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Review Article

Antibiotics Removal from Aqueous Solution and Pharmaceutical Wastewater by Adsorption Process: A Review

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ABSTRACT

With the widespread use of antibiotics, pharmaceutical effluents containing antibiotics have recently attracted wide attentions since it has potential adverse effects. Although the injuriousness of antibiotics is not so intuitive like other environmental pollution, residues of the antibiotic drug have become a seriously ignored problem. The abuse of antibiotics can damage the immune function of animals, when again infected, and then they need more antibiotics to treat. In this review article the authors presented up to-date development on the application of adsorption in the removal of antibiotics from aqueous solution. This review article provides extensive literature information about antibiotics, its classification and toxicity, various treatment methods, and antibiotics adsorption characteristics by various adsorbents. The effectiveness of various adsorbents under different physico-chemical process parameters and their comparative adsorption capacity towards antibiotics adsorption has also been presented. This review paper also includes the affective adsorption factors of antibiotics such as solution contact time, initial antibiotics concentration, adsorbent dosage, and temperature. The applicability of various adsorption thermodynamic models and isotherm models for antibiotics removal by wide range of adsorbents is also reported here.

Key words: Adsorbent, Antibiotics, Adsorption, Wastewater, Thermodynamic.

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INTRODUCTION

Antibiotics are widely used in the treatment of diseases in animals and humans, as well as applied in food rations in order to increase animal growth rates.[1-3] Antibiotics have high antimicrobial activity associated it's the aromatic structure containing the naphthol chemical group that is antibacterial.[4] However, approximately 50-90% of the doses of antibiotics administered in health treatment procedures is not absorbed by organisms and is eliminated by humans and animals in sewage systems.[5] These molecules have a complex chemical structure and the natural environmental and sewage conditions are not sufficient to decompose their chemical structure.[6] Thus, the amount of antibiotics accumulated in sewage can be a serious environmental problem.[7] Due to the chemical structure of antibiotics, they are act as a resistant to many chemicals, oxidizing agents, and heat, and are biologically non-degradable.[8] So it is difficult to removal the effluents, once released into the aquatic environment.[9] Many of the methods are available for the removal of pollutants from water, the most important of which are reverse osmosis, ion exchange, precipitation and adsorption.[10]

Adsorption is used as top quality treatment procedures for the removal of dissolved organic pollutants like antibiotics from industrial waste water.[11] Adsorption is defined as concentration of materials on the surface of solid bodies.[12] Adsorption is a surface phenomenon which deals primarily with the utilization of surface forces.[13] When a solution having absorbable solute, also called as adsorbate, comes into contact with a solid, called as adsorbent, with highly porous surface structure liquid-solid intermolecular forces of attraction causes the solute to be concentrated at the solid surface.[14] Adsorption is one of the unit operations in the chemical engineering processes used for the separation of industrial wastewater pollutants.[15]

The present state of the art on the application of adsorption in the removal of antibiotics from aqueous solution is presented in this paper. The main goal of this review article is to provide up-to-date development on the application of commercial activated carbon and various sustainable low cost alternative adsorbents such as agricultural solid waste (azolla,Lemna minor, canola and …) , industrial solid waste, agricultural by-products, and biomass based cost effective activated carbon, and various natural materials in the removal of antibiotics from aqueous phase. This review article also critically analyses the effectiveness of various adsorbents under different physicochemical process parameters and their comparative adsorption capacity is also presented. A compilation of relevant published data with respect to adsorption kinetics, isotherm models, thermodynamics and adsorption capacity under various process conditions along with important findings is presented here.

Although there are a couple of review articles such as low cost adsorbents for the removal of organic pollutants from wastewater,[16-18] but all are dealing with specific system only and also not relatively presented with up-to date information. Therefore, this present review article was undertaken in order to provide more comprehensive up-to-date and critical review information on the adsorption of various antibiotics from aqueous solution by wide range of adsorbents. The new aspect of this review article is to cover up-to-date research result presentation on various antibiotics adsorption and its adsorptive effectiveness in the removal of various antibiotics and also to critically analyzed and identify various operation conditions and their maximum adsorption capacity. Authors also tried to analyze the scattered available information on antibiotics adsorption by wide range of adsorbents since the last two decades.

