REVIEW PAPER

Adsorption Method for Removal of Pharmaceuticals from Wastewater: Review

Ali Hosseinian Naeini[1,*], Seyed Ali Hosseini Moradi[2]

* *hosseinian_ali22@yahoo.com*

[1] Department of Chemical and Polymer Engineering, South Tehran Branch, Islamic Azad University, Tehran, Iran
[2] Khatam Al-Anbia University, Tehran, Iran

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Abstract: *The growth of industries, populations, and industrial activities includes environmental pollutants. Pollution causes problems such as reduced light transmission, anaerobic conditions, and complications such as allergies and cancer for humans and other living organisms. The adsorption method is one of the most attractive, and efficient methods for removing environmental pollutants such as pharmaceuticals. Among the standard methods for wastewater treatment, adsorption is more efficient than other methods and is more economical. They have a meager price. Adsorption of pollutants can be an excellent way to remove toxic substances from polluted waters and industrial effluents. In this review, pharmaceutical removal by adsorption process was reviewed in detail.*

Keywords: *Adsorption, Pharmaceutical, Wastewater treatment.*

1. INTRODUCTION

Pharmaceuticals are an essential, and integral part of modern life, and are used to treat human and animal diseases. They are one the environmental pollutants. In the last decade, few countries have studied the harmful effects of these pollutants on living organisms. Recent studies on the toxicity of this pharmaceutical show its harmful effects, even at low concentrations. Therefore, the development of effective technologies to remove these pollutants is necessary. Studies show that biological treatment is not enough to decompose and prevent contamination of natural waters. However, chemical processes such as advanced oxidation methods, in particular, can break down analgesics into molecules of simpler compounds or mineralize them, still, processes are complicated, and expensive to remove complex compounds such as analgesics completely. Physical techniques are the most appropriate way to purify these materials. The adsorption method has several advantages. It is the most efficient among physical methods for removing organic compounds from industrial wastewater. Also, the operation of the adsorption method is straightforward and does not produce toxic substances, nor is it expensive. Therefore, the adsorption method is an effective and economical method that causes the separation of organic compounds from aqueous media [1-13]. However, the adsorption process suffers from some limitations. Low adsorption capacity and low regeneration ability adsorbent are the disadvantages of the adsorption technology. Thus, scientists and engineers focus on synthesizing the high adsorption capacity and high regeneration ability of adsorbent.

1.1. The Status of Pharmaceutical Use in the World and Iran

According to the World Health Organization, the daily consumption of antibiotics is 7700 kg, and their annual consumption globally is between 100,000 and 200,000 tons. Iran is one of the top 20 pharmaceutical users in the world and ranks second in Asia after China in this regard. On average, every Iranian takes pharmaceuticals 339 times a year, four times the global figure. In total, approximately 43% of Iranians use pharmaceuticals arbitrarily. The average growth of pharmaceutical use in Iran is 11.5%, which is 9% higher than the global average [14].

1.2. Commonly Used Pharmaceuticals: The Types, Chemical Structures, and their Applications

Approximately 3000 pharmaceutical substances are in the European Union. The most widely used molecules are antibiotics for human and veterinary pharmaceuticals. Their consumption has reached 12,500 tons per year over the last decade. Ibuprofen, scientifically named 4-isobutylphenyl- 2-propionic acid, is one of the

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most widely used NSAIDs worldwide. It appears to inhibit cyclo-oxygenase in the central nervous system without peripheral action, which is why it does not have anti-inflammatory effects. Naproxen (NPX) is one of the most effective analgesics, a non-steroidal anti-inflammatory pharmaceutical (NSAID. It has been found in both surface moisture and wastewater at concentrations ranging from 20 ng/L to several mg/L. NPX has an excellent cardiac profile; however, it has been reported that people who ingest trace amounts of NPX have a higher risk of heart attack or a higher potential of urinary bladder cancer. [15-20].

1.3. Removal of Pharmaceuticals

There exists a common distinction between pharmaceuticals and food and materials providing nutrients. The pharmaceuticals were consumed in various ways, such as sublingual administration, injection, inhalation, ingestion, smoking and absorption through a patch, or a suppository. A pharmaceutical is a chemical material utilized for treating, curing, preventing, diagnosing a condition, or enhancing health. In the beginning, pharmaceuticals were extracted from different plants, yet they were currently synthesized organically. Pharmaceutical pharmaceuticals are taken either for a particular amount of time or regularly in case of chronic diseases. They are typically categorized into different groups; these types might be based on similarity in chemical formation, identical action mechanisms (attaching to the same biological target), a similar action mode, and whether they are employed for treating the same condition. The Anatomical Therapeutic Chemical Classification System (ATC) is currently the most common pharmaceutical classification system. It gives a particular alphanumeric code to pharmaceuticals, assigning them to a particular pharmaceutical category in the ATC system. Biopharmaceutics Classification System is another prevalent classification system that categorizes pharmaceuticals based on solubility, permeability, or absorption features. Psychoactive pharmaceuticals influence the performance of the central nervous system by changing the mood, consciousness, or perception. They were classified into various categories, such as antidepressants, depressants, antipsychotics, anxiolytics, hallucinogens, and stimulants. These pharmaceuticals are known to help treat myriad mental diseases. Nicotine, alcohol, and caffeine are pharmaceuticals with the highest service. They are further known as recreational pharmaceuticals because their use is mainly limited to pleasure.

