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Chitosan sorbents used for dye removal

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ABSTRACT

The rapid increase in the amount of dye-containing wastewater produced in various industries is a major environmental concern and a challenge to existing conventional wastewater treatment systems. Among them, adsorption is considered to be one of the most efficient methods due to its high dye removal efficiency, easy operation, cost effectiveness, and recyclability of adsorbents. With this in mind, this article presents the characteristics of various types of dyes and sorbents used to remove them. Chitosan, methods of its modification and sorption efficiency of anionic and cationic dyes depending on the method of chitin/chitosan sorbent preparation are described in detail. The paper explains the mechanism of dye adsorption. In the second part of the article, mathematical models of adsorption – kinetic equations, mono- and multi-layers and isotherms flow models were collected and characterized.

Keywords: Dyes; Chitin; Chitosan; Modifications; Adsorption isotherms

1. Introduction

There are many known ways of industrial wastewater treatment containing dyes. Conventional methods used for their removal such as: chemical precipitation, photochemical degradation, membrane filtration, ozonation, Fenton reagents, advanced oxidation, ion exchange, UV irradiation, electrocoagulation or nanofiltration, ultrafiltration and reverse osmosis [1–6] are often uneconomical despite their high efficiency. Because of that, cheaper, more effective and safer for the environment (involving biosorbents – materials of biological origin) methods are being sought. As biosorbents, bacteria, algae and fungi directly obtained from nature are used; waste products from the industry of microorganisms raised specially only for the purpose of biosorption. Regardless of the origin, biosorbents should characterize with high adsorption effectiveness of dyes from the solutions and ease of desorption with the use of cheap desorbents.

A practical use of the process of adsorption for the dye removal from wastewater still encounters a number of restrictions. The most important is lack of universal adsorbent, which regardless of the type of the dye (anionic, cationic) would show high effectiveness and could be used in flow conditions. What plays an important role are also costs related to the separation of the adsorbent in the dust or flake form from the treated solution and mechanical durability allowing multiple use of the adsorbent in continuous cycles of sorption and desorption.

These disadvantages might be eliminated for example through various modifications of chitosan. Chitosan has numerous valuable physicochemical properties, such as: biocompatibility, biodegradability, non-toxicity, ability to create polycations in acidic environment, ease in modification, high affinity to dyes, hydrophilicity, ability to create films etc. [7]. These features allow chitosan to be used in various branches of the industry, that is, in environmental protection, processes of water treatment, producing textiles cosmetics food, plastics, pharmaceutics, etc. [8,9].

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Chitosan, however, has also a number of physicochemical properties which limits its use. This polymer swells in water (especially in acidic environment), what reduces its mechanical durability, dissolves in acidic solutions but does not dissolve in many solvents. In order to change the adverse properties of chitosan and expand the possibilities of use, among others, to increase: its solubility in water, the ability to bind various substances and chemical and mechanical strength, but decrease its ability to dissolve in acidic environment, it is subjected to various processes of chemical and physical modification. The modification of the chitosan molecule through the insertion of the functional group or crosslinking reactions (linking macromolecular chains with each other) leads to the formation of chitosan derivatives with better properties: greater adsorption capacity and resistance to adsorption under extreme conditions. In case of grafting reactions, additional functional groups added on chitosan increase the number of adsorption sites, and consequently, the adsorption capacity.

The scope of this work was to characterize the types of most frequently used dyes in various branches of the industry and types of chitosan adsorbents used for the dye removal. The mechanisms of dye binding on chitosan adsorbents were discussed and mathematical equations used for the description of kinetics and most used models of adsorption were presented.

2. Dyes

The process of fabrics dyeing was already known in ancient times, but it wasn't until the 19th century that the rapid development of the textile industry led to an increase in the demand and use of dyes.

Dyes are compounds that have the ability to intensively absorb and convert the energy of electromagnetic radiation in the visible and near UV range and near infrared. Dyes are used to transfer these properties to other substances. The practical use and specificity of dyes depends on to the type of transformation of absorbed energy. The dye molecules contain chromophore groups, thanks to which these compounds selectively absorb electromagnetic radiation in the visible range and auxochromes giving dyes affinity to dyed materials. The chromophore group is a configuration of radicals forming double bonds [10]. In their structure, the dyes contain chromophore groups such as: azomethine –N=CH–, carbonyl =C=O, azo –N=N–, ethylene =C=C=, nitrosic –N=O, azox $–N=N(\rightarrow O)–$ as well as functional groups such as amino $–NH_2$, sulfone $–SO_3H$, hydroxyl –OH, and nitric $–NO_2$. The chemical classification of dyes is based on the type of chromophore group (Table 1).

There are over 100,000 dyes available in the industry [11,12]. The textile industry is the major consumer of dyes. The mass of synthetic colorants used by this industry is estimated at the level of $1 \div 3 \times 10^5$ tons, in comparison with the total annual consumption of around 7×10^5 tons worldwide [13,14].

Dyes can be classified according to various criteria, such as chemical structure, application class or use [15]. Due to the method of dyeing, dyes are divided into: direct, acid, alkaline, reactive, ice, ladle, mortar, and others. Dyes, can also be divided into anionic (direct, acidic, and reactive azo), cationic (basic), and nonionic (suspension/dispersion) [16].

The classification of dyes is presented in Table 2.

3. Dye adsorption

High cost of sorbents and difficulties in regeneration result in a number of restrictions still present in the practical use of adsorption for the wastewater treatment. The reason is most often the high cost of the adsorbent, disproportionate to the economic effects of treatment. The hope for the change of this situation is finding cheap adsorbent, which would be easily regenerated and allow to be used multiple times or which would have price low enough to not need to be regenerated, and the used adsorbent would not be harmful for the environment.

The search concentrates on the obtaining of effective, cheap, and easily available sorbents. The literature overview shows, that for the adsorption of dyes some types of the active carbon [17,18], fly ashes [20,21], kaolinite, bauxite, and diatomaceous earth [22], dolomite [23], modified peat resin [24], rice husks, areca nut husk [25,26], eucalyptus bark [27] lemongrass leaf [28], wastes from the galvanizing industry [29], peat [30], sawdust [31,32] as well as chitin and chitosan [33–42] were used. The use of industrial waste from various industries for wastewater treatment can not only solve the problem of waste utilization, but also be economically beneficial.

Sorption is a general term describing two processes: absorption, which involves the penetration of one substance from one phase inside another in a process of diffusion, as well as adsorption, consisting of binding the removed contamination (adsorbates) on the surface of adsorbent.

The process of adsorption can be divided into the chemical adsorption or so-called chemisorption, where binding forces are so strong, that the process is practically irreversible and physical adsorption, where forces are weaker (e.g., Van der Waals forces) and the process in reversible. During the physical adsorption, the particles of adsorbate are transiently placed in active sites on the surface of the adsorbent. Being in the zone of influence of these centers they can move along the surface of the adsorbent. In case of physical adsorption, the adsorbate can be easily removed from the surface of the adsorbent. With chemisorption the removal of contamination is hard and requires much more drastic measures [15,43].

