbent removed other metals from smelting wastewater. The model included the size of ferrihydrite's reductive dissolution to recompose the natural siderite, which was then re-oxidized to maghemite. As a result, at the dosage of 12.5 g L$^{-1}$, a removal efficiency around 99% of Cu$^{2+}$, Zn$^{2+}$, Pb$^{2+}$, and Cd$^{2+}$ was attained (Zhu et al., 2018).

Siderite has been applied as a pristine mineral (Erdem and Özerdi, 2005; Haji et al., 2019; Wang and Reardon, 2001), as well as the principal constituent in iron-rich sludge adsorbents (Qu et al., 2020; Sharma et al., 2013b; Zhu et al., 2018, 2019). By using stirred flow-through reactor experiments, siderite (90 m$^2$ g$^{-1}$) adsorption of As(III), Cr(VI), and competitive As(III)/Cr(VI) was reinvestigated. As Cr sorption isothersms fit the Langmuir model. Its competitive sorption responded to a sigmoidal Hill model. The maximum uptake for each pollutant was around 60 mg g$^{-1}$ (Hajji et al., 2019). Conversely, by submitting the wasted iron mud to hydrothermal treatment, a magnetic adsorbent removed other metals from smelting wastewater. The modification acted upon ferrhydrite's reductive dissolution to recompose the natural siderite, which was then re-oxidized to maghemite. As a result, at the dosage of 12.5 g L$^{-1}$, a removal efficiency around 99% of Cu$^{2+}$, Zn$^{2+}$, Pb$^{2+}$, and Cd$^{2+}$ was attained (Zhu et al., 2018).

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Moreover, magnesite, smithsonite, aragonite, and bastnasite have all been applied to the wastewater treatment to some extent. Magnesite was employed in phosphate from municipal effluents (Masindi et al., 2016; Mavhungu et al., 2019) and as an adsorbent for cationic and anionic dyes (Ngulube et al., 2018). Lead (Zhang et al., 2019a), iron (Deng et al., 2017), and 8-hydroxyquinoline onto smithsonite have bastnasite was explored (Millero et al., 2001).
3. Clays

Clays are phyllosilicate minerals with layered structural units, constituted of one or two tetrahedral silica sheets around an octahedral aluminum sheet (Brigatti et al., 2006; Velde, 1995). They present small particle sizes, typically of less than 2 μm, and high specific surface areas, as a result of their complex porous structures, which facilitates physical and chemical interactions with dissolved species (Bertagnolli et al., 2011; Djomouge and Njopwouo, 2013; Luo and Daniel, 2003). Moreover, some specific factors determine how the adsorption process will occur onto clay minerals. Besides some of its specific properties, the contact time, clay dosage, and pH, play important roles (Otonuala and Ololade, 2020).

Two essential topics on clay adsorption are its cation exchange capacity (Chapman, 2016) and specific surface area (Carter et al., 2018), because in this case, it is understood that they rule its adsorption capability (Dabrowski, 2001). Both properties are related: while cation exchange capacity translates as the total negative charge (Ammann et al., 2005; Lipson and Stortzky, 1983), the specific surface area is the total surface area with available adsorption sites (Kuila and Prasad, 2013; Macht et al., 2011). The larger the surface area, the greater is the cation exchange capacity (Ersahin et al., 2006; Kuila and Prasad, 2013). Besides, it is attractive to the point that variations found in these properties determinations can be attributed to the fact that some clay minerals have only external layers, such as kaolinite and illite, and others have internal and external layers, such as smectites and attapulgite (Hepper et al., 2006).

Another critical variable in adsorption studies is the contact time, which is how long the adsorbent needs to be in the same medium as the pollutant to achieve maximal removal efficiency (McKay, 1982; Sülesiştah Hartami and Tuheteru, 2020; Yang et al., 2009). The adsorption rate of clays tends to increase with the increased contact time, remaining constant until equilibrium is reached (Yin and Zhu, 2016). Moreover, the contact time varies according to clay dosage (Otonuala and Ololade, 2020). There are no specific guidelines determining clay dosage for wastewater treatment; therefore, previous studies and literature search is needed before application. It has been discussed that a small dosage, around 1 to 3 g L⁻¹, of clay minerals, is enough to adsorb reasonable concentration pollutants from contaminated effluents (Kausar et al., 2018; Lazaratou et al., 2020).

Moreover, observations on the influence of the pH of the system demonstrated that, as pH increases, there is an immediate increase in the rate of adsorption (Åkpmamn and Dawodu, 2016; Chen et al., 2011b; Es-Sahbany et al., 2019; Otonuala and Ololade, 2020; Potgieter et al., 2006). However, it must be emphasized that pH also regulates other processes, such as the chemical equilibrium of the target pollutant molecule with the clay (Beattie, 1956; Hackling and Garnett, 1985). Therefore, even though generally basic pH enhances the clays’ adsorption capacity, this is not a rule (Çiyöfı et al., 2020; Hamza et al., 2020; Maleki and Karimi-Jashni, 2020; Obayomi et al., 2020; Romdhane et al., 2020).

3.1. Kaolinite

One of the most currently applied geological materials for adsorption belongs to the hydrous silicates class: kaolinite (Velde, 1995). Its general molecular formula is Al₂Si₂O₅(OH)₄. Kaolinite is a layered silicate mineral, with one tetrahedral sheet of silica linked through oxygen atoms to one octahedral sheet of alumina octahedral (Essington and Stewart, 2015; Kuila and Prasad, 2013; Sadri et al., 2018).

Ghorbanzadeh et al. (2015) reported on the removal of arsenate and arsenite from aqueous solution. Kaolinite surface area was determined as 10.1 m² g⁻¹. Adsorption isotherms were conducted with initial arsenic concentrations of 0.05, 0.06, 0.1, 0.15, and 0.2 mmol L⁻¹, with 27 g L⁻¹ of the adsorbent. The equilibrium was studied for 24 h. Optimal adsorption pH for As⁵⁺ was found to be around 5 (99.9%), with the efficiency rates decreasing as pH increased. For As³⁺ adsorption, at pH 7, the maximum adsorption capacity reached was 380 μg g⁻¹. Both As (V) and As(III) adsorption isotherms fit the Langmuir model (R² = 0.968 and 0.979, respectively), and qmax values of 0.203 and 0.241 mg g⁻¹ (Ghorbanzadeh et al., 2015). Mohapatra et al. (2007) observed similar responses while studying pH for As(V) adsorption onto kaolinite, and maximum adsorption was also achieved at pH 5.0. Equilibrium was reached within 3 h, and qmax value of 0.86 mg g⁻¹ was found by fitting the Langmuir equation to the adsorption isotherms (R² = 0.98). The authors also observed an adverse effect of an increase in temperature on As(V) adsorption; therefore, interactions are exothermic. The electrokinetic behavior of kaolinite was modified in the pollutant’s presence, which can be concluded as inner-sphere surface complexation and strong specific ion adsorption (Mohapatra et al., 2007).