1.3.1. Antibiotics

The discovery of antibiotics helped rescue many lives. Significant amounts of antibiotics are being utilized as antimicrobial medications around the globe. Antibiotic pharmaceuticals are mainly employed for treating bacterial disorders in people, as animal medications for preventing conditions related to animal husbandry, and as growth promoters, particularly in livestock. If these pharmaceuticals are utilized excessively, there will be an augment in the antibiotic residues released into nature. Nonetheless, it is only recently that scientists have been concerned with the level of contamination that antibiotics cause in the service. This is mainly because large amounts of antibiotics exist in the marine ecosystem, they are widely utilized in creating state-of-the-art and accurate analytical tools, and antibiotic residues are poisonous with long-lasting impacts. Aquatic ecosystem Instead of being fully metabolized in the body, antibiotics are released in urine, manure, or faeces as metabolites, water-soluble conjugate compounds, or parent compounds, which explains their augmented concentration in the aquatic ecosystem. The agricultural runoff and manufacturing industries emitting unutilized antibiotic pharmaceuticals are other antibiotic pharmaceutical sources in nature. In various investigations, antibiotics were observed in industrial effluents, hospital wastewater, groundwater, surface water, sediments, drinking water, and the influents and effluents of wastewater treatment plants. When antibiotics are released into the aquatic ecosystem, bacteria are more likely to obtain antibiotic-resistant genes that readily travel to other bacteria via lateral gene transfer. The presence of antibiotic-resistant genes bacteria makes the microbes resistant to traditional antibiotics that were previously effective. Antibiotic-resistant bacteria were detected in effluents, surface water, and wastewater treatment plants. Hospitals typically utilize antibiotics, so their effluents are the source of pharmaceutical-resistant bacteria. Fluoroquinolones, macrolides tetracycline, and

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sulphonamides are among highly prevalent antibiotics in the aquatic ecosystem. Such pharmaceuticals are mainly found in ground, and surface water, overland moisture systems, and municipal wastewater. A large body of research has corroborated that traditional wastewater treatment merely partially eliminates antibiotics from wastewater. Adsorption through activated carbons and other substances, nanofiltration, reverse osmosis, chlorination, flocculation, ultraviolet (UV) irradiation filtration, and ozonation are among the techniques utilized so far. Nonetheless, a majority of the preceding approaches were created to eliminate heavy metals and hydrophobic pharmaceuticals and for the treatment of microbial pollutants instead of pharmaceutically active compounds like antibiotic pharmaceuticals. Some drawbacks are further associated with photodegradation via UV/catalysts and adsorption through carbon nanotubes, clays, and ion exchange which were mainly created to eliminate antibiotics. Alumina, zeolite, biosorbents, agricultural waste, activated carbon, silica, mesoporous silica, functionalized mesoporous silica, and metal-organic frameworks are some substances utilized in removing antibiotic pharmaceuticals. Therefore, to eliminate antibiotic pharmaceuticals from marine ecosystems, it is still necessary to develop effective, economical, and environmentally friendly substances in aquatic ecosystems. A large number of studies are being conducted to invent cost-effective techniques. Owing to their efficaciousness and adaptability for eliminating various contaminants from the aquatic ecosystem, bio-materials have gained a great deal of scientific attention among the adsorbents [21-66].

2. TYPES OF PHARMACEUTICALS

A Pharmaceutical in English science refers to any substance is used to treat, relieve symptoms, diagnose or prevent disease affect the structure or function of an organism, and correct the body's function once it enters the body. It becomes. In another definition, a pharmaceutical is a substance that, by acting on a particular receptor inside, outside, or the cell wall, triggers or inhibits a particular function. The potency of the Pharmaceutical is directly proportional to the amount and number of this interaction. Of course, medications with a topical effect, including antacids, topical disinfectants, and contrast agents, are not included in this definition.