Practically every solid body might be a potential adsorbent, however, its physical and chemical properties have crucial influence on the course of the adsorption process. Because the adsorption is a surface process, its effectiveness depends on the surface area of the adsorbent available for adsorbate. Usually it is assumed, that it consists of the following stages: (1) external diffusion where the adsorbate molecules/ions migrate from the bulk of the solution to the material surface (bulk diffusion); (2) diffusion in the pores of the adsorbent, the molecules diffuse through the boundary layer to the surface of the material (film diffusion); (3) intraparticle diffusion – the adsorbate diffuses from the surface to the interior of the particle (pore diffusion); (4) finally the molecules reacts with the active sites on the surface of the material (physical adsorption, chemical reaction) [44].

Table 1
Classification of dyes by type of chromophore group

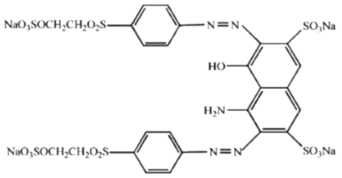
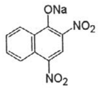
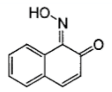
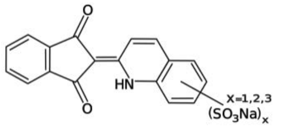
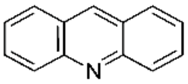
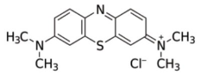
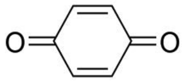
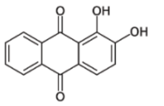
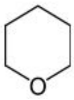
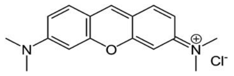
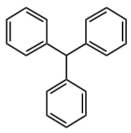
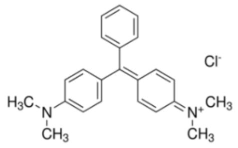
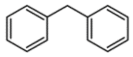
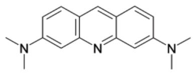
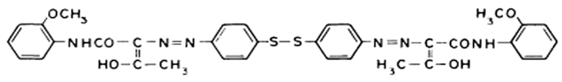
Dye class	Chromophore group	Dye example
Azo	–N=N–	 Reactive Black 5
Nitric	$–NO_2$	 Acid yellow 24
Nitrosic	–NO–	 Pigment Green 8
Polyene	(–C=C–)n	 Food Yellow 13
Azine		 Methylene Blue
Chinoid	$O=C_6H_4=O$ 	 Alizarin red
Pyrone		 Pyronin G
Triphenylmethane		 Basic Green 4
Diphenymethane		 Basic Orange 14
Disulfide	–S–S–	 4,4′diamino-2,2′dichloro diphenyl disulfide

Table 2
Classification of dyes

Dyes									
Soluble in water					Insoluble in water				
Anionic			Cationic	Direct	Sulfuric	Ladle	Disperse	Created directly on the material	
Reactive	Acidic	Chrome-acidic						Azo	Oxidized

The process of adsorption lasts in particular conditions up until the moment, when the concentration of the substance dissolved in the solution will reach the dynamic equilibrium with the concentration of this substance on the surface of the adsorbent. The time needed for the reach of the equilibrium state depends on the size of the particles of the dissolved substance and its susceptibility for the process of sorption. For big particles this time is higher. Adsorption is a selective process, which means that one component might be adsorbed better than the other. The selectivity results mostly from the affinity of the dissolved substance to the adsorbent and the solubility of the substance in the solvent.

3.1. Chitosan

An important feature of chitosan is its deacetylation degree (DD). Although the heterogeneous alkaline deacetylation of chitin would appear to be a simple one, it is still being studied and modified [45,46]. The conditions of deacetylation mainly involve the use of 50% (wt./wt.) NaOH and the relatively high temperatures of 100°C–120°C. There has been a trend towards lower temperatures and reduction in the amounts of NaOH used, together with a considerable amount of research into enzymatic deacetylation using chitin deacetylases [47].

Higher deacetylation degree causes higher sorption effectiveness [48,49]. The process of deacetylation of chitin is based on the exchange of acetamide groups (cementing the structure of chitin) for amino groups, influencing the change in the chemical and physical properties. Higher content of amino groups (higher degree of deacetylation) causes chitosan to be a polymer of higher solubility and results in its wider range of use, for example, through the possibility of using chitosan in the form of beads or membranes. Chitosan as one of the few biopolymers shows basic character. Chitosan owes this property to the presence of free groups ($-NH_2$). Thanks to having amino functional groups, chitosan shows very good sorption ability in relation to anionic dyes [49,50].

The use of chitin and chitosan as adsorbents is beneficial from economical point of view. Both chitin and chitosan are adsorbents, that can be found in nature in significant amounts, and obtaining them does not require large financial outlays. Chitin is a material obtained from natural resources, while obtaining chitosan is associated with the use of cheap chemical reagents. This versatility allows to use both chitin and chitosan in various forms such as: flakes, gel, various types of beads or fibers, and membranes.

Chitosan easily subjects to the process of biodegradation and is a non-toxic compound. What is more, it shows number of other properties such as: high chemical reactivity, high bioactivity, high stability, and high sorption capacity. The sorption properties of chitosan are used for the removal of the dye, heavy metals, and other toxic substances causing water contamination.

Chitosan drew special attention as complexing compound due to low costs compared to activated carbon and numerous functional groups – amino and hydroxyl. Biosorbents basing on chitin and chitosan are an effective material and have very high affinity to a lot of classes of dyes, what is proven by numerous literature positions [51–55].

The research upon chitosan as an adsorbent for the acidic dye removal were presented by numerous authors [33,40,51,56–59] and obtained sorption capacities exceeding 1,000 mg/g of sorbent confirm its usefulness for the dye removal. The use of chitosan is restricted by its solubility in acidic environment, what makes it impossible to use at low pH and requires chemical and physical modification. One of the most often used solutions might be crosslinking. Biosorbents based on chitosan after crosslinking are insoluble in acidic and basic solutions as well as in organic solvents, more resistant to high temperature and low pH. Chemical modification of chitosan might be also used for the improvement of effectiveness and selectiveness of removed dyes, the control of diffusion properties and the lowering of sorption sensitivity for the conditions of the environment.

3.1.1. Chitosan as sorbent

Chitosan sorbents might be in the form of dust, flakes, or hydrogel beads. The advantage of chitosan in the form of flakes or dust is relatively low time of production and low cost. These sorbents have dense structure. Polysaccharide chains of chitosan in the form of flakes closely adhere to each other, impeding the sorbate reaching the inside of the sorbent. Serious downside of chitosan in these two forms is difficulty in separation of sorbent form purified solution. These sorbents hardly sediment and the use of dense strainers is effective only in case of flakes.

Chitosan in the form of hydrogel beads is more expensive and harder to produce. The advantage of this form of sorbent is loose and at the same time elastic structure. Polysaccharide chains of hydrogel structure are apart from each other and the spaces between them are filled with water. This system allows the sorbates to enter into the inside of the sorbent as well as more effective use of sorption centers. Contrary to chitosan in the form of flakes and beads, the sorption of contamination on hydrogel beads is in most part the result of absorption.