Chantawong et al. (2003) investigated the adsorption of Cd²⁺, Cr³⁺, Cu²⁺, Ni²⁺, Pb²⁺, and Zn²⁺ by thai kaolinite. Except for Ni²⁺, adsorption increased as pH increased. Isotherms fit the Freundlich model, with R² ranging from 0.93 to 0.99, for each ion. Adsorption followed the order: Cr > Zn > Cu ≈ Cd ≈ Pb > Ni, with maximum removal capacity of 1.13 × 10⁻³, 1.07 × 10⁻³, 4.20 × 10⁻⁴, 6.22 × 10⁻⁴, 7.73 × 10⁻⁴, and 5.11 × 10⁻⁵ mmol g⁻¹, respectively (Chantawong et al., 2003). Liu et al. (2016a) focused on a wide range of individual Pb, Zn, and Cu concentrations, varying from 0.1 to 100 mM, at different pH conditions. Again, the best results were obtained in basic pH. Also, the isotherms fit the Freundlich and Langmuir models for kaolinite. The maximum removal capacity for Cu was 1.82 mg g⁻¹, for Zn was 6.19 mg g⁻¹, and Pb was 14.47 mg g⁻¹ (Liu et al., 2015). Also, Coles and Yong (2002) conducted batch equilibrium tests on kaolinite suspensions adjusted to pH 4 and pH 6, aiming to remove PbCl₂ and CdCl₂. Better results were obtained at pH 6. Interestingly, by studying the equilibrium curves of both metal retention versus suspension pH, combined with an analysis of the speciation of the metals, it was evidenced that both divalent (Pb²⁺ and Cd²⁺) and monovalent (PbCl⁺ and CdCl⁺) species were adsorbed (Coles and Yong, 2002).

Ghosh and Bhattacharyya (2002) employed raw kaolinite obtained from a local deposit focusing on methylene blue adsorption. The raw adsorbent showed considerable adsorption, superior to the calcinated version of the material. Experiments were conducted considering contact time of 3 h, pH 10, initial methylene blue concentration of 15 mg L⁻¹, and adsorbent dosage of 0.8 g L⁻¹. In this condition, raw kaolinite uptake reached 13.99 mg g⁻¹, and the isotherms fit well the Langmuir model (Ghosh and Bhattacharyya, 2002). Doğan et al. (2009) addressed Maxilon Yellow 4GL and Maxilon Red GRL dyes kinetic adsorption. The equilibrium was set after 150 min. The adsorption kinetics followed pseudo-second-order for both dyes, with k values up to 107.87 × 10⁻⁴ g mol⁻¹ min⁻¹ for Maxilon Yellow and 72.09 × 10⁻⁴ g mol⁻¹ min⁻¹ for Maxilon Red (Doğan et al., 2009). Despite kaolinite usual small surface area, several studies have been published on its efficiency towards dyes adsorption: aniline blue (Unuabonah et al., 2008a), basic fuchsin (Khan et al., 2015), crystal violet (Çiftçi et al., 2017; Dobrogowska et al., 1991; Khan et al., 2015; Sarma et al., 2019; Yariv et al., 1991), solophenyl yellow GFL (Kamel et al., 1991), solophenyl red 6BL (Kamel et al., 1991), diphenyl pink BF (Kamel et al., 1991), 9-aminoacridine (Harris et al., 2001, 2006a–c), 3,6-diaminoacridine (Harris et al., 2001, 2006a, 2006b, 2006c), azeure A (Harris et al., 2001, 2006a, 2006b, 2006c), safranin O (Harris et al., 2001, 2006a, 2006b, 2006c), rhodamine B (Batista et al., 2014; Khan et al., 2012; Rosales et al., 2018), methylene blue (Ghosh and Bhattacharyya, 2002; Greathouse et al., 2015; Hang and Brindley, 1970; Mukherjee et al., 2015), malachite green (Castellini et al., 2008; Sarma et al., 2019), reactive red 120 (Abidi et al., 2017), congo red (Bhattacharyya et al., 2015; Shaban et al., 2018), and many others.

Moving on further than dyes, one study investigated their adsorption alongside to other 23 organic pollutants, such as acridine, 8-amino quinoline, quinoline, and pyridine (Harris et al., 2001). Organic pollutants are of great concern due to their ubiquitous occurrence,
even in remote ecosystems (Lu and Astruc, 2020; Sun et al., 2020; Zhang et al., 2003). Among them, pesticides are of great concern (Bache et al., 1996; Sharma et al., 2020). Clausen et al. (2001) investigated atrazine (6-chloro-N2-ethyl-N4-isopropyl-1,3,5-triazine-2-diamine), isoproturon ([3-(4-isopropyl phenyl)-(1,1-dimethylurea)]), mecoprop ([RS]-2-(4-chloro-2-methyl phenoxy)propiocnic acid), 2,4-D (2,4-dichloro-phenoxy-acetic acid), and bentazone (3-isopropyl-1H-2,1,3-benzothiadiazin-4-(3H)-one 2,2-dioxide) adsorption towards kaolin. Specific surface area and mineral surface charge proved important factors: detectable adsorption of anionic pesticides was only measured when positive sites were present on the mineral surface. When an electrolyte was added, detectable adsorption of mecoprop and 2,4-D was also measured on kaolinite, probably due to the formation of surface complexes. However, the adsorption of the uncharged pesticides, atrazine, and isoproturon, did not suffer interferences. Despite their efforts, pesticides adsorb weakly to pure kaolin in aqueous solutions (Clausen et al., 2001).

3.2. Montmorillonite

Montmorillonite is a clay mineral, whose molecular formula can be described as Na<sup>+</sup>(Na, Ca<sub>3.33</sub>)(Al, Mg)<sub>2</sub>(Si<sub>4</sub>O<sub>10</sub>)(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>n</sub>, with substantial isomorphous substitution. On behalf of adsorption, this mineral presents peculiar characteristics, such as fast cationic exchange and interlaying swelling (Bhattacharyya and Gupta, 2008). Cations such as Na<sup>+</sup> and Ca<sup>2+</sup> tend to form surface complexes; therefore, they are easily exchanged with soluble ions (Dähn et al., 2002). In its structure, interlayer swelling occurs in aqueous media. This process depends on valences and the atomic radius of the exchangeable cations (Hennig et al., 2002), which leads to additional inner-sphere complexation and adsorption (Elzinga and Sparks, 1999). Although there is a conflict in the literature about whether bentonites are a sub-group of montmorillonites or simply the same thing, this review article will approach both subjects together. When it comes to writing reports on different knowledge areas, there is a deficiency sometimes in standardizing terms, which can result in less visibility for several relevant and well-performed studies, just because the authors know a specific material by a name other than the usual one, but that still is scientifically accepted (Malamas and Katsou, 2013).