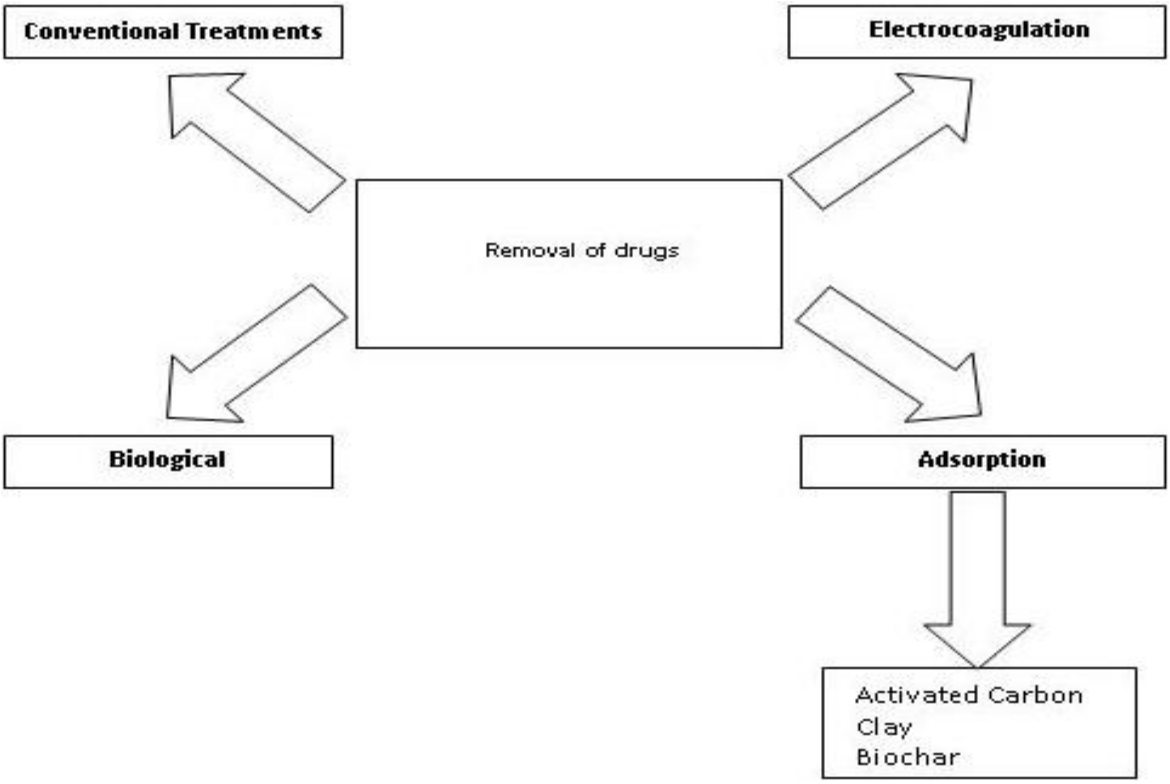

Fig. 1. Removal of pharmaceuticals by different treatment methods

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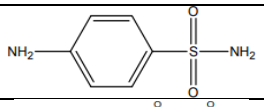
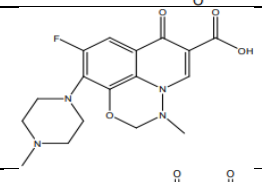
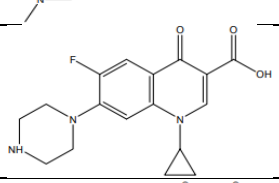
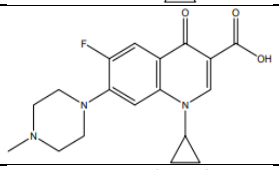
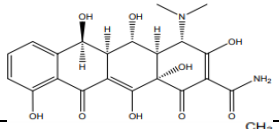
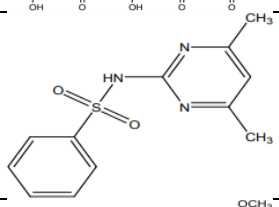
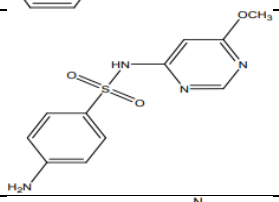
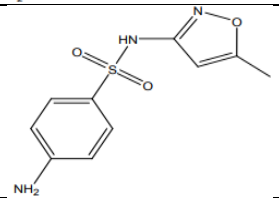
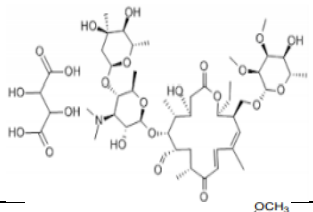
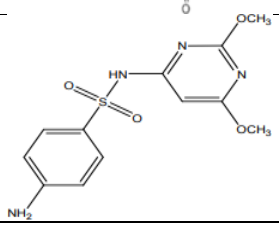
Table 1. Molecular structure and physicochemical properties of selected analytes

Number	Name of pharmaceuticals	Structure	Reference
1	Sulphanilamide		67
2	Marbofloxacin		68
3	Ciprofloxacin		69, 70
4	Danofloxacin		75
5	Oxytetracycline		72, 73
6	Sulphamerazine		73
7	Sulphamonomethoxine		70, 74
8	Sulphamethoxazole		75, 70
9	Tylosin tartrate		72
10	Sulphadimethoxine		74

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The Pharmaceutical may be of natural (plant or animal) origin or may be synthetic. Chemical medications are usually discovered in the laboratory by pharmacists and sometimes by other scientists or doctors and are produced in pharmaceutical factories after adequate research and approval by official authorities. The pharmaceutical may be taken orally (tablets and syrups), rubbed (ointments, and drops), inhaled (inhaled), or injected (ampoules). The place where the pharmaceutical is sold is called the pharmacy. Pharmaceuticals come in four forms: mineral, animal, herbal, and chemical.
Pharmaceuticals can also be classified into authorized and unauthorized categories (like some narcotics). Medications should generally be stored in particular conditions and have a particular expiration date. How to take the Pharmaceutical and how much to take (dose) is particular in the prescription of the treating physician. Some manufactured Pharmaceuticals, also called galenic Pharmaceuticals, are made in pharmacies with a doctor's prescription and from a combination of several Pharmaceuticals [77].