The advantage of chitosan in the form of hydrogel beads is its ease of application and removal of the sorbent from the solution after the process of treatment. The use of chitosan in the form of hydrogel gives an additional possibility of simple modification of the sorbent as well as incorporation into the structure of the bead other materials, for example, sawdust or fly ashes.

The disadvantage of chitosan as a sorbent is its lability in acidic solutions ($pH < 5$). At low pH most of the amino groups of chitosan become protonated. Positively charged polysaccharide chains of chitosan repels each other what results in the swelling of the sorbent. At $pH < 5$ the electrostatic effect is strong enough to dissolve chitosan and make it lose the possibility of sorption [60]. This makes it hard to use chitosan for the treatment of the solutions with low pH. The commercial use of chitosan for the contamination removal in wide range of pH requires the stabilization of the sorbent structure.

The modification of chitosan through crosslinking leads to the fixation of biosorbent and allows to use it in acidic environment. During crosslinking, the crosslinking agent reacts with at least two polysaccharide chains of chitosan, creating a bridge between them. Joined with each other chitosan chains create durable three dimensional web, thanks to which the crosslinked chitosan gains higher mechanical durability and stays stable in wide range of pH [61].

The properties of crosslinked chitosan depend largely on the amount of crosslinking agent as well as its type. Depending on the crosslinking agent used, crosslinking by covalent or ionic bonds is distinguished.

The covalent crosslinking of chitosan is a chemical reaction, that results in the creation of permanent covalent bonds between the crosslinking agent and polysaccharide chains. The covalent crosslinking bond might be any compound having at least two functional groups capable of the reaction of condensation with the polymer. The most used covalent crosslinking agents include dialdehydes such as glutaraldehyde or glyoxal [62]. Aldehyde groups of dialdehydes react with first order amino groups of chitosan creating Schiff alkalines. However, the reactions of dialdehydes with hydroxyl groups also cannot be excluded. Among the popular crosslinking agents there are also compounds having epoxy groups such as epichlorohydrin or diglycidyl ether of ethylene glycol (Quetol 651). During crosslinking the epoxy ring of the compound is broken and the reaction of condensation usually occurs with the participation of chitosan hydroxyl groups. Covalent crosslinking of chitosan is an irreversible reaction [63]. Covalently crosslinked chitosan sorbent stays stable even in a very acidic environment (pH 1). A serious disadvantage of covalent crosslinking of chitosan is, however, the negative influence on the mechanical durability of the sorbents. Covalently crosslinked chitosan is not flexible and brittle, making it more susceptible to destruction [64].

During ion crosslinking, between the crosslinking agent and the chitosan chains, the electalenic (ionic) bonds are formed. Ionic crosslinking agent in aqueous solution has the opposite charge to the one of the modified polymer. The electrostatic attraction of polymer chains to the ionic crosslinking agent produces the ionic crosslinking effect.

Ionic crosslinking agent in terms of chitosan might theoretically be every compound having at least two functional groups, creating negative charge in water, for example, $-COO^-$, $-SO_3^-$, and $-O-PO_3^{2-}$. Citrates and polyphosphates are the most commonly used ionic crosslinking agents. Sodium oxalate and sulfosuccinic acid can also be included to this group. The polysaccharide of chitosan connected with ion bonds are responsible for compact structure of the sorbent. Ionically crosslinked chitosan in comparison with covalently crosslinked chitosan is less durable in acidic solutions (pH 2–3). The structure of ionically crosslinked chitosan hydrogel is however more elastic and resistant to mechanical damage.

The methods of chitosan modifications include also methods involving the introduction of side groups into the substitution chain, methods leading to chain elongation, and depolymerization methods.

The modification of chitosan particle might also be based on the inclusion of functional groups, what leads to the creation of chitosan derivatives of better properties – adsorption capacity increases, chitosan can be used in wider range of pH. Grafting might change physical and mechanical properties, but does not affect valuable properties such as biocompatibility and biodegradability. Through grafting of chitosan, the diffusion properties can be controlled and the sensitivity of adsorption to environmental conditions might be reduced [48].

A large group of chitosan derivatives makes up the derivatives containing in their structure phosphorus or sulfur. One of the most frequently tested derivatives of chitosan is carboxymethylochitosan [65]. This polymer contains two types of functional groups in its chain: basic amino groups and acidic carboxyl groups.

In case of grafting, additional functional groups added to the chitosan molecule increase the number of sorption sites. The properties of grafted copolymers depend largely on the chemical character of side chains, their length (average particle mass) and their number in chain (content in copolymer) [66].

The method of improvement of chitosan sorption capability might also be impregnation. For this purpose, surfactants can be used. They might join with chitosan throughout electrostatic interactions, giving the chitosan and surfactant complexes as a result [67]. Use of surfactants might improve electrostatic interactions, because they create chemical bound with chitosan with the use of hydrophilic groups of surfactants and chitosan. Hydrophobic interactions might also take place between chitosan backbone and hydrophobic part of surfactant, what would increase sorption capacity of chitosan [68]. It has significant meaning in case of cationic dyes sorption. Because chitosan has cationic character, the adsorption capability of cationic dyes is low due to the repulsion of the charge between chitosan and dye. Impregnation with anionic surfactant introduces anionically charged groups on the surface of the bead what allows to bind dyes of cationic character.

4. Mechanism of the dye adsorption

The explanation of the mechanism of dye adsorption on chitin and chitosan is connected with the fact, that interactions of various kind such as ion exchange, hydrophobic attraction, physical adsorption, and others might happen simultaneously. The differences in the adsorption degree might result from the differences in the chemical structure of the dyes.

Adsorption of anionic dyes most efficiently occurs at low pH. Amino groups of chitosan were protonated due to the reaction:

$$\text{R–NH}_2 + \text{H}^+ \leftrightarrow \text{R–NH}_3^+ \quad (1)$$

Simultaneously, the dissociation of the reactive dye particle:

$$\text{D–SO}_3\text{Na} \rightarrow \text{D} - \text{SO}_3^- + \text{Na}^+ \quad (2)$$

As a result the process of adsorption takes place through the electrostatic interactions between the two molecules: R–NH_3^+ and D–SO_3^-.

$$\text{R–NH}_3^+ + \text{D–SO}_3^- \leftrightarrow \text{R–NH}_3^+ - \text{SO}_3^- - \text{D} \quad (3)$$

The increase in pH of the solution decreases the electrostatic interactions as a result of the deprotonation of amino groups. In strongly basic environment deprotonation of hydroxyl groups and anion dye binding is as follows:

$$-\text{CH}_2\text{OH} + \text{OH}^- \leftrightarrow \text{CH}_2\text{O}^- + \text{H}_2\text{O} \quad (4)$$

$$-\text{CH}_2\text{O}^- + \text{D–Cl} \rightarrow -\text{CH}_2\text{–O–D} + \text{Cl}^- \quad (5)$$