METHODOLOGY

This systematic review aimed to study the antibiotics adsorption from aqueous solutions using different adsorbent. Studies published in electronic form in international database of Google Scholar, Scopus, PubMed, Web of Science and Science Direct from 2000 until end of the 2019 year, was investigated. Search using antibiotic, adsorption, efficacy and removal keywords with AND/OR operators in title and abstract was conducted.

RESULTS

Table 1 shows the reported studies on the effect of adsorbent dosage on the percentage of antibiotics removal. Table 2 showed the compilation of results of various studies on the effect of temperature on the antibiotics adsorption by various adsorbents. Table 3 shows the various isotherm results of antibiotics adsorption by various adsorbents. Table 4 also shows the maximum adsorption capacity (q_m) of different adsorbents in the field of antibiotic removal obtained from the Langmuir equation.

DISCUSSION

The term adsorption refers to the accumulation of a substance at the interface between two phases (liquid–solid interface or gas–solid interface).[103] The substance that accumulates at the interface is called adsorbate and the solid on which adsorption occurs is adsorbent.[104] Adsorption can be classified into two types: chemical sorption and physical sorption. Chemical adsorption or chemisorption is illustrated by the formation of strong chemical associations between molecules or ions of adsorbate to adsorbent surface, which is generally due to

Table 1: **The results of various reported studies on the effect of adsorbent dose on antibiotics adsorption by various adsorbents.**

Adsorbents	Antibiotics name	Adsorbent dosage	%Removal	References
Carbon materials	Amoxicillin	0.05-0.5 g/L	39.5-75.6	19
AC-vine wood	Cephalexin	0.1-1 g/L	44.5-87.2	20
Bentonite	Amoxicillin	0.25-2.5 g/L	41.8-94.6	21
AC-siris seed	Metronidazole	0.15-0.8 g/L	35.2- 64.2	22
AC	tetracycline	0.05-0.6 g/L	44.6-78.9	23
Montmorillonite	Penicillin G	0.4-2 g/L	64.8-98.2	24
AC-lignocellulosic	Cephalexin	0.15-0.7 g/L	21.9-92.1	25
NiO nanoparticle	Amoxicillin	0.1-0.5 g/L	54.3-87.9	26
AC- pyrolysis char	Tetracycline	0.0.2-1 g/L	71.5-91.8	27
AC commercial	Ibuprofen	0.25-1.5 g/L	61.4-97.4	28
Maize stalks	Tetracycline	0.5-4 g/L	54.6-94.2	29
Azolla filiculoides	Tetracycline	0.5-5 g/L	69.8-87.9	30
AC-macadamia shells	Tetracycline	0.3-1.5 g/L	71.4-87.2	31
Granular sludge	Oxytetracycline	0.4-2 g/L	39.8-79.8	32
Chestnut shell	penicillin G	0.5-3 g/L	28.7-81.4	33

Table 2: **The effect of temperature on the adsorption of Antibiotics using various adsorbents.**

Adsorbents	Antibiotics name	Temperature (K)	Results	References
Grapheme oxide magnetic	Tetracycline	273-323	Endothermic	34
Activated alumina	Metronidazole	273-303	Exothermic	35
Rice husk	Metronidazole	273-303	Endothermic	36
MWCNT	Metronidazole	288-318	Endothermic	37
Azolla Filiculoides	Cephalexin	293-333	Endothermic	38
mesoporous silica	Tetracycline	273-313	Exothermic	39
Cu-13X	Tetracycline	288-318	Endothermic	40
MWCNT	Tetracycline	283-313	Exothermic	41
Zero-valent iron	Tetracycline	273-313	Endothermic	42
AC-apricot nut shells	Tetracycline	273-323	Endothermic	43
AC commercial	Quinolone	283-313	Endothermic	44
NiO nanoparticle	Amoxicillin	288-318	Exothermic	45
CuO nanoparticles	Ciprofloxacin	288-323	Endothermic	46
MWCNT	Amoxicillin	273-323	Endothermic	47
Graphene oxide	Tetracycline	283-313	Exothermic	48

Table 3: Various isotherm studies of antibiotics adsorption by various adsorbents.