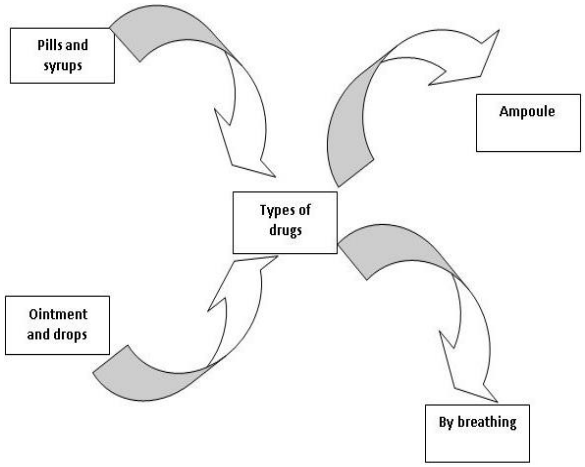

Fig. 2. Types of medication for consumption

3. MATHEMATICAL MODELING

The adsorption process has offered particular upsides with motivated scientists to better understand the process by utilizing it. Anticipating how packed bed column behaves can help create a novel process according to this approach. Yoon and Nelson have created an empirical model for predicting how activated carbon-based packed beds behave. However, it is costly and time-consuming to create these empirical models for various bed kinds; furthermore, these models only function under particular operation situations and cannot be categorized as a universal model for full bed columns. Thus, it is beneficial to create mathematical models that accurately explain the behavior of packed beds. It is easy to solve the governing equations in such models; however, they are limited to particular hypotheses to be considered when the system is being modelled, resulting in more valid models. Several scientists have recently attempted to model various methods of adsorption which will be discussed in the following sections. To better fathom the natural features of a system, the adsorption method is mainly divided into two types: liquid-phase, and gas-phase. Hence, the governing equations regarding each type are expressed separately [78].

4. THE ADSORPTION METHOD

The adsorption method is a process that is widely used for chemical species from the fluid phase to the solid or liquid surface. Concrete surfaces in adsorption have active and energetic sites that can be used in aqueous solutions using their particular electronic properties with different solutes. The solid substance that gives the surface to absorb is called the adsorbent, and the interested species are called the adsorbent. The adsorption process was influenced by the nature of the adsorbent, and adsorbent, pH, temperature, contact time, the concentration of contaminants, adsorbent particle size, the presence of other wastes and test conditions. Suppose the experiments in the experimental conditions compared the two adsorbents. Studies on the use of adsorbents to remove pharmaceuticals show that pharmaceuticals with hydrophobicity are more prone to hydrophilicity. Most adsorbents used in wastewater treatment are activated carbon, zeolite, clay, and agricultural waste [86-90].

4.1. Carbon Adsorbents

There are some materials contain activated carbon, and graphite, which are obtained from materials including coal, and coconut shell. High surface area and easy availability make activated carbon the adsorbent studied in removing pharmaceuticals from water. In carbon adsorbents, activated carbon is most used in wastewater treatment. Activated carbon is low in efficiency, and cost.

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Table 2. A lot of pharmaceuticals are by Formulation & Molar mass & Structure chemical

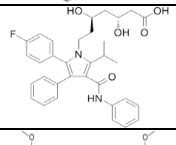
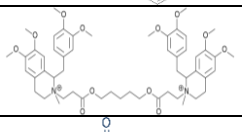
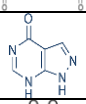
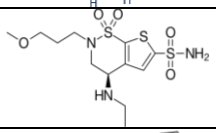
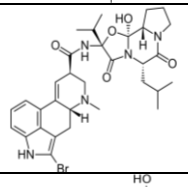
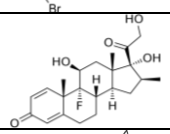
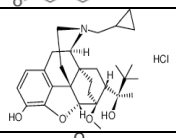
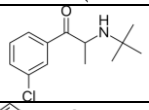
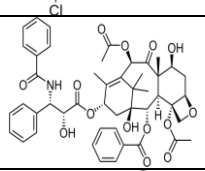
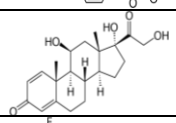
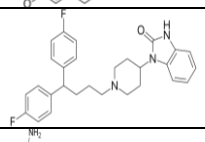
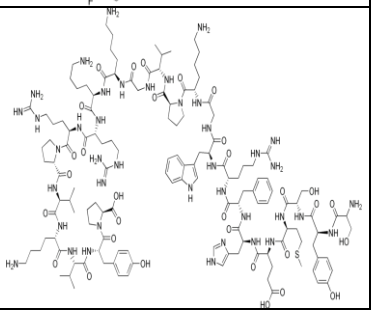
Number	Name of pharmaceuticals	Formula	Molar mass	Structure
1	Aspirin	$C_9H_8O_4$	180.158 g/mol	
2	Atorvastatin	$C_{33}H_{35}FN_2O_5$	558.64 g/mol	
3	Atracurium	$+C_{53}H_{72}N_2O_{12}$	929.145 g/mol	
4	Allopurinol	$C_5H_4N_4O$	136.112 g/mol	
5	Brinzolamide	$C_{12}H_{21}N_3O_5S_3$	383.51 g/mol	
6	Bromocriptine	$C_{32}H_{40}BrN_5O_5$	654/595 g/mol	
7	Betamethasone	$C_{22}H_{29}FO_5$	392/461 g/mol	
8	Buprenorphine	$C_{29}H_{41}NO_4$	467.64 g/mol	
9	Bupropion	$C_{13}H_{18}C_lNO$	239.7425 g/mol	
10	Paclitaxel	$C_{47}H_{51}NO_{14}$	853/906 g/mol	
11	Prednisolone	$C_{21}H_{28}O_5$	360/444 g/mol	
12	Pimozide	$C_{28}H_{29}F_2N_3O$	461.56g/mol	
13	Tetracosactrin	$C_{136}H_{210}N_{40}O_{31}S$	2933/44g/mol	