Several studies report on montmorillonite adsorption towards metals (Álvarez-Ayuso and García-Sánchez, 2003; Andini et al., 2006; Angove et al., 1998; Bhattacharyya and Gupta, 2007a; Donat et al., 2005; Gupta et al., 2003; Gupta and Bhattacharyya, 2006; Jain and Sharma, 2002; Jobstmann and Singh, 2001; Kandah, 2004; Karapinar and Donat, 2009; Liu and Jiang, 2010; López et al., 1998; Mathiagalan and Viraraghavan, 2002; Putro et al., 2017; Ullman et al., 2003; Wasewar et al., 2010). Gupta and Bhattacharyya (2006) reported the adsorption of Cd<sup>2+</sup> onto raw and modified montmorillonite. The removal efficiency reached 94.5% for raw montmorillonite, compared to 64.8%, 81.0%, and 99.3% for ZrO/montmorillonite, tetraethylammonium/montmorillonite and acid-activated montmorillonite, respectively. This removal efficiency can be translated as an adsorption capacity of 32.7 mg g<sup>−1</sup>. Again, the adsorption of Co<sup>2+</sup> was only slightly superior onto acid activated montmorillonite in comparison to the raw material, reaching 29.7 and 28.6 mg g<sup>−1</sup> of adsorption capacity (Bhattacharyya and Gupta, 2007b). Considering the time, effort, and cost, modified montmorillonite is not offset by raw montmorillonite efficiency (Gupta and Bhattacharyya, 2006). In Table 4, several studies on montmorillonite adsorption towards metals are summarized.

The adsorption of several dyes onto both natural and modified montmorillonites has been studied over the years, such as methylene blue (Benhouria et al., 2015; Feddal et al., 2014; Hong et al., 2009; Kahr and Madsen, 1995; Wei et al., 2018; Zhang et al., 2019a), methyl violet (Fabryanty et al., 2017; Guiza et al., 2012; Puri and Sumana, 2012; Zhang et al., 2019b), methyl orange (Chen et al., 2011b), naphtol green (Zhang et al., 2019c), direct red 23 (Mahvi and Dalvand, 2020), diamond fast brown KE (El-Defrawy et al., 2019), reactive red 120 (Mahmoodi et al., 2019; Tabak et al., 2010) and acid fuchsin (Cao et al., 2017; Gong et al., 2018). Data on dye adsorption can be summarized in results obtained by Fil et al. (2014), who studied Red Violet 3RN color removal in simulated wastewater using montmorillonite clay. They concluded that the process efficiency rate increased with increasing pH, temperature, dye concentration, and agitation speed but decreased with increased ionic strength and adsorbent dosage. Langmuir model better represented the equilibrium data. Also, kinetics fit the pseudo-second-order model (Fil et al., 2014).

Chang et al. (2015) investigated tetracycline adsorption, an antibiotic onto high-charge Ca-montmorillonite and low-charge Na-montmorillonite. The adsorption data obeyed Langmuir isotherm, with maximum pollutant adsorption of 468 and 404 mg g<sup>−1</sup> on Ca and Na-montmorillonites, respectively. The adsorption was endothermic, suggesting strong physical adsorption, which is expected for organic molecules adsorbers with high surface area and a small pore size ratio (Chang et al., 2015). Also, concerning natural montmorillonite, Thiebault and Boussafir (2019) explored the adsorption of the psychoactive drugs codeine, diazepam, and oxazepam onto Na-montmorillonite. At pH = 7.5, codeine cation exchange resulted in the highest amount adsorbed among the tests (q<sub>max</sub> = 0.381 mmol g<sup>−1</sup>). Therefore, their significant contribution was proving that variation in pH strongly impacts the pollutant and sorbent affinity (Thiebault and Boussafir, 2019). Also, studies report atenolol (Chang et al., 2019) and nortriptyline (Sadri et al., 2018) in raw Ca-montmorillonite, while 4-aceaminophenol (Chu et al., 2019), amoxicillin, and diclofenac (Khan et al., 2020) removal were reported for modified montmorillonite.

At last, pesticides adsorption onto montmorillonite was reported and verified as well, demonstrating that it acts as a natural scavenger of pesticides due to the abundant availability, large specific surface area, and high adsorptive and ion exchange properties (Bhardwaj et al., 2014; Cabrera et al., 2008; Kovacevic et al., 2011; Ozcan et al., 2012; Park et al., 2014; Suciu and Capri, 2009). Carbaryl, aldrin, malathion, 2,4-D, and dimethoate adsorption capacity onto raw montmorillonite were 3.70, 14.96, 7.95 mg g<sup>−1</sup> and 0.90, 0.96 μg kg<sup>−1</sup>, respectively (Al Kuisi, 2002; Chen et al., 2009; Ozcan et al., 2012; Pal and Vanjara, 2001; Park et al., 2019); 8-quinoline carboxylic acid adsorption capacity onto Na<sup>+</sup>, acidic- and organo-montmorillonite was 65.4, 67.6 and 75.9 mg g<sup>−1</sup> (Mekhloufi et al., 2013); Na- and Ca-montmorillonite adsorption capacity towards phosmet reached 1.04 × 10<sup>−3</sup> and 1.648 × 10<sup>−3</sup> mg g<sup>−1</sup> (Sánchez Camazano and Sánchez Martín, 1983), while K-, Na- and Ca-montmorillonite towards phosdrin reached 1.882 × 10<sup>−3</sup>, 3.548 × 10<sup>−3</sup> and 2.150 × 10<sup>−3</sup> mg g<sup>−1</sup> (Sánchez Camazano and Sánchez Martín, 1983).

3.3. Illite

The term illite was proposed by (Grím et al., 1997) as a general term, not as a specific clay mineral name, to designate mica-like clay minerals of Illinois. Since then, the illite definition was progressively improved (Meunier and Velde, 2010). Thus, Illite is understood as a group of closely related non-expanding phyllosilicate. Its chemical formula is given as [K<sub>2</sub>Na<sub>2</sub>H<sub>2</sub>Al<sub>2</sub>Mg<sub>3</sub>Si<sub>10</sub>O<sub>20</sub>(OH)<sub>2</sub>·2H<sub>2</sub>O], with considerable ion substitution (Meunier et al., 2004; Meunier and Velde, 2010). In addition to the surface hydrogen bonds, illite cleavage releases potassium ions, which results in the surface of high-density ionic bonds. Thus, cleaved illite surfaces are moderately hydrophilic (Park et al., 2019; Zhang et al., 2018).