In case of cationic dyes adsorption increases along with the increase in the pH. Amino groups protonated at low values of pH, at which chitosan is positively charged, cause strong coulomb repulsion between protonated chitosan and cationic dye because of positive charge of basic dyes. The increase in the pH weakens strongly repulsive forces and causes the amino groups of chitosan to deprotonate. The adsorption od basic dyes increases:

$$-\text{CH}_2\text{OH} + \text{OH}^- \leftrightarrow \text{CH}_2\text{O}^- + \text{H}_2\text{O} \quad (6)$$

$$-\text{CH}_2\text{O}^- + \text{D–N}^+ \rightarrow -\text{CH}_2\text{–O–D–N} \quad (7)$$

The process of desorption from chitin and chitosan is as follows:

$$\text{R–NH}_3^+ - \text{D–SO}_3^- + \text{OH}^- \rightarrow \text{R–NH}_2 + \text{D–SO}_3^- + \text{H}_2\text{O} \quad (8)$$

$$-\text{CH}_2^- - \text{O–D–N}^+ + \text{H}_3\text{O} \rightarrow -\text{CH}_2\text{OH} + \text{D–N}^+ + \text{H}_2\text{O} \quad (9)$$

5. Sorption of anionic and cationic dyes on various chitosan sorbents

5.1. Anionic dyes

Comparison of sorption capacities of various chitosan sorbents in relation to anionic dyes is presented in Table 3.

According to the literature data (Table 3), the most preferred form of sorbent is hydrogel bead. The efficiency of dyes sorption on sorbents in powder, flake or fiber form is much lower. It may be related to the spatial structure of the sorbent and its crystalline structure. Densely packed polysaccharide chitosan chains are a difficult barrier for dyes to penetrate. The main mechanism for binding dyes on chitosan sorbents with a "dense structure" is the adsorption process occurring mainly on the surface. In case of hydrogel, the dye has the ability to penetrate the sorbent structure more easily. The adsorption process is therefore accompanied by a process of diffusion into the structure. For this reason, the use of sorption centers of the sorbent is much larger, which leads to the greater sorption capacity.

Research shows that crosslinking of chitosan sorbents can have a large impact on their sorption capacity in relation to anionic dyes. The ionic cross-linking agents such as sodium citrate and sulfosuccinic acid are the examples of compounds that increase the sorption capacity of chitosan. It might be proven by comparing the sorption efficiency of anionic dyes on CIT-CHz, SSA-CHz, and CHz. Effect of pentasodium tripolyphosphate on the sorption efficiency of anionic dyes was low. Covalent crosslinking of chitosan with glutaraldehyde limited the sorption capacity of the obtained sorbent. The negative effect of GLA on the sorption properties of CHz has also been described by other authors [69]. In contrast to glutaraldehyde, cross-linking of chitosan with epichlorohydrin in most cases had a positive effect on the sorption of anionic dyes [41,54,70].

5.2. Cationic dyes

Analysis of the data presented in the Table 4 indicates the relationship between the form of chitosan sorbent and the sorption efficiency of cationic dyes. The dye sorption efficiency on chitosan powder is greater than on chitosan in the form of flakes. However, as with anionic dyes, the best form of sorbent turned out to be hydrogel beads. This relationship is particularly visible in case of BV3, BB9, and BY37 dyes.

The influence of chitosan crosslinking on the sorption of cationic dyes is inconsiderable. The optimal pH of sorption of cationic dyes within the pH range of 6–10 suggests that the use of crosslinked chitosan is economically unjustified. Crosslinked chitosan remains stable at pH 6–10 and crosslinking of sorbent only increases its costs.

6. Mathematical description of adsorption

The practical use of adsorption requires mathematical description of the process. While modeling the process of adsorption, it is assumed that there will be simplifications. In case of adsorption models the equations have empirical character. The adsorption kinetics is described with equations of pseudo-first and pseudo-second order and equilibrium models. Adsorbents have a finite number of active sites, so it is possible to determine the maximum sorption capacity.

The adsorption kinetics depends on interactions between adsorbate and adsorbent and the state in which the system is in. The speed of adsorption of dissolved substance determines the adsorption time, which can be calculated form the analysis of the process kinetics. In 1898, Lagergren presented first order kinetic equation of adsorption of oxalic and malonic acid on activated carbon. It was the first equation describing adsorption in liquid-solid system based on

Table 3
Comparison of sorption capacities of various chitosan sorbents against anionic dyes

Nr	Chitosan sorbent	Anionis dye		Dye weight (mg/mol)	Sorption capacity (mg/g)	Sorption time (h)	pH sorption	Temperarure (°C)	References
1	Chitosan (powder)	Acid Green 25	AG25	622.6	**43.0**	0.5	2	25	[71]
2	Chitosan (powder)	Acid Orange 10	AO10	452.4	**95.0**	2	7	25	[72]
3	Chitosan (powder)	Acid Red 73	AR73	556.6	**121.8**	>1 h	6	25	[73]
4	Chitosan (powder)	Acid Violet 5	AV5	678.6	**160.0**	12	–	25	[74]
5	Chitosan (powder)	Acid Blue 9	AB9	792.9	**210.0**	3	3	25	[75]
6	Chitosan (powder)	Acid Yellow 25	AY25	549.6	**220.0**	12	–	25	[74]
7	Chitosan (powder)	Acid Blue 113	AB113	681.7	**250.0**	12	–	25	[74
8	Chitosan (powder)	Food Yellow 3	FY3	452.4	**295.0**	1	3	25	[56
9	Chitosan (powder)	Acid Yellow 23	AY23	534.4	**350.0**	–	3	25	[75]
10	Chitosan (powder)	Reactive Black 5	RB5	991.8	**440.0**	12	–	25	[74]
11	Chitosan (powder)	Food Red 17	FR17	496.4	**529.0**	8	6.6	25	[52]
12	Chitosan (powder)	Acid Green 25	AG25	622.6	**645.1**	24	4	25	[52]
13	Chitosan (powder)	Acid Red 18	AR18	604.5	**693.2**	24	4	25	[52]
14	Chitosan (powder)	Acid Red 73	AR73	566.5	**728.2**	24	4	25	[52]
15	Chitosan (powder)	Acid Black 1	AB1	616.5	**800.0**	12	–	25	[74]
16	Chitosan (powder)	Acid Green 25	AG25	622.6	**850.0**	12	–	25	[74]
17	Chitosan (powder)	Acid Orange 10	AO10	452.4	**922.9**	24	4	25	[52]
18	Chitosan (powder)	Acid Orange 12	AO12	350.3	**973.3**	24	4	25	[52]
19	Chitosan (powder)	Reactive Black 5	RB5	991.8	**1,000.0**	-	–	25	[76]
20	Chitosan (flakes)	Acid Yellow 73	AY73	376.3	**0.2**	–	3	30	[77]
21	Chitosan (flakes)	Reactive Red 141	RR141	1,774.2	**67.9**	–	2–5	20	[78]
22	Chitosan (flakes)	Reactive Blue 19	RB19	626.5	**76.9**	–	2	–	[79]
23	Chitosan (flakes)	Reactive Violet 5	RV5	735.6	**122.0**	2	4	25	[80]
24	Chitosan (flakes)	Reactive Blue 81	RB81	808.5	**123.0**	2	4	25	[81]
25	Chitosan (flakes)	Reactive Yellow 81	RY81	667.4	**126.0**	2	4	25	[81]
26	Chitosan (flakes)	Reactive Red 141	RR141	1,774.2	**156.0**	–	2–5	60	[78]
27	Chitosan (flakes)	Congo Red	CR	696.7	**173.0**	8	4	25	[82]
28	Chitosan - GLA (crosslinked flakes)	Reactive Blue 222	RB222	1,357.5	**199.0**	–	–	30	[83]
29	Chitosan - GLA (crosslinked flakes)	Reactive Yellow 145	RY145	1,026.2	**188.0**	–	–	30	[83]
30	Chitosan - GLA (crosslinked flakes)	Reactive Red 222	RR222	940.2	**339.0**	–	–	30	[83]
31	CHs (non-crosslinked beads)	Reactive Red 120	RR120	1,470	**4.4**	8	5	25	[84]
32	CHs (non-crosslinked beads) – 0.4 mm	Reactive Black 5	RB5	991.8	**91.5**	24	6.7	30	[85]
33	CHs (non-crosslinked beads)	Congo Red	CR	696.7	**93.4**	10	6	20	[86]
34	CHs (non-crosslinked beads) – 0.4 mm	Reactive Black 5	RB5	991.8	**97.1**	24	8.5	30	[85]
35	CHs (non-crosslinked beads) – 0.4 mm	Reactive Black 5	RB5	991.8	**100.0**	24	9.5	30	[85]