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Table 3. List of formula (permission of Dr. Rama Rao Karri) [79-85]

Number	Formula
1	$\frac{(qe,meas-qe,cal)^2}{\sum(qe,meas-qe,cal)^2 + (qe,meas-qe,cal)^2}$
2	$\sum_{i=1}^{n}(qe,meas - qe,cal)^2$
3	$\sum_{i=1}^{n}\lvert qcal - qexp\rvert i$
4	$\frac{100}{n}\sum_{i=1}^{n}\lvert\frac{qcal-qexp}{qexp}\rvert i$
5	$\sqrt[100]{\frac{1}{n-p}\sum_{i=1}^{n}(\frac{qcal-qexp}{qexp})^2}\ i$
6	$\sum_{i=1}^{n}(\frac{qe,cal-qe,meas}{qe,meas})^2$
7	$\frac{100}{n}\sum_{i=1}^{n}[\frac{(qe,cal-qe,meas)^2}{qe,meas}]\ i$
8	$1-\frac{6\sum_{i=1}^{n}\frac{(qe,meas-qe,cal)^2}{n(n-1)}i}{n(n-1)^2}$
9	$\sqrt{\frac{\sum_{i=1}^{n}\lvert(qe,meas-qe,cal)i-AREi^2\rvert}{n-1}}$

The physical and chemical properties of activated carbon depend on precursors and their preparation methods. The adsorption of pharmaceuticals on inexpensive activated carbon shows that increasing the pH reduces the pharmaceutical adsorption from the solution, and increases the temperature in the range of 4-40°C [89, 91, 92, 93].

4.2. Adsorption Mechanism

Tetracycline (TC) and Doxycycline (Dox) as common antibiotics were used to study the adsorption ability of the MIL-53/NH_2-Chitosan composite [94]. The removal experiments were carried out at natural pH (5.4) conditions. Fig. 3 shows that the adsorption capacity of MIL-53/NH_2-Chitosan composite to TC and Dox was 388 and 264 mg/g, respectively. The MIL-53/NH_2-Chitosan could provide multiple non-covalent interactions to remove various organic contaminants, in which both π-π interactions/ stacking and H- bonding are responsible for the TC and Dox removal.

4.3. Adsorption Isotherm, Kinetic, and Thermodynamic

There are different isotherm models to investigate the adsorption data [94-98]. Commonly three isothermal models (the Langmuir, Freundlich, and Tempkin) are studied. The isotherm coefficients for pollutant removal by chitosan and MIL-53/NH_2-Chitosan are summarized in Table 7. The degree of fitness and compatibility of each isotherm model was estimated by the correlation coefficient (R^2) values indicating that pollutant removal followed the Langmuir model.

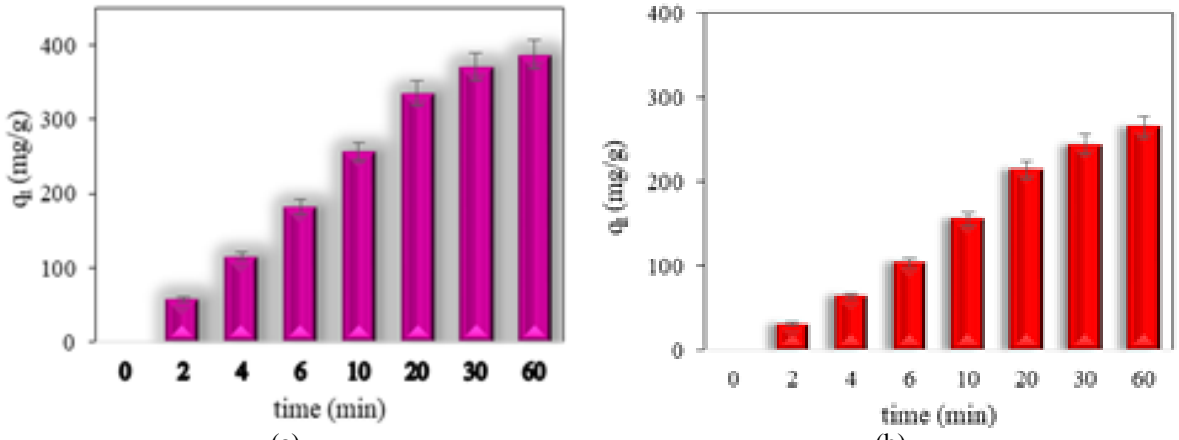

Fig. 3. Removal of (a) tetracycline and (b) doxycycline by the MIL-53/NH_2-Chitosan [94].