Picolram, a herbicide adsorbed on illite, was studied under pH variation. Batch tests were performed with an adsorbent dosage of 16 g L<sup>−1</sup> and pollutant concentrations ranging from 0.2 to 5.0 mmol L<sup>−1</sup>. The adsorption isotherms well-fit both Langmuir and Freundlich models, with q<sub>max</sub> values of 14 ± 2, 12 ± 3, and 11 ± 1 mmol g<sup>−1</sup> at pH 3, 5, and 7, respectively (Marco-Brown et al., 2019). The picolram molecule interactions with illite surfaces exhibited anionic profile adsorption, with a decrease in adsorption when the pH increases, which
is very interesting, considering that the illite point of zero-charge is around 2.8 (Marco-Brown et al., 2019; Park et al., 2019). Tetracycline is a semi-synthetic antibiotic commonly detected in soils due to animal-produced slurry applications as fertilizer (Agersø et al., 2006). Chang et al. (2012) reported illite adsorption capacity towards tetracycline adsorption at 32 mg g\(^{-1}\), at pH 5–6. Adsorption equilibrium data obeyed the Freundlich isotherm model. Therefore, considering the \(q_{\text{max}}\) value reported in this study, illite may act as an essential environmental material on fate, routes, and transportation of antibiotics in soils (Chang et al., 2012). Although the studies discussed above, as well as the study carried out by Fil et al., 2016 regarding methyl violet dye, point to non-linear adsorption models, it has also been reported that for larger molecules, such as microcystin-LR, the application of linear isotherms might be proven more suitable (Liu et al., 2019).

Ionic adsorption onto illite has been inspected as well. For example, uranium sorption characteristics tend to be dominated by chemical ion-exchange, an endothermic and spontaneous process that increases entropy (Liao et al., 2020). Fernandes and Baeyens (2019) modeled lead adsorption considering two sites protolysis non-electrostatic surface complexion and cation exchange, and reported maximal uptake values 4.0 \(\times 10^{-2}\) to 2.0 \(\times 10^{-3}\) mol kg\(^{-1}\) (Fernandes and Baeyens, 2019). Moreover, investigations on copper and nickel adsorption on illite/smectite systems were reported by Du et al., 1997, 2019. Moreover, investigations on copper and nickel adsorption on illite/smectite systems were reported by Du et al., 1997, 2019. In addition to illite ionic adsorption, thallium and strontium adsorption have been investigated as well, but will not be explored in this review for our scope is environmental remediation, and such metals are not yet considered environmental relevant contaminants (Galamboš et al., 2013; Wick et al., 2018; Zhang et al., 2016).

### 4. Zeolites

Zeolites of natural origin are formed due to volcanic activity, either by water or deposition of volcanic dust in saline deposits (Delkash et al., 2015; Malamis and Katsou, 2013). They are complex, microporous inorganic polymers formed by an infinitely extensive three-dimensional structure of silicon and aluminum tetrahedrons linked together by sharing oxygen (Hong et al., 2019; Niu et al., 2020). The most commonly found natural types are mordenite, chabazite, and clinoptilolite (Dehghan and Anbia, 2017; Flanigen, 1991). The zeolite crystal structure's inner cavities are generally in the range of 0.5–1.2 nm, a factor determined by formation route and different Si/Al ratios. This Si/Al ratio acts directly on the thermal resistance of zeolites and cation exchange properties: low-silica zeolites with Si/Al ratio below 2 have excellent ion exchange capacity; however, the higher the aluminum content, the less stable tends to be the zeolite (Jiang et al., 2018; Wen et al., 2018). Unlike geopolymers, zeolites, despite having the same constitution, are highly crystalline materials with higher thermal and chemical resistance. Another difference is that zeolites need a higher amount of water present in their formation reaction medium. The synthesis reactions take longer than that of the geopolymers, much due to the crystallization stage (Fernández-Jiménez et al., 2005).

Jafari-zare and Habibi-yangjeh (2010) studied the adsorption of rhodamine B and methylene blue in both single and binary component systems, using natural zeolite formed predominantly by clinoptilolite. The experiments were carried out at pH 12, with an adsorbent dosage of 0.2 g L\(^{-1}\) and initial dye concentration of 6 \(\times 10^{-6}\) mol L\(^{-1}\). Results showed that the maximum capacity of clinoptilolite for the dyes methylene blue and rhodamine B was 7.95 \(\times 10^{-5}\) and 1.26 \(\times 10^{-5}\), respectively, with both isotherms being better described by the Langmuir model, with determination coefficients (\(R^2\)) greater than 0.991. A reduction in the adsorption capacity of both dyes was verified in the binary system due to the competition of the molecules for the active sites available in the adsorbent; thus, the \(q_{\text{max}}\) value for rhodamine B was 2.2 \(\times 10^{-5}\) mol g\(^{-1}\), while for methylene blue was 7.44 \(\times 10^{-5}\) mol g\(^{-1}\), fitted again by Langmuir model (\(R^2\) of 0.984 for the rhodamine B and 0.997 for the methylene blue) (Jafari-zare and Habibi-yangjeh, 2010).

Natural zeolites can also be used as adsorbents to remove pharmaceuticals in an aqueous solution. de Sousa et al. (2018) removed azithromycin, ofloxacin, and sulfamethoxazole using faujasite zeolites

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Different montmorillonites adsorption response on metal ions removal efficiency.</th>
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<tbody>
<tr>
<td>Type</td>
<td>Dosage</td>
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<tr>
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<td>--------</td>
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<tr>
<td>Acid-activated</td>
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<td>2</td>
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<td>Illite system</td>
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<tr>
<td>K10</td>
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<td></td>
<td>1</td>
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<td></td>
<td>2</td>
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<tr>
<td></td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Tetrabutylammonium</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td>ZrO</td>
<td>2</td>
</tr>
</tbody>
</table>
with different Si/Al ratios. The zeolite FAU-1 had a Si/Al ratio of 30 and a surface area of 914 m$^2$ g$^{-1}$ while the FAU-2 had a Si/Al ratio of 82 and a surface area of 899 m$^2$ g$^{-1}$. The adsorption tests were carried out with initial concentrations of antibiotics ranging from 10 to 400 µg L$^{-1}$, for 360 min, with a solution volume of 30 mL. The results showed that the FAU-1 zeolite, with greater surface area, showed greater adsorption capacity for both antibiotics, within the range of 8.5 mg g$^{-1}$ for azithromycin to 31.32 mg g$^{-1}$ for ofloxacin. A study simulating an effluent containing the three antibiotics, under conditions of pH 7.25, an adsorbent dosage of 10 mg L$^{-1}$, a contact time of 2 h, initial concentration of azithromycin, ofloxacin, and sulfamethoxazole of 391, 378, and 78.6 ng L$^{-1}$, respectively, showed that zeolite FAU-1 responds well against the treatment of effluents contaminated with pharmaceuticals, removing up to 60% of azithromycin, 76% of ofloxacin, and 44% of sulfamethoxazole (de Sousa et al., 2018).