(continued)

Table 3 Continued

Nr	Chitosan sorbent	Anionis dye		Dye weight (mg/mol)	Sorption capacity (mg/g)	Sorption time (h)	pH sorption	Temperarure (°C)	References
36	CHs (non-crosslinked beads) – 1.7 mm	Reactive Black 5	RB5	991.8	**103.1**	24	6.7	30	[85]
37	CHs (non-crosslinked beads) – 0.4 mm	Reactive Black 5	RB5	991.8	**111.1**	24	6.7	45	[85]
38	CHs (non-crosslinked beads) – 0.2 mm	Reactive Black 5	RB5	991.8	**119.0**	24	6.7	30	[85]
39	CHs (non-crosslinked beads) – 0.4 mm	Reactive Black 5	RB5	991.8	**130.0**	24	6.7	60	[85]
40	CHs (non-crosslinked beads)	Acid Blue 25	AB25	416.4	**178.6**	–	4	27	[87]
41	CHs (non-crosslinked beads)	Reactive Black 5	RB5	991.8	**103.1**	<1 h	6.7	30	[49]
42	CHs (non-crosslinked beads)	Reactive Black 5	RB5	991.8	**201.9**	–	6	30	[88]
43	CHs (non-crosslinked beads)	Acid Red 37	AR37	524.4	**357.1**	–	6	27	[87]
44	CHs (non-crosslinked beads)	Reactive Blue 19	RB19	626.5	**398.0**	24	–	25	[89]
45	CHs (non-crosslinked beads dried)	Acid Orange 51	AO51	860.8	**494.0**	72	6.9	30	[90]
46	CHs (non-crosslinked beads)	Reactive Black 5	RB5	991.8	**605.0**	–	5	25	[70]
47	CHs (non-crosslinked beads)	Acid Orange 51	AO51	860.8	**656.0**	72	6.9	30	[90]
48	CHs (non-crosslinked beads)	Reactive Black 5	RB5	991.8	**753.8**	–	5	35	[70]
49	CHs (non-crosslinked beads)	Reactive Yellow 176	RY176	1,025.3	**928.0**	4	2	25	[91]
50	CHs (non-crosslinked beads)	Reactive Red 189	RR189	828	**950.0**	–	6	30	[41]
51	CHs (non-crosslinked beads)	Reactive Red 222	RR222	940.2	**1,026.0**	>6 h	–	30	[92]
52	CHs (non-crosslinked beads dried)	Reactive Red 222	RR222	940.2	**1,214.0**	72	6.1	30	[90]
53	CHs (non-crosslinked beads)	Reactive Red 189	RR189	828	**1,189.0**	48	6	30	[54]
54	CHs (non-crosslinked beads)	Reactive Red 222	RR222	940.2	**1,498.0**	72	6.1	30	[90]
55	CHs (non-crosslinked beads)	Reactive Black 5	RB5	991.8	**1,506.0**	24	4	25	[93]
56	CHs (non-crosslinked beads)	Reactive Red 222	RR222	940.2	**1,965.0**	>3 h	6.5	25	[94]
57	CHs (non-crosslinked beads)	Reactive Black 5	RB5	991.8	**2,307.3**	504	4	25	[93]
58	GLA-CHs (crosslinked beads)	Acid Red 37	AR37	524.4	**166.7**	–	6	27	[87]
59	GLA- CHs (crosslinked beads)	Reactive Yellow 145	RY145	1,026.2	**885.0**	–	–	30	[83]
60	GLA-CHs (crosslinked beads)	Reactive Black 5	RB5	991.8	**974.7**	24	3	25	[93]
61	GLA- CHs (crosslinked beads)	Reactive Blue 222	RB222	1,357.5	**1,009.0**	–	–	30	[83]
62	GLA-CHs (crosslinked beads)	Reactive Orange 16	RO16	617.5	**1,060.0**	3	4	25	[95]
63	GLA- CHs (crosslinked beads)	Reactive Black 5	RB5	991.8	**1,459.9**	168	3	30	[96]
64	GLA- CHs (crosslinked beads)	Reactive Red 222	RR222	940.2	**1,653.0**	–	–	30	[83]
65	GLA-CHs (crosslinked beads)	Reactive Black 5	RB5	991.8	**2,157.7**	504	3	25	[93]
66	GLA- CHs (crosslinked beads)	Reactive Orange 16	RO16	617.5	**1,852.4**	168	3	30	[96]
67	GLA- CHs (crosslinked beads)	Indigo carmine	IND	466.4	**303.0**	2		30	[117]
68	GLA-CHs (crosslinked beads with Fe)	Reactive Red 120	RR120	1,470	**290.7**	1	3.6	25	[98]
69	ECH-CHs (crosslinked beads)	Reactive Black 5	RB5	991.8	**1,430.0**	24	3	25	[93]
70	ECH-CHs (crosslinked beads)	Reactive Black 5	RB5	991.8	**1,754.1**	120	3	30	[97]