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It means that contaminant removal is limited to the formation of single-layer coverage of adsorbent surface [94].

Different kinetic models are investigated in the literature for pollutant adsorption [94-98]. Kinetic model curves and parameters at various adsorbent dosages are presented in Table 8. From Table 7, it is clear that the R^2 value for PSO was relatively high, which signified that the adsorption mechanism obeyed the PSO kinetic model.

Table 4. Comparison of adsorbent, pharmaceuticals, isotherm, kinetic, q_{max}, Thermodynamic

Number	Adsorbent	Pharmaceutical	q_{max}	isotherm	kinetic	Thermodynamic	Ref.
1	Fe_3O_4-chitosan	Metronidazole	97.06	Langmuir	Pseudo-first-Order	ΔG°=-3.371 Δs°=499.255 ΔH°=144.405	67
2	magnetic activated carbon	Erythromycin		Langmuir, Freundlich, Temkin , Dubinin-Radushkevich	Pseudo-first-order, Pseudo-second-order, Elovich model, Intraparticle diffusion model (step 1, step 2, step 3)	ΔG°=-3.4 Δs°=+1 ΔH°=+28.3	68
3	starch, chitosan, and β-cyclodextrin	ibuprofen	328, 360, 479, 420	Langmuir, Freundlich, D-R model	Pseudo-first order, Pseudo-second order	ΔG°(mesoporous silica)= 1.2, 1.25, 1.35, 1.47, 1.52, 1.63, 1.7 ΔS°(mesoporous silica)=-17.7 ΔH°(mesoporous silica)=-4.19 ΔG°(mesoporous silica/starch)= 1.1, 1.2, 1.31, 1.42, 1.5, 1.59, 1.66 ΔS°(mesoporous silica/starch)= -4.8 ΔH°(mesoporous silica/starch)= -19.45 ΔG°(mesoporous silica/chitosan)= 0.12, 0.22, 0.32, 0.41, 0.48, 0.55, 0.62 ΔS° (mesoporous silica/chitosan)= -16.26 ΔH° (mesoporous silica/chitosan)=-4.9 ΔG° (mesoporous silica/β-cyclodextrin)= 0.66, 0.76, 0.86, 0.95, 1.03, 1.11, 1.18 ΔS° (mesoporous silica/β-cyclodextrin)= -17.5 ΔH° (mesoporous silica/β cyclodextrin)= -4.63	69
4	chitosan/ tripolyphosphate /graphene oxide hydrogel	Sumatriptan Succinate	45.4	Langmuir Temkin Ferundlich	–	ΔG°= -3.322, -3.712, -3.907, -4.102 ΔH°= 8.3 Ln K= 1.36, 1.46, 1.52, 1.57	70
5	Chitosan based magnetic	tetracycline	215.31	Langmuir, Freundlich, Temkin,	Pseudo- First Order, Pseudo-second order nonlinear model, Intra-	–	71

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	nanocomposite			Dubinin–Radushkevich	particle diffusion, Elovich model		
6	Magnetic nanocomposite (cobalt-based ferrite)	Diclofenac sodium	18.4	Langmuir,: Freundlich, Temkin, Dubinin–Radushkevich	Pseudo first-order, Pseudo second-order, Elovich, Bangham	ΔH° cobalt-based ferrite =20.75 ΔS° cobalt-based ferrite= 74.37 ΔG° 288 cobalt-based ferrite= −0.67 ΔG° 298 cobalt-based ferrite= −1.41 ΔG° 308 cobalt-based ferrite = −2.15 ΔG° 318 cobalt-based ferrite=−2.90	72
7	Magnetic nanocomposite (graphene oxide@ cobalt based ferrite)	Diclofenac sodium	32.4	Langmuir,: Freundlich, Temkin, Dubinin–Radushkevich	Pseudo first-order, Pseudo second-order, Elovich, Bangham	ΔH° graphene oxide@cobalt based ferrite= 15.61 ΔS° graphene oxide@cobalt based ferrite= 70.22 ΔG° graphene oxide@cobalt based ferrite= −4.61 ΔG° 298 graphene oxide@cobalt based ferrite= −5.31 ΔG° 308 graphene oxide@cobalt based ferrite= −6.02 ΔG° 318 graphene oxide@cobalt based ferrite= −6.72	73
8	bentonite/ biopolymer composites	5-fluorouracil	114, 230, 273, 310	Langmuir, Freundlich, Dubinin–Radushkevich	Zero-order mode, First order model, Higuchi model, Hixson-Crowell model, Korsmeyer-peppas mode	ΔG° bentonite= −9.68 to −9.78 ΔH° bentonite= 9.1 Δs° bentonite= −1.93 ΔG° bentonite/ chitosan= −7.44 to −7.24 ΔH° bentonite/ chitosan= 9.38 Δs° bentonite/ chitosan= 6.74 ΔG° bentonite/ Co-Poly 2-hydroxyethyl methacrylate-methyl methacrylate= −6.95 to −6.86 ΔH° bentonite/ Co-Poly 2-hydroxyethyl methacrylate-methyl methacrylate= 8.12 Δs° bentonite/ Co-Poly 2-	74