Due to zeolite's tetrahedral aluminum structure, a negative surface charge is created in the mineral network structure. The presence of cations can counterbalance this charge, usually, Ca$^{2+}$, Na$^+$, and K$^+$, located in the cavities; therefore, these cations are exchangeable with other cations, including environmental pollutant metals ions (Malamis and Katsou, 2013; Sprynskyy et al., 2006). For further understanding, the ions, including environmental pollutant metals ions (Malamis and Katsou, 2013; Sprynskyy et al., 2006), for metal ions removal up to 60% of azithromycin, 76% of ofloxacin, and 44% of sulfamethoxazole (de Sousa et al., 2018).

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5. Geopolymers

Geopolymers are amorphous or semi-crystalline materials formed from polymerization reactions between geological originated materials containing aluminum and silicon, such as clays and fly ash, and an activating agent, usually strong bases as sodium or potassium hydroxide (Alouani et al., 2018; Bagci et al., 2017). Initially, geopolymers were used as additives to Portland cement because they improved their mechanical properties and durability since geopolymers are highly resistant to acid attacks and are resistant to frost/defrost cycles and fire-resistant (Ati et al., 2015; Komnitas, 2011).

The large OH$^{-}$ ion concentration in the reaction medium of geopolymer preparation is responsible for the amorphous three-dimensional network's dissolution, commonly found in the starting materials (Khale and Chaudhary, 2007). In more detail, the activating agent breakdown the solid aluminosilicate by repulsion caused by the strong base cations (Na$^+$ or K$^+$). In monomers, Al is tetrahedrally coordinated, and polycondensation reactions follow, forming a network composed of SiO$_4$ and AlO$_4$ tetrahedrons linked together by oxygen atoms. In this network, the alkali agent cation acts as a charge compensator in the geopolymer structure, enhancing adsorption possibilities (Duxson et al., 2007; Rahier et al., 2007). Studies involving the use of geopolymers as adsorbents for environmental remediation purposes, despite recent, are widely disseminated in literature, as presented in Table 6, and mainly focus on the removal of dyes molecules of aqueous solutions (Acisili et al., 2020; Alouani et al., 2018; Barbosa et al., 2018; Hua et al., 2020; Li et al., 2006; Rossatto et al., 2020; Schadeck Netto et al., 2019; Syal et al., 2018) and towards metal ions (Al-Zboon et al., 2011; Chen et al., 2019; Cheng et al., 2012a; Kara et al., 2017; Liu et al., 2016c; Naghsh and Shams, 2017).

Barbosa et al. (2018) prepared a geopolymer using calcined kaolinite and rice husk ash as precursor materials and tested it versus methyl violet dye adsorption from aqueous solutions. The 62 m$^2$ g$^{-1}$ surface area as-synthesized geopolymer showed a $q_{\text{max}}$ capacity of 277 mg g$^{-1}$ at pH 4.5, at a temperature of 328 K, and an adsorbent dosage of 1.5 g L$^{-1}$. Isotherms were better described by the Sips model, with $R^2$ of 0.995, 0.989, 0.993, and 0.996 for the respective temperatures of 298, 308, 318, and 328 K (Barbosa et al., 2018). The endothermic character, which guarantees an improvement in the adsorption capacity by greater exposure of the geopolymer's active sites, was also reported by Alouani et al. (2018). They synthesized a geopolymer from fly ash from a thermoelectric plant for the adsorption of crystal violet dye. After 120 min, pH 5, and adsorbent dosage of 1 g L$^{-1}$, the maximum adsorption capacity of 37 mg g$^{-1}$ was found, with the Langmuir model best describing the adsorption isotherms, with $R^2 = 0.999$, much higher.
if compared to the fit of Freundlich ($R^2 = 0.694$), Temkin ($R^2 = 0.866$) and Dubinin-Radushkevich ($R^2 = 0.555$) models (Alouani et al., 2018).

The addition and impregnation of magnetic agents, such as magnetite or zero-valent iron, was presented as a viable and innovative alternative to facilitate the separation of the adsorbent from the aqueous medium (Schadeck Netto et al., 2019; Hua et al., 2020). Rossatto et al. (2013) native to facilitate the separation of the adsorbent from the aqueous medium. The addition and impregnation of magnetic agents, such as magnetite or zero-valent iron, was presented as a viable and innovative alternative to facilitate the separation of the adsorbent from the aqueous medium (Schadeck Netto et al., 2019; Hua et al., 2020). Rossatto et al. (2013) native to facilitate the separation of the adsorbent from the aqueous medium.

Table 6

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorbate</th>
<th>Surface area ($m^2 g^{-1}$)</th>
<th>$q_{max}$ ($mg g^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash</td>
<td>Methylene blue</td>
<td>-</td>
<td>37.04</td>
<td>Alouani et al., 2018</td>
</tr>
<tr>
<td></td>
<td>Pb^{2+}</td>
<td>20.48</td>
<td>118.6</td>
<td>Liu, Huang, et al., 2016</td>
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<tr>
<td></td>
<td>Cd^{2+}</td>
<td>130.45</td>
<td>26.246</td>
<td>Vazquez et al., 2015</td>
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<tr>
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<td>Cs^{+}</td>
<td>114.16</td>
<td>15.24</td>
<td>Lee et al., 2016</td>
</tr>
<tr>
<td>Linz Donawitz converted slag</td>
<td>Ni^{2+}</td>
<td>30.84</td>
<td>85.29</td>
<td>Barbosa et al., 2018</td>
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<td>Mesoporous</td>
<td>Methyl violet</td>
<td>62</td>
<td>276.9</td>
<td>Fumba et al., 2014</td>
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<td>Metakaolin</td>
<td>Methyl Orange</td>
<td>35.66</td>
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<td>NH_{4}^{+}</td>
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<td>21.07</td>
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<td>Cd^{2+}</td>
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<td>75.74</td>
<td>Cheng et al., 2014</td>
</tr>
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<td>Cu^{2+}</td>
<td>39.24</td>
<td>69.23</td>
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<td>Mn^{2+}</td>
<td>39.24</td>
<td>72.34</td>
<td>Cheng et al., 2014</td>
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<tr>
<td>Metakaolin spheres</td>
<td>Cu^{2+}</td>
<td>53.95</td>
<td>52.63</td>
<td>Singhal et al., 2017</td>
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<tr>
<td></td>
<td>Pb^{2+}</td>
<td>100.99</td>
<td>629.21</td>
<td>Singhal et al., 2017</td>
</tr>
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<td>Mn-CuO/Graphene bottom ash</td>
<td>Direct sky blue</td>
<td>18.45</td>
<td>0.497</td>
<td>Singh et al., 2017</td>
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<td>Modified metakaolin</td>
<td>Cu^{2+}</td>
<td>216</td>
<td>40</td>
<td>Singh et al., 2017</td>
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</table>

6. Modified materials and composites

This final section presents an overview of the most relevant topics on modified geological originated materials. This straightforward approach was chosen to illuminate future perspectives while still focusing on natural and raw forms of application. Nevertheless, there are many ways of modifying geological originated materials aspiring to increase in adsorption capacity compared to the raw mineral.