71	ECH-CHs (crosslinked beads)	Reactive Red 189	RR189	828	**1,834.0**	–	3	30	[41]
72	ECH-CHs (crosslinked beads)	Reactive Red 189	RR189	828	**1,936.0**	48	3	30	[54]
73	ECH-CHs (crosslinked beads)	Reactive Black 5	RB5	991.8	**2,043.1**	–	3	35	[71]
74	ECH-CHs (crosslinked beads)	Reactive Black 5	RB5	991.8	**2,083.2**	504	3	25	[93]
75	ECH-CHs (crosslinked beads)	Reactive Black 5	RB5	991.8	**515.7**	–	5	25	[70]
76	SSA-CHs (crosslinked beads)	Reactive Black 5	RB5	991.8	**2,004.9**	504	3	25	[93]
77	SSA-CHs (crosslinked beads)	Reactive Black 5	RB5	991.8	**2,065.7**	24	3	25	[93]
78	CIT-CHs (crosslinked beads)	Reactive Black 5	RB5	991.8	**2,208.8**	24	3	25	[93]
79	CIT-CHs (crosslinked beads)	Reactive Black 5	RB5	991.8	**2,085.3**	504	3	25	[93]
80	TPP-CHz (crosslinked beads)	Reactive Black 5	RB5	991.8	**1,247.3**	24	3	25	[93]
81	TPP-CHz (crosslinked beads)	Reactive Black 5	RB5	991.8	**2,163.5**	504	3	25	[93]
82	H_2SO_4-CHs (crosslinked beads with H_2SO_4)	Acid Blue 25	AB25	416.4	**102.5**	–	4	27	[87]
83	H_2SO_4-CHs (crosslinked beads with H_2SO_4)	Acid Red 37	AR37	524.4	**139.3**	–	6	27	[87]
84	GLA-CHs – (nanoparticles)	Acid Yellow 23	AY23	534.4	**292.0**	3	3	25	[99]
85	ECH-CHs with palm oil (composite)	Reactive Blue 19	RB19	626.5	**416.7**	48	6	30	[51]
86	Chitozan with PVA (beads)	Congo Red	CR	696.7	**467.3**	36	4	25	[100]
87	GLA-CHs – (nanoparticles)	Acid Blue 9	AB9	792.9	**475.6**	3	3	25	[99]
88	CHs (beads with polyethyleneimine)	Reactive Black 5	RB5	991.8	**709.3**	–	6	30	[88]
89	ECH-CHs (modified with benzaldehyde)	Reactive Blue 19	RB19	626.6	**991.3**	–	6	25	[101]
90	CHs (beads with polyacrylamide)	Reactive yellow 86	RY86	667.4	**1,000.0**	6	4	30	[102]
91	ECH-CHs (modified with benzaldehyde) modyfikowany benzaldehydem)	Reactive Yellow 15	RY15	634.6	**1,174.6**	–	6	25	[101]
92	GLA-CHs modified with N-vinyl	Remazol Red 3BS	RR	1,085.8	**1,219.0**	24	2	25	[103]
93	CHs (beads with polyacrylamide)	Reactive violet 5R	RV5	735.6	**1,428.6**	6	4	30	[102]
94	ECH-TPP-CHs (double crosslinked beads)	Reactive Blue 15	RB15	1,283	**722.0**	10	4	30	[104]
95	ECH-TPP-CHs (double crosslinked beads)	Metanil Yellow	MY	375.5	**1,334.0**	6	4	30	[104]
96	ECH-TPP-CHs (double crosslinked beads)	Reactive Yellow 86	RY86	596	**1,911.0**	–	3	30	[55]
97	ECH-TPP-CHs (double crosslinked beads)	Acid Orange 7	AO7	350.3	**1,940.0**	–	4	30	[55]
98	ECH-TPP-CHs (double crosslinked beads)	Acid Red 14	AR14	502.4	**1,940.0**	–	3	30	[55]
99	ECH-TPP-CHs (double crosslinked beads)	Acid Orange 12	AO12	350.3	**1,954.0**	–	3	30	[55]
100	ECH-TPP-CHs (double crosslinked beads)	Reactive Red 2	RR2	615.3	**2,422.0**	–	3	30	[55]
101	ECH-TPP-CHs (double crosslinked beads)	Reactive Yellow 2	RY2	873	**2,436.0**	–	4	30	[55]
102	ECH-TPP-CHs (double crosslinked beads)	Reactive Blue 2	RB2	774.2	**2,498.0**	–	3	30	[55]
103	Chitosan – (scaffold)	FD&C Yellow 6	FY6	452.4	**788.0**	–	6	25	[105]
104	Chitosan – (scaffold)	Acid Yellow 23	AY23	534.4	**1,078.0**	–	6	25	[105]
105	Chitosan – (scaffold)	Acid Red 27	AR27	604.5	**1,552.0**	–	6	25	[105]
106	Chitosan – (scaffold)	FD&C Blue 2	FDCB2	466.4	**3,032.0**	–	6	25	[105]
107	Chitosan – (scaffold)	Food Red 17	FR17	496.4	**3,316.0**	–	6	25	[106]

(continued)

Table 3 Continued

Nr	Chitosan sorbent	Anionis dye		Dye weight (mg/mol)	Sorption capacity (mg/g)	Sorption time (h)	pH sorption	Temperarure (°C)	References
108	Chitosan (foil/membrane)	FD&C Blue 2	FDCB2	466.4	**153.3**	2	7	25	[107]
109	Chitosan (foil/membrane)	FD&C Blue 2	FDCB2	466.4	**154.8**	2	7	25	[108]
110	Chitosan (foil/membrane)	Acid Red 18	AR18	604.5	**239.0**	2	7	25	[107]
111	Chitosan (fiber)	Reactive Blue 19	RB19	626.6	**454.5**	1.5	3.5	25	[106]
112	Chitosan (fiber)	Acid Orange 7	AO7	350.3	**1,678.0**	–	4	25	[109]
113	Chitosan-TiO_2 (composite)	Benzopurpurin 4 B	BP4B	724.7	**5.4**	24	4	45	[110]
114	Chitosan-TiO_2 (composite)	Benzopurpurin 4 B	BP4B	724.7	**11.7**	24	4	25	[110]
115	Chitosan-bio-silicate (composite)	Acid Red 88	AR88	400.4	**25.8**	4	3	25	[111]
116	Chitosan-kaolin-Fe_2O_3 (composite)	Oranż metylowy	MO	327.3	**34.9**	8.3	2.9	37	[112]
117	Chitosan with lignin (composite 1:1)	Reactive Blue 19	RB19	626.5	**111.1**	–	2	–	[79]
118	Chitosan-IPN (composite)	Oranż Metylowa	MO	327.3	**202.0**	>6	2	25	[113]
119	Chitosan – methyl methacrylate(composite)	Reactive Blue 81	RB81	808.5	**204.0**	2	4	25	[81]
120	Chitosan-IPN (composite)	Acid Orange 7	AO7	350.3	**243.3**	>6	2	25	[113]
121	Chitosan- methyl methacrylate (composite)	Reactive Yellow 81	RY81	667.4	**263.0**	2	4	25	[81]
122	Chitosan with polyaniline (composite)	Reactive Blue 19	RB19	626.5	**303.0**	1	3	25	[114]
123	Chitosan with polyaniline (composite)	Congo Red	CR	696.7	**322.6**	1	3	25	[114]
124	Chitosan with polyaniline (composite)	Coomassie Brilliant Blue	CBB	826.0	**357.1**	1	3	25	[114]
125	Chitosan-IPN (composite)	Acid Red 18	AR18	604.5	**358.4**	>6	2	25	[113]
126	Chitosan with nanotubes (composite)	Congo Red	CR	696.7	**370.4**	10	5	30	[115]
127	Chitosan-karboxymetyl (composite)	Congo Red	CR	696.7	**375.9**	10	7	30	[116]
128	Chitosan- methyl methacrylate (composite)	Reactive Violet 5	RV5	735.6	**384.0**	2	4	25	[81]
129	Chitosan- clay (composite)	Reactive Red 222	RR222	940.2	**1,912.0**	>3 h	6.5	25	[94]
130	Xanthated chitosan/cellulose sponge	Congo Red	CR	696.7	**289.9**	10	6	30	[118]
131	Citosan-sodium alginiate (composite foam)	Acid Black 172	AB172	993.7	**817.0**	84	3	25	[119]