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						hydroxyethyl methacrylate-methyl methacrylate= 4.02 ΔG° bentonite by an organic surfactant= −7.64 to −7.75 ΔH° bentonite by an organic surfactant = Δs° bentonite by a 6.58 organic surfactant= −3.33	
9	Chitin and lignin	Ibuprofen (500)	type 1 (400.39) type 2 (256.41), type 3 (314.33), type 4 (334.55)	Langmuir isotherm (type 1, 2, 3, 4), Freundlich	a pseudo-first-order model (PFO) (Bartczak et al., 2016), a pseudo-second-order model (PSO) (Ho and McKay, 1999) and an intra-particle diffusion	ΔH°=−5.515 ΔS° =−12.180 ΔG°=−1.87, −1.83−1.80, −1.68	76
10	Chitin and lignin	Ibuprofen (1000)	type 1 (400.39) type 2 (256.41), type 3 (314.33), type 4 (334.55)	Langmuir isotherm (type 1, 2, 3, 4), Freundlich	a pseudo-first-order model (PFO) (Bartczak et al., 2016), a pseudo-second-order model (PSO) (Ho and McKay, 1999) and an intra-particle diffusion	ΔH°=−5.715 ΔS° =−13.980 ΔG°=−1.55, −1.48, −1.41 −1.34	76
11	chitin and lignin	Acetaminophen (500) Acetaminophen (1000)	type 1 (267.07) type 2 (111.11), type 3 (158.21), type 4 (204.24)	Langmuir (type 1, 2, 3, 4), Freundlich	a pseudo-first-order model (PFO) (Bartczak et al., 2016), a pseudo-second-order model (PSO) (Ho and McKay, 1999) and an intra-particle diffusion	ΔH°=−5.161 ΔS°=−19.73 ΔG°=0.71, 0.83 0.90, 1.02	76
12	chitin and lignin	Acetaminophen (1000)	type 1 (267.07) type 2 (111.11), type 3 (158.21), type 4 (204.24)	Langmuir (type 1, 2, 3, 4), Freundlich	a pseudo-first-order model (PFO) (Bartczak et al., 2016), a pseudo-second-order model (PSO) (Ho and McKay, 1999) and an intra-particle diffusion	ΔH°=−1.225 ΔS°=−12.49 ΔG°=2.49, 2.55 2.64, 2.67	76

Table 5. Comparison adsorbent, pharmaceutical, characterizations

Number	Adsorbent	pharmaceutical	characterizations	Ref.
1	magnetic activated carbon	Erythromycin	XRD, SEM, TEM, Raman, VSM, TGA, BET	68
2	Oligochitosan	Ibuprofen binding-releas	DSC, DLS, ITC	69
3	chitosan/tripolyphosphate/ graphene oxide hydrogel	Sumatriptan Succinate	SEM, TEM, AFM, TGA, XRD, FT-IR	70
4	Chitosan based magnetic nanocomposite	tetracycline	FTIR, TGA, BET, XRD, Raman, XPS, FESEM, HRTEM	71
5	Magnetic nanocomposite (cobalt-based ferrite)	Diclofenac sodium	XRD, SEM, TEM, X-ray , XPS, VSM, UV_Vis	72
6	bentonite/ biopolymer composites	5-fluorouracil	XRD, FT-IR, BET, BJH, TEM, SEM	73
7	Tannin and 3-Aminopropyltriethoxysilane	Methotrexate	FTIR, SEM, TEM, XRD	76

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Table 6. Comparison adsorbent, pharmaceuticals, Condition adsorption, correlation coefficient

Number	adsorbent	pharmaceuticals	Condition adsorption	removal efficiency	Ref.
1	Chitosan based magnetic nanocomposite	Tetracycline	Temperature= 298, 308, 318 K), concentration= 0.05 g adsorbent dosage, 60 mg/L	Langmuir isotherm (0.9845, 0.9207, 0.9283), Freundlich isotherm= (0.9232, 0.83.18, 0.8396), Temkin isotherm= (0.8327, 0.8548, 0.8671), Dubinin–Radushkevi= (0.9700, 0.9758, 0.9748), First order= 0.9921, Second order= 0.9957, Intra-particle diffusion= 0.7490, Elovich model= 0.8045	73
2	Oligochitosan	Ibuprofen binding-releas	Concentrations of Ibuprofen binding-release, oligochitosan, in the initial mixture, were 3.77, 5.0, and mg/mL, (pH= 7.2), oligochitosan concentration is = 4.5,5 mg/mL	–	76

Table 7. The contaminant adsorption isotherm coefficients at different adsorbent doses [94].