Adsorbents	Antibiotics name	studied isotherms	best isotherm	References
Chitosan	Amoxicillin	Langmuir-Freundlich-Temkin-D-R	Langmuir	49
Composite iron nano	Ibuprofen	Langmuir-Freundlich-Temkin-R-P	D-R	50
Carbon xerogel	Ciprofloxacin	Langmuir-Freundlich-BET-D-R	Langmuir	51
Polyoxometalates-NP	Tetracycline	Langmuir-Freundlich-Temkin-BET	BET	52
Fe_3O_4-graphene	Tetracycline	Langmuir-Freundlich-BET-D-R	D-R	53
Hydroxyapatite	Tetracycline	Langmuir-Freundlich-Temkin- D-R	D-R	54
Magnetic-MWCNT	Amoxicillin	Langmuir-Freundlich-Temkin-BET	Langmuir	55
Rice husk ash	Tetracycline	Langmuir-Freundlich-Temkin-BET	Temkin	56
MWCNT	Cephalosporins	Langmuir-Freundlich-Temkin-D-R	Langmuir	57
MWCNT	Tetracycline	Langmuir-Freundlich-Temkin-BET	Temkin	58
SWCNT	Ibuprofen	Langmuir-Freundlich-Temkin-R-P	Freundlich	59
Granular AC	Trimethoprim	Langmuir-Freundlich-Temkin- D-R	Langmuir	60
Coal fly ash	Norfloxacin	Langmuir-Freundlich-Temkin	Langmuir	61
Coal fly ash	Ciprofloxacin	Langmuir-Freundlich-Temkin- D-R	Langmuir	62
Activated sludge	Tetracycline	Langmuir-Freundlich-Temkin	Temkin	63
Canola	Amoxicillin	Langmuir-Freundlich-Temkin-R-P	Freundlich	64
Montmorillonite	Tetracycline	Langmuir-Freundlich-Temkin-BET	Langmuir	65

Table 4: Adsorption capacity of different adsorbents in the field of antibiotic removal.

Adsorbents	Antibiotics	Q_m(mg/g)	Ref	Adsorbents	Antibiotics	Q_m(mg/g)	Ref
NH_4Cl-AC	Amoxicillin	28.24	66	Iron particles	Ampicillin	41.17	67
Azolla filiculoides	Ampicillin	19.45	68	Aluminum oxide	Tetracycline	71.49	69
Fe–Mn oxide	Tetracycline	82.57	70	Goethite	Tetracycline	35.79	71
Activated sludge	Tetracycline	41.43	72	Chitosan	Tetracycline	28.64	73
$MnFe_2O_4$/AC	Tetracycline	73.96	74	Titania–silica	Tetracycline	41.72	75
Azolla -AC	Amoxicillin	98.47	76	Magnetic-CNT	Amoxicillin	148.2	77
Lemna minor	Penicillin G	29.47	78	Montmorillonite	Tetracycline	36.94	79
Kaolinite	Tetracycline	41.56	80	Illite	Tetracycline	38.74	81
Cay minerals	Tetracycline	35.68	82	Lemna minor algal	Tetracycline	36.47	83
Wheatstalks	Tetracycline	21.79	84	Corylus -AC	Ciprofloxacin	125.9	85
Azolla-AC	Sulfamethoxazole	119.7	86	Alumina-CNT	Tetracycline	264.8	87
Graphite	Tetracycline	84.35	88	Grapheme oxide	Tetracycline	114.6	89
Bntonite	Ampicillin	61.74	92	Palygorskite	Tetracycline	146.5	91
Silica	Tetracycline	48.14	92	Polyaniline-NP	Metronidazole	36.94	93
Zirconium Oxide-NP	Ciprofloxacin	219.8	94	Zeolite A	Clinoptilolite	181.2	95
siris seed pods- AC	metronidazole	81.46	96	NH_4Cl- AC	Tetracycline	92.17	97
Ativated carbons	Tetracycline	95.27	98	SiO_2-NP	Ciprofloxacin	84.91	99
Red mud	Ciprofloxacin	52.14	100	Plm bark	Amoxicillin	29.65	101
MAC	Ciprofloxacin	156.4	102	Cu-13X	Tetracycline	64.81	40
Fe_3O_4-graphene	Tetracycline	54.62	53	Canola	Amoxicillin	24.19	64