ECH - epichlorohydrin; GLA - glutaraldehyde; TPP - trimethylopropane triglycidyl ether; CIT - sodium citrate; SSA - sulfosuccinic acid

Table 4
Comparison of sorption capacities of various chitosan sorbents against cationic dyes

Nr	Chitosan sorbent	Cationics dye		Dye weight (mg/mol)	Sorption capacity (mg/g)	Sorption time (h)	pH sorp- tion	Temperarure (°C)	References
1	Chitosan (powder)	Basic Yellow 1	BY1	318.9	**25.1**	2	–	25	[120]
2	Chitosan (powder)	Basic Violet 3	BV3	408.0	**31.7**	72	–	25	[121]
3	Chitosan (powder)	Basic Blue 9	BB9	319.9	**44.2**	2	–	25	[120]
4	Chitosan (powder)	Basic Blue 66	BB66	589.3	**47.9**	2	–	25	[120]
5	Chitosan (flakes)	Basic Violet 3	BV3	408.0	**28.5**	4	8	25	[122]
6	Chitosan (flakes)	Basic Yellow 37	BY37	359.5	**254.0**	24	10	25	[91]
7	Chitosan – $NaCNBH_3$ (powder)	Basic Blue 3	BB3	359.9	**166.5**	0.7	3	25	[123]
8	CHs (non-crosslinked beads)	Basic Green 4	BG4	364.9	**35.5**	2	3	25	[124]
9	CHs (non-crosslinked beads)	Basic Violet 3	BV3	408.0	**76.9**	72	7	30	[125]
10	CHs (non-crosslinked beads)	Basic Green 4	BG4	364.9	**93.6**	5	8	30	[126]
11	CHs (non-crosslinked beads)	Basic Blue 9	BB9	319.9	**99.0**	-	-	25	[127]
12	CHs (non-crosslinked beads)	Basic Yellow 37	BY37	359.5	**137.0**	4	10	25	[91]
13	CHs (non-crosslinked beads)	Basic Blue 9	BB9	319.9	**202.0**	72	6.9	30	[90]
14	CHs (non-crosslinked beads)	Basic Violet 10	BV10	479.0	**240.0**	2	6	25	[128]
15	CHs (non-crosslinked beads)	Basic Blue 3G	BB3	359.9	**254.0**	24	10	25	[89]
16	CHs (non-crosslinked beads)	Basic Yellow 37	BY37	359.5	**589.0**	24	10	25	[91]
17	GLA-CHs (crosslinked beads)	Basic Green 4	BG4	364.9	**19.3**	2	3	25	[124]
18	GLA-CHs (crosslinked beads)	Basic Green 4	BG4	364.9	**56.1**	2	5	25	[124]
19	GLA- CHs (crosslinked beads)	Malachite Green	MG	365.0	**714.3**	2	–	–	[117]
20	CHs (dried crosslinked beads)	Basic Blue 9	BB9	319.9	**222.0**	72	6.9	30	[90]
21	Chitosan intercalated with montmorillonite	Basic Yellow 1	BY1	318.9	**45.9**	2	–	25	[120]
22	Chitosan intercalated with montmorillonite	Basic Blue 9	BB9	319.9	**48.9**	2	–	25	[120]
23	Chitosan intercalated with montmorillonite	Basic Blue 66	BB66	589.3	**49.2**	2	–	25	[120]
24	CHs (beads with fly ash)	Basic Violet 10	BV10	479.0	**70.0**	2	6	25	[128]
25	CHs (beads with polyacrylamide)	Basic Blue 9	BB9	319.9	**106.7**	>1 h	5.5	25	[129]
26	Chitosan modified with ethyl acrylate	Basic Red 18	BR18	426.3	**158.7**	2	11	40	[127]
27	Chitosan modified with ethyl acrylate	Basic Blue 41	BB41	482.6	**217.4**	2	9	40	[130]
28	CHs (beads formed in SDS)	Basic Blue 9	BB9	319.9	**226.2**	-	–	25	[130]
29	CHs (beads with sawdust)	Basic Violet 10	BV10	479.0	**270.0**	2	6	25	[128]
30	CHs (beads with polyacrylamide)	Basic Yellow 37	BY37	359.5	**314.0**	24	10	25	[91]
31	CHs (beads with acrylic acid)	Basic Yellow 37	BY37	359.5	**556.0**	24	10	25	[91]
32	Chitosan-TiO_2 (komposite)	Basic Blue 9	BB9	319.9	**0.5**	24	8	45	[129]
33	Chitosan-TiO_2 (kompositet)	Basic Blue 9	BB9	319.9	**1.2**	24	8	25	[129]
34	Chitosan – (film/foil)	Red No 3	R3	879.9	**194.6**	2	7	25	[108]
35	Xanthated chitosan/cellulose sponge	Methylene Blue	MB	319.9	**213.2**	2	7	30	[118]
36	Chitosan-sodium alginiate – composite foam	Methylene Blue	MB	319.9	**1,488**	11	3	25	[119]

the volume of the solid, unlike the kinetic equation using the concentration of the solution and adsorption capacity of the adsorbent. The Lagergren equation is called the pseudo-first-order equation [131].

The graphic dependence lnqt = f(t) is a straight line and indicates, that the reaction is of pseudo-first-order. In 1995, Ho proposed kinetic equation of pseudo-second-order connecting reaction rate constant and the amount of ions adsorbed on the surface of adsorbent, instead of the relation to the concentration of adsorbent substance. In model presented by Ho, the speed of occupying available active sites by adsorbate is proportional to the number of unoccupied sites squared. The number of occupied sites is proportional to adsorbed ions of the sorbate [132].

The graph presenting the dependence t/q_t = f(t), created based on experimental data is a straight line with a slope of $1/q_e$ and at the intersection with the coordinate axis at $1/(kq_e^2)$.

The order of reaction and reaction rate constants were presented in the Table 5. The determination of reaction rate constants with a graphic method from linearized forms of kinetic equations consists of plotting in a rectangular coordinate system the concentration values on the y-axis and the time of reaction values on the x-axis. If the graph is a straight line, then the reaction is of n-order, and the reaction rate constant k can be determined from the slope of the line.