Although in several studies previously discussed, the $q_{max}$ values reported were adequate for untreated materials, many other comparative studies have shown that modifications, such as metal impregnation, or treatments, such as thermal or acid-base activation, can critically enhance adsorption capacity (Bhatcharyya et al., 2015; Bhatcharyya and Gupta, 2008; Bhatcharyya and Sen Gupta, 2009; Carvalho et al., 2008; Kausar et al., 2018; Martín et al., 2019; Obayomi et al., 2020; Park et al., 2014; Sen Gupta and Bhatcharyya, 2014; Singhal et al., 2017; Suci and Capri, 2009; Unuabonah et al., 2008a,b; Wu et al., 2011). Even simple pre-treatments can extract soluble organic compounds and enhance chelating efficiency (Gaballah et al., 1997). Modifications comprise various kinds of modifying agents: bases, such as sodium hydroxide, calcium hydroxide, and sodium carbonate; mineral and organic acid solutions, such as hydrochloric acid, nitric acid, sulfuric acid, tartaric acid, citric acid, and thioglycolic acid, organic compounds, such as ethylenediamine, formaldehyde, epichlorhydrin, and methanol, and even oxidizing agents, such as hydrogen peroxide (Wan Ngah and Hanafiah, 2008).

6.1. Metal ions

Aiming U(VI) adsorption, Li et al. (2014) prepared thermally activated sodium by calcinating micron Na-feldspar at 450 °C for 45 min, which resulted in a material with a larger specific surface area and larger porosity than the original. The prepared material presented maximum adsorption capacity of 200 mg L$^{-1}$ of U$^{6+}$, the equivalent to 95.49%, at pH 5.0, 318 K, and contact time of 600 min. The relationship between $q_{max}$ and equilibrium concentration, $Ce$, was well described by the Freundlich model (Li et al., 2014). Ahmad and Mirza (2017) synthesized a novel ecofriendly alginiate/Au/mica bio nanocomposite with remarkable environmental remediation capacity of Pb$^{2+}$ and Cu$^{2+}$ in single and binary system. The biocomposites data best fit the Freundlich isotherm model for Pb$^{2+}$, whereas for Cu$^{2+}$ Langmuir isotherm model was more suitable, both single and binary systems, with a maximum adsorption capacity of 224.97 mg g$^{-1}$ and 169.817 mg g$^{-1}$, respectively. Adsorption process was found to be endothermic and spontaneous, thus, the nanocomposite can be applied successfully to industrial wastewaters.

Hematite and ilmenite modified composites have been studied and proposed by several authors (Chen et al., 2017; Kang et al., 2018; Lee et al., 2013a; Ma et al., 2018; Sengupta et al., 2017; Shu et al., 2019; Waanders et al., 2016; Wang et al., 2019a; Xu et al., 2017, 2018; Yousef, 2017). Sengupta et al. (2017) prepared a mesoporous composite consisting of hematite micro sheets modified and decorated with tetragonal zirconia nanocrystallites, useful for adsorbing cationic pollutants from water, by a simple hydrothermal method. It exhibited improved adsorption behavior of various metal ions, with about 99% removal efficiency reached for Cu$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$ at an initial concentration ranging from 5 to 20 mg L$^{-1}$, in comparison to unmodified zirconia and hematite. Wang et al., 2019b synthesized using ilmenite...
and NaOH as starting materials a nanosized titanate composite by the solid-state route. After calcination at 900 °C, the final molecular formula of the composite was reached: Na$_{0.79}$−$\nu_{0.08}$Ti$_{0.07}$−$\nu_{0.08}$Mg$_{0.07}$−$\nu_{0.08}$Mg$_{0.07}$Mg$_{0.07}$. The adsorption of Cu$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$ ions fit pseudo-second-order adsorption kinetics and the Langmuir adsorption model. At 20 °C, the maximum adsorption capacities of the as-synthesized nanocomposite for Cu$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$ were 13.8, 8.8, and 20.3 mg g$^{-1}$, respectively. The thermodynamic parameters also revealed that these ions’ adsorption was spontaneous and endothermic (Wang et al., 2019b). Interestingly, on the contrary to hematite and ilmenite, magnetite is usually used to cover other adsorbents to increase their magnetization purposes, as by Mahdavian and Mirrahimi (2010). They proposed anchoring polyacrylic acid on superparamagnetic magnetite nanoparticles for the adsorption of Cu, Pb, Cd, Cr, and Ni ions, and even Pt (Abou-El-Sherbini and Hassaniel, 2010; Begg et al., 2013; Bhattacharyya and Sen Gupta, 2009; Cruz-Guzmán et al., 2006; Goncharuk et al., 2010; Karamanis and Assimakopoulos, 2007; Liu et al., 2016a; Ma et al., 2015; Na et al., 2010; Oubagaranadin et al., 2010; Park et al., 2012; Sen Gupta and Bhattacharyya, 2009; Soltermann et al., 2013; Vinuth et al., 2015; Xu et al., 2008; Yu et al., 2008, 2009; Pereira et al., 2013). Organically modified montmorillonite clay was used to remove Cu$^{2+}$, $q_{\text{max}}$ = 62.5 μg g$^{-1}$ (Abou-El-Sherbini and Hassaniel, 2010). Montmorillonites modified with natural organic cations were synthesized and tested for the adsorption of Pb$^{2+}$ and Hg$^{2+}$ by Cruz-Guzmán et al. (2006). Carbon modified aluminum-pillared montmorillonite has shown good uptake of Cd$^{2+}$ from an aqueous system, $q_{\text{max}}$ = 161.75 g L$^{-1}$ (Yu et al., 2008). Al-13 pillared montmorillonites were also prepared with different Al to clay ratios to remove Cd$^{2+}$ and PO$_4^{3-}$ from aqueous solution (Ma et al., 2015). Aluminum-pillared-layered montmorillonites also proved their potential as a sorbent in removing Cu$^{2+}$ and Cr$^{3+}$ from aqueous solutions (Karamanis and Assimakopoulos, 2007). Acid-activated montmorillonite-illite was examined for removing Cu$^{2+}$ and Zn$^{2+}$ from industrial wastewater containing Pb$^{2+}$ at low concentration (Oubagaranadin et al., 2010). Calcium tetrabutylammonium bromide modified montmorillonite was prepared and used for the adsorption of Fe$^{3+}$, Co$^{2+}$, and Ni$^{2+}$ from aqueous solution (Bhattacharyya and Sen Gupta, 2009).