Isotherm	parameter	Adsorbents	
		Chitosan	MIL-53/NH_2-Chitosan
Langmuir $C_e/q_e=1/K_L\ q_L + C_e/q_L$	q_L	3703	12500
	K_L	0.0418	0.1142
	R^2	0.9797	0.9909
Freundlich $\log q_e=\log K_f + 1/n \log C_e$	K_F	1729	7219
	n	8	11
	R^2	0.5490	0.8117
Temkin $qe=B_1 \ln k_T + B_1 \ln C_e$	K_T	1.856×10^{-20}	2.467×10^{-15}
	B_1	-25	-195
	R^2	0.5497	0.7875

Table 8. The kinetics coefficients of organic pollutant adsorption at different adsorbent doses [94].

Dose (g)	$(q_e)_{Exp}$	Pseudo-first order (PFO)			Pseudo-second-order (PSO)			Intraparticle diffusion (ID)		
		$\log (q_e-q_t) =\log q_e-(k_1/2.303) *t$			$t/q_t=1/k_2*q_e^2 + t/q_e$			$q_t=k_p * t^{0.5} + I$		
		$(q_e)_{Cal}$	k_1	R^2	$(q_e)_{Cal.}$	k_2 ($\times10^{-5}$)	R^2	k_p	I	R^2
Chitosan										
0.0005	3360	5011	27	0.8677	3703	5	0.9824	424	630	0.8122
0.0010	3212	4088	18	0.9736	3333	30	0.9929	321	12583	0.6670
0.0015	3252	2258	57	0.9320	3448	10	0.9967	311	1225	0.7599
0.0020	3205	2141	36	0.8649	3333	18	0.9993	215	1846	0.7317
MIL-53/NH_2-Chitosan										
0.0005	11590	9931	25	0.8822	12500	10	0.9998	721	7051	0.7292
0.0010	10396	5280	34	0.8630	1111	12	0.9998	422	7650	0.8428
0.0015	9725	3377	33	0.8921	10000	10	0.9999	265	8044	0.7584
0.0020	9261	3573	29	0.7597	10000	5	1.0000	207	7965	0.7440

Thermodynamic parameters (ΔG: Gibbs energy, ΔH: enthalpy, and ΔS: entropy) are used to study the application of an adsorption process. The values of these parameters indicate what process

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will occur spontaneously. The thermodynamic parameters are investigated using the following equations: 47

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

$$Kc = CA/CS \quad (2)$$

$$\ln Kc = (\Delta S/R) - (\Delta H/RT) \quad (3)$$

Where Kc is the equilibrium constant, CA is the amount of contaminant adsorbed on the adsorbent at equilibrium (mol/L), and CS is the equilibrium contaminant concentration in the solution (mol/L). The positive ΔH value indicates an endothermic process. The positive ΔS value shows the increased randomness at the solid/solution interface during the adsorption of the contaminant onto the adsorbent. The negative ΔG values present the spontaneous adsorption [95, 96].

4.4. Regeneration of Adsorbent

Contaminant removal was investigated by various materials [94-101]. The adsorbent regeneration ability is a crucial issue for its practical applications. The regeneration of MIL-53/NH_2-Chitosan was studied via regeneration of the used adsorbent particles. In each cycle, after the removal process, the particles of the pollutant-adsorbed material were collected, washed with ethanol and dried before the reuse. The recovered adsorbent was reused in the next removal cycle (Fig. 4). The results showed that the MIL-53/NH2-Chitosan regeneration efficiency diminished slightly over the five runs of operations [94].

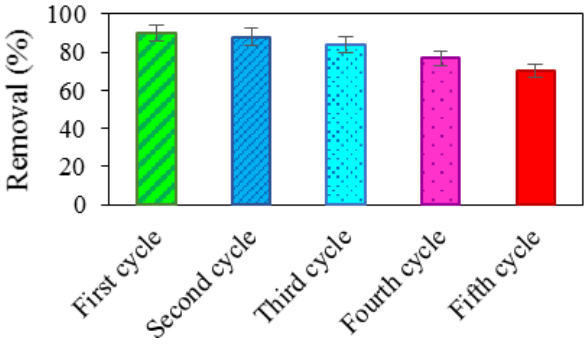

Fig. 4. Regeneration of MIL-53/NH_2-Chitosan after 5 cycles [94].

5. CONCLUSIONS, PROSPECTS, AND CHALLENGES

The use of waste moisture has led to widespread pollution of moisture by dangerous pharmaceuticals or pharmaceuticals and has raised concerns for human health, and the environment. Various experiments have been performed to reduce the presence of pharmaceuticals in moisture to protect the environment and the human body. To remove medicinal products from water, many methods were considered, including the adsorption method. In this study, we showed that there is no use of technology for the treatment of pharmaceutical wastewater to remove all pharmaceuticals before complete discharge. Pharmaceuticals have also been found in rivers and lakes. The adsorption process has been developed to demonstrate promising potential as the following generation of moisture treatment. The adsorption processes can be a great way to eliminate pharmaceutical products such as antibiotics, and analgesics at low concentrations. Various techniques have been considered in this study to reduce the toxicity of pharmaceuticals in moisture to humans through fresh drinking moisture or food, as well as on the environment (lakes, and rivers). This study also shows a combination of different treatment methods to achieve a high percentage of pharmaceutical elimination in a short time up to 100%. The adsorption method adsorption of several low-cost materials such as clay, activated carbon, and olive waste can be used as adsorbents.

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