the exchange of electrons and thus chemical sorption generally is irreversible.[105] Physical adsorption or physisorption is characterized by weak Van der Waals intraparticle bonds between adsorbate and adsorbent and thus reversible in most cases[22]. Adsorption on most of the adsorbent including agricultural by-products is controlled by physical forces with some exception of chemisorption.[106] The main physical forces controlling adsorption are Van der Waals forces, hydrogen bonds, polarity, dipole–dipole ∏–∏ interaction, etc.[107] This process provides an attractive alternative for the treatment of polluted waters, especially if the sorbent is inexpensive and does not require an additional pretreatment step before its application.[24] As for environmental remediation purpose, adsorption techniques are widely used to remove certain classes of chemical contaminants from waters, especially those that are practically unaffected by conventional biological wastewater treatments.[25] Adsorption has been found to be superior to other techniques in terms of flexibility and simplicity of design, initial cost, insensitivity to toxic pollutants and ease of operation.[26] Adsorption also does not produce harmful substances.[28] Factors that influence the adsorption efficiency include adsorbate–adsorbent interaction, adsorbent surface area, adsorbent to adsorbate ratio, adsorbent particle size, temperature, pH and contact time and etc.

Adsorbent dosage is an important process parameter to determine the capacity of an adsorbent for a given amount of the adsorbent at the operating conditions.[108] Generally the percentage of antibiotics removal increases with increasing adsorbent dosage, where the quantity of sorption sites at the surface of adsorbent will increase by increasing the amount of the adsorbent.[109] The effect of adsorbent dosage gives an idea for the ability of a antibiotics adsorption to be adsorbed with the smallest amount of adsorbent, so as to recognize the capability of a antibiotics from an economical point of view.

Effect of temperature is another significant physico-chemical process parameter because temperature will change the adsorption capacity of the adsorbent.[108] If the amount of adsorption increases with increasing temperature then the adsorption is an endothermic process.[109] This may be due to increasing mobility of the antibiotics molecules and an increase in the number of active sites for the adsorption with increasing temperature.[110] Whereas the decrease of adsorption capacity with increasing temperature indicates that the adsorption is an exothermic process.[111] This may be due to increasing temperature decreasing the adsorptive forces between the antibiotics species and the active sites on the adsorbent surface as a result of decreasing the amount of adsorption.[112] Table 2 showed the compilation of results of various studies on the effect of temperature on the antibiotics adsorption by various adsorbents.

The adsorption isotherm is significant for the explanation of how the adsorbent will interact with the adsorbate and give an idea of adsorption capacity. They play an important role in understanding the mechanism of adsorption. The surface phase may be considered as a monolayer or multilayer. Several isotherm models are presented in the literature.[113] Langmuir and Freundlich models are the most widely used to describe the adsorption isotherm. The Langmuir adsorption isotherm model assumed that adsorption takes place at specific homogeneous sites within the adsorbent, and it has been used successfully for many adsorption processes of monolayer adsorption.[114] The Freundlich adsorption isotherm model considers a heterogeneous adsorption surface that has unequal available sites with different energies of adsorption.[115]

CONCLUSION

Is review article presented a wide range of adsorbents such as nanoparticles, carbon nano tubes, various agricultural adsorbent, activated carbon, biomass-based activated carbon, biosorbents, various other inorganic oxides, and clay minerals in the removal of antibiotics from aqueous solution. From the large number of published literature reviewed here, it is observed that the mechanism and kinetics of adsorption of antibiotics on various adsorbents depend on the chemical nature of the materials and various physico-chemical experimental conditions such as initial antibiotics concentration, adsorbent dosage, and temperature of the system. Therefore, these factors are to be taken into account while evaluating the adsorption capacity of different adsorbents. This review article also reveals that the Langmuir and Freundlich adsorption isotherm models are usually used to evaluate the adsorption capacity of various adsorbents.

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