The reports on montmorillonites modifications also include thermal (Aytas et al., 2009; Zuo et al., 2017), acid/base chemical treatment (Akporomie and Dawodu, 2016; Shawabkeh et al., 2007), polymeric-aromatic hydrocarbon (Biswas et al., 2016), phosphate (Park et al., 2012), polyethyleneimine (Goncharuk et al., 2010), Ti-pillared (Ma et al., 2010), chitosan-beads (Arvand and Pakseresht, 2013; Liu et al., 2015; Pereira et al., 2013), cystein (El Adra et al., 2017; Stathi et al., 2007), goethite (Olu-Owolabi et al., 2010), alkyl benzene sulfonate (Sandy Maramis et al., 2012), 3-aminopropyltrimethoxysilane (Guerra et al., 2013) and 3,2-aminoethylamino-propyl-trimetoxisilane (Guerra et al., 2013), manganese oxide (Eren and Afsin, 2008), amine and carboxylate (Anirudhan et al., 2012), aluminum pillaring (Arfaoui et al., 2008), thermal-hydro-chemical (Lee et al., 2013b), magnesium ferrite nanoparticles (Kaur et al., 2015) and humic acid (Wu et al., 2011).

Zeolites modifications can be separated into two larger groups: organic and inorganic treatments. For the first group, reports include hexadecytrimethylammonium bromide-modified NaY zeolite for both cationic and anionic metal ions (Chao and Chen, 2012), amine-modified zeolite for Pb and Cd ions adsorption (Wingenfelder et al., 2005), surfactant-modified natural zeolites for As$^{3+}$ adsorption (Chutia et al., 2009), thiourea modified synthetic zeolite X and its adsorption of Cd$^{2+}$ (Zhang et al., 2019a), cetylpyridinium bromide modified zeolite for Hg ion adsorption (Liu et al., 2016b), ethyleneelaminede and monoethanolamine modified synthesized -zeolite for adsorption of Pb$^{2+}$ (Motlagh Bahadory Esfahani and Faghhiian, 2014), hexadecylypyridinium bromide modified zeolite for Cr$^{6+}$ adsorption (Zeng et al., 2010), surfactant modified zeolite for the selective adsorption of Pb$^{2+}$ and Cd$^{2+}$ (Ren et al., 2016b) and Cu$^{2+}$ (Zhan et al., 2013), dithionaze-immobilized zeolite for Hg$^{2+}$ adsorption (Mudasis et al., 2016), poly(methacrylic acid)/iron-oxide-coated zeolite for removal of Mn$^{2+}$, Fe$^{3+}$ and As$^{3+}$ (Pak et al., 2018), humic acid-immobilized surfactant-modified zeolite for the adsorption of Cu$^{2+}$ (Lin et al., 2011), and polyacrylamide-zeolite composite modified by phytic acid for the adsorption of UO$_2^{2+}$, Ti$^{4+}$, Pb$^{2+}$, Ra$^{2+}$, Bi$^{3+}$ and As$^{3+}$ (Şimşek and Ulusoy, 2004). The inorganic modifications comprehend mostly changes and procedures of coating, layering, or supporting metals on
zeolites, aiming to improve some specific adsorption sites towards contaminants removal (Alswat et al., 2016; Jiménez-Cedillo et al., 2011; Kazansky and Pidko, 2005; Luo et al., 2019; Medina-Ramírez et al., 2019; Onyango et al., 2003; Pahlavanzadeh and Motamedi, 2020; Qiu et al., 2018; Salam et al., 2020; Simsek et al., 2013; Venkata Ramana et al., 2013; Zhang et al., 2019).

6.2. Organic molecules

6.2.1. Dyes

Yazdani et al. (2014) synthesized chitosan/feldspar bio-based beads and tested for the removal of Acid Black 1 dye from aquatic phases in 31 different batch experiments. The results showed uptake of 19.85 mg g$^{-1}$ under the optimum conditions of pH 3, the temperature at 15 °C, initial dye concentration of 125 mg L$^{-1}$, and an adsorbent dosage of 2 g L$^{-1}$, which was very close to the predicted maximum adsorption amount by the statistical model of 21.63 mg g$^{-1}$. The mathematical modeling on the dyes’ adsorption behavior illustrated that the process followed Langmuir isotherm, as well as pseudo-second-order kinetics. Langmuir’s maximum sorption capacity was found to be 17.86 mg g$^{-1}$. The thermodynamic parameters were evaluated and revealed that the adsorption process was exothermic and favorable (Yazdani et al., 2014).

Saipaneendra et al. (2017) used hematite and magnetite nanoparticles to functionalize reduced graphene oxide sheets via a facile one-step co-precipitation technique. It has been postulated that both minerals’ co-existence on the graphene sheet causes synergistic effects to enhance adsorption. For comparison purposes, the authors studied the adsorption behavior of pure graphene oxide, reduced graphene oxide, reduced graphene oxide/hematite composite (surface area = 230 m$^2$ g$^{-1}$), reduced graphene oxide/magnetite composite (surface area = 231 m$^2$ g$^{-1}$), and reduced graphene oxide/magnetite/hematite composite (surface area = 216 m$^2$ g$^{-1}$) against methylene blue adsorption. The adsorption kinetics was well described by the pseudo-second-order model, and Langmuir isotherm for the equilibrium adsorption behavior of rGO-Fe$_2$O$_3$-Fe$_3$O$_4$. The maximum adsorption capacity was determined to be 72.8 ± 2.7 mg g$^{-1}$ (Saipaneendra et al., 2017). Kang et al. (2018) provided a novel approach to “waste eliminates waste” by using ilmenite’s acid leachate as the precursor in its structure tailoring. They reported that the final product’s morphology and structure could be controlled, originating from nanoparticles, microcubes, rhombohedrons to the microsphere, by merely varying synthetic parameters. Due to its large surface area ($152.3$ m$^2$ g$^{-1}$) and large functional groups, Fe$_3$O$_4$ microspheres efficiently removed organic dyes from aqueous solutions. The maximum adsorption capacities obtained by Sips model ($R^2 = 0.9820$) fit were 723.8, 150.7, and 54.5 mg g$^{-1}$ for Congo red, Methyl orange, and Methylene blue, respectively, with 0.3 g L$^{-1}$ of adsorbent, at pH of 7.2 ± 0.1 and at 25 °C (Kang et al., 2018).

Thermally treated, modified, and calcined dolomites have been used for dye adsorption. In 2010, Dolomite was thermally treated at 1000 °C, going from a surface area of 1.82 to 11.36 m$^2$ g$^{-1}$. The batch adsorption experiments were performed at 25 °C, 0.06 g L$^{-1}$ of adsorbent, and aqueous orange I solution in a concentration range of 20–200 mg L$^{-1}$. The synthesized material’s final uptake was 25 mg g$^{-1}$ (Boucif et al., 2010). In 2018, the adsorption of reactive black 5 and Congo red by dolomite treated at 900 °C was investigated in single and binary solutions. At equilibrium, Congo red was more strongly coadsorbed than reactive black 5, with maximum adsorption capacities of 229.18 and 72.37 mg g$^{-1}$ at 40 °C, respectively (Ziane et al., 2018). At last, in 2019, low-cost porous calcined dolomite microspheres were prepared by simple spray drying and subsequent calcination. The material was tested against methylene blue removal in the conditions of 20 g L$^{-1}$ of adsorbent and 100 mg L$^{-1}$ of dye. The adsorption kinetics followed the pseudo-second-order, while the isotherm data fit the Langmuir model. In this context, the microspheres’ removal efficiency reached 95.6% (Yan et al., 2019).

Mahmoodi and Saffar-Dastgerdi (2019) prepared sodalite zeolite nanoparticles, subsequently modified by different amounts of 3-aminopropyl-triethoxy-silane, resulting in products with 2.3 wt.%, 4.4 wt.%, and 6.5 wt.% of the organic modifier, named 0.5, 1, and 1.5 zeolites, respectively. The surface-modified products were used for adsorption of Direct Red 23 and Direct Red 80 from simulated wastewater. After initial tests, 0.5 zeolite was elected as the best, and it was tested furtherly. Equilibrium data followed Langmuir isotherm and pseudo-second-order kinetic. The adsorption capacity of the 0.5 composite reached expression 2415 and 4842 mg g$^{-1}$ for Direct Red 80 and Direct Red 23, respectively. Thermodynamics was studied and measured Gibbs free energies at 298, 313, 323, and 333 K were −12.53, −14.68, −16.12, and −17.55 kJ mol$^{-1}$ for Direct Red 23, and −9.27, −11.73, −13.37, and −15.01 kJ mol$^{-1}$ for Direct Red 80, respectively. The adsorption process was physisorption, exothermic, and spontaneous (Mahmoodi and Saffar-Dastgerdi, 2019).

6.2.2. Pharmaceuticals

Martín et al. (2019) modified natural montmorillonite and a synthetic mica with cationic octadecylamine by a cation-exchange reaction and explored its potential use adsorbent for ibuprofen removal. The adsorption equilibrium isotherm was fitted with the Langmuir and Freundlich mathematical models ($R^2 > 0.999$). The adsorption rate of C$_8$-montmorillonite (removal efficiency = 99.9%) was not dependent on ibuprofen concentration (0.1–80 mg L$^{-1}$), but C$_{18}$-mica behaved contrarily (from 99.9% at 0.1 mg L$^{-1}$ to 67% at 80 mg L$^{-1}$). Variations in pH ranging from 4 to 9 did not affect the process. Pseudo-second-order kinetic model best described the adsorption of ibuprofen ($R^2 > 0.993$), reaching equilibrium, with outstanding efficiency up to 100%, in less than 5 and 60 min for C18-montmorillonite and C$_{18}$-mica, respectively (Martín et al., 2019).

Azizi (2020) studied a green preparation method of iron oxide/cellulose nanocomposite, used to remove metronidazole, an antibiotic, from aquatic solutions in the form of an aqueous extract of spent tea waste, regarding its effective and magnetic separation capability. The prepared nanocomposite had spherical particles with an average size of 15.5 nm. At pH 5, the metronidazole concentration of 10 mg L$^{-1}$, the adsorbent dosage of 25 mg L$^{-1}$, and contact time of 30 min, the pollutant’s removal efficiency was 97.04%. Langmuir isotherm determined the maximum adsorption capacity of 332 mg g$^{-1}$, pseudo-first-order kinetic constant rate of 1.15 L min$^{-1}$, with the determination coefficient of 0.97 (Azizi, 2020).

The adsorption and advanced oxidation of diverse pharmaceuticals and personal care products from the water were studied by Masud et al. (2020). Interestingly, they started assuming that their model pollutants are found as a complex mixture in wastewater and the environment and used reduced graphene oxide as a support for nanozerovalent iron against a complex mixture of 12 diverse personal care products (including antibiotic, anti-inflammatory, anti-seizure, and antidepressant pharmaceuticals). This approach is exciting for most studies on removing personal care products results with only one pollutant at a time, typically at high initial concentrations, not environmentally relevant. Considering starting concentration of 200 μg L$^{-1}$, an adsorbent dosage of 533 mg L$^{-1}$, pH 3, and after a contact time of 30 min, final removal efficiencies for venlafaxine, citalopram, paroxetine, lamotrigine, sulfamethoxazole, and caffeine reached 88.5%, 98.92%, 99.58%, 98.71%, 97.92%, 88.55%, 99.25%, 82.97%, 85.75%, 95.23%, 74.13% and 93.12%, respectively (Masud et al., 2020).

De Oliveira et al. (2020) investigated micro and mesoporous silica prepared with coal fly ash as starting material and used as an adsorbent to remove parabens. The composite prepared at pH 7 presented higher adsorption capacity, with a surface area of 396 m$^2$ g$^{-1}$. Adsorption kinetics were carried out in a batch system with a 40 mL multicomponent
paraben solution at 5 mg L\(^{-1}\), 2 mg adsorbent mass, pH 3, agitation at 300 rpm for 30 min at room temperature (28 ± 2 °C). The same conditions were used in equilibrium tests, but the multicomponent parabens concentrations varied from 1 to 20 mg L\(^{-1}\). The adsorption capacity was determined as 0.01, 0.07, 0.54, and 1.31 mg g\(^{-1}\) for methylparaben, ethylparaben, propylparaben, and butylparaben, respectively, by fitting the data obtained to Freundlich isotherm \((R^2 > 0.999)\) (De Oliveira et al., 2020).

Differently than the previous minerals, modified clays have been prepared by several different research groups and applied for the adsorption of many pharmaceuticals, such as amoxicillin (Pierucci et al., 2017), atenolol (Seema, 2013), carbamazepine (Dordio et al., 2009; Lawal and Moodley, 2018; Liu et al., 2011), trimethoprim (Bekçi et al., 2015), mefanamic acid (Dordio et al., 2017), metronidazole (Calabrese et al., 2017), cinnamic acid (Calabrese et al., 2017), ciprofloxacin (Hamilton et al., 2014), diclofenac (Pierucci et al., 2017; Styszko et al., 2015), flurosemide (Machado et al., 2017), gemfibrozil (Dordio et al., 2017), ibuprofen (Dordio et al., 2009; Styszko et al., 2015), ketoprofen (Styszko et al., 2015), mefanamic acid (Dordio et al., 2017), metronidazole (Galihar et al., 2013; Al-Zboon, K., Al-Harahsheh, M.S., Hani, F.B., 2011. Fly ash-based geopolymer for Pb removal from aqueous solutions with clinoptilolite. Microporous Mesoporous Mat. 94, 99–104. https://doi.org/10.1016/j.saa.2014.02.092.

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