A commonly recognized form of adsorbate separation description (between solution and adsorbent phases) is to present the amount of dissolved substance adsorbed per mass unit of adsorbent as a function of concentration of dissolved in solution substance at equilibrium state at constant temperature. This is called adsorption isotherm, which can be presented as:

$$Q = \mathrm{f}(C)_T \tag{10}$$

where Q is the amount of adsorbed adsorbant per 1 g of adsorbent, C is the concentration in the phase of adsorbate, and T is the temperature.

Brunauer divided the isotherms describing the equilibrium of physical adsorption into five types (Fig. 1).

- Type I – is the equivalent of the Langmuir adsorption isotherm and is characterized by monotonic approaching to border adsorption, which is a complete monomolecular layer.
- Type II – characteristic for physical adsorption and results from multilayer adsorption.
- Type III – not very widespread, in this type, the adsorption heat is smaller or equal the heat of condensation of pure adsorbate ($Q_{\mathrm{ads}} < Q_{\mathrm{con}}$).
- Types IV and V – connected with types II and III and with the fact, that the maximum of adsorption is obtained at lower pressures than the pressure of saturated steam p_0. It is assumed, that what occurs there is so-called capillary condensation.

Isotherm of type I is used for dimensioning microporous adsorbents. Type II and III isotherms are obtained for adsorbents with a broad pore distribution. Type IV indicates the formation of two layers on the surface, and type V occurs with high intramolecular interactions [133].

6.1. Adsorption isotherms

6.1.1. Langmuir isotherm

The Langmuir theory is based on the assumption, that even at the complete coverage of the surface, the number of adsorbed particles cannot be bigger than the number of active sites. The resulting adsorption layer isolates the action of adsorption forces, which prevents the formation of subsequent layers [134].

In the conditions of low concentrations of adsorbate bC_e << 1 then $q_e = q_{\max} \cdot bC_e$. The adsorption is directly proportional to the concentration of the solution. When the concentration of adsorbent is very high $q_e \sim q_{\max}$, at the beginning, the adsorption is rising proportionally to the concentration, and then slows down, to reach constant value at the very high concentration of adsorbate (graphically the "plateau" effect is obtained). Constants b and $q_{\max}$ determined from the Langmuir equation reflect the nature of the adsorbent and allow comparison of adsorption. The b constant determines how steep is the isotherm, so the affinity of the adsorbent to adsorbate. If, after the linearization of the Langmuir isotherm, the broken line is obtained, it indicates that the substance is bound on adsorbent by more than one type of active sites. In double model of Langmuir it was assumed, that the surface of the adsorbent is energetically heterogenous and has adsorption sites of various energy of bonding of adsorbate particles. Each type of active sites is described by the Langmuir isotherm equation [135]. Total sorption capacity ($q_{\max}$) equals the sum of maximum adsorption capacity determined in active sites of first (I) and second (II) type ($q_{\max} = q_{\max1} + q_{\max2}$). Constants b_1 and b_2 characterize the adsorption affinity of dye to active sites of respectively first and second type and correspond to the inverse of the equilibrium concentration of the adsorbate at which the adsorption capacity is more than half the maximum capacity $q_{\max1}$ or $q_{\max2}$. Higher values of b constant indicate the increase of the adsorbate affinity to the active sites of the adsorbent.

6.1.2. Freundlich isotherm

For the description of the adsorption equilibrium indicating the heterogenous character of the surface, the Freundlich equations are used [136]. The Freundlich isotherm is an empirical equation indicating, that the presence of sites bound with free adsorption energy decreases exponentially with the increase of free energy [137].

If $n = 1$, all the sites are equal and the adsorption depends linearly on concentration of adsorbate in equilibrium solution. The more heterogenous surface, the closer the value of n is to zero. The Freundlich isotherm provides realistic description of adsorption through the organic matter, because it includes the diversity of active sites.

6.1.3. Redlich–Peterson isotherm

Redlich and Peterson connected the assumptions of Langmuir and Freundlich models into a single equation,

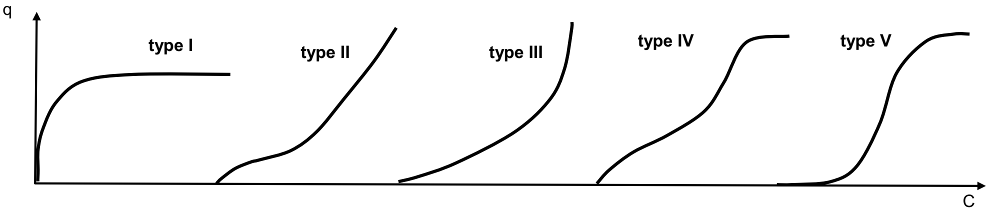


Fig. 1. Types of isotherms of physical adsorption: q is the amount of adsorbate bound per mass unit of adsorbent; C is the concentration of adsorbate in liquid phase.

which modifies the Langmuir and Freundlich isotherms. The model of Redlich–Peterson isotherm determines the equilibrium of adsorption in wide range of concentrations. It might be used because of its elasticity in case of homogenous surface as well as heterogenous systems. The Redlich–Peterson equation describes isotherms of I and III type [138].

6.1.4. Sips isotherm

Sips isotherm is a connection between the Langmuir and Freundlich isotherm [139]. It is used to describe heterogeneous adsorption systems, avoiding the disadvantages of the Freundlich isotherm associated with the increasing concentration of adsorbate. At low concentrations of adsorbate the Sips isotherm is reduced to Freundlich isotherm. At high, it has the form of monolayer adsorption isotherm of Langmuir. The parameters of the equation depend on the operation conditions, such as the change of temperature and pH as well as concentration of the adsorbate [140].

6.1.5. Dubinin–Radushkevich isotherm

Dubinin–Radushkevich isotherm describes the adsorption in small pores or so-called micropores with diameters comparable with the sizes of the adsorbate particle. Adsorption in small pores is much stronger than on chemically identical flat surface (bigger amount of adsorbate atoms interacts closely with adsorbent) and is most often described with the use of Dubinin–Radushkevich equation [141,142].

6.1.6. Radke–Prausnitz isotherm

Radke–Prausnitz isotherm is an experimental three parameter adsorption isotherm used most commonly for the description of adsorption of organic substances from diluted aqueous solutions. The equation of Radke–Prausnitz isotherm is not a monolayer isotherm – it does not comply with Langmuir model – is used usually in case of adsorption on strongly heterogenous adsorbents, most commonly on active carbons. The Radke–Prausnitz equation for low concentrations comes down to the linear dependence, and for high concentrations to Freundlich isotherm, whereas in case of $n = 0$, it becomes the Langmuir isotherm. This model provides good fit in wide range of concentrations [143].

The purpose of the creators was to modify the Freundlich isotherm in such a way, that for low concentrations it resembled Henry isotherm. It was achieved by adding to the inverse of Freundlich isotherm the inverse of Henry isotherm, what causes that both components of the equation smoothly pass into each other. Similar properties to = Radke–Praunitz isotherm in the range of low concentrations has the Tóth isotherm, however, for the high concentrations the Tóth equation displays monolayer features. The Radke–Praunitz isotherm might be, similarly to most of the other equations, used for the description of gas and vapor adsorption.

6.1.7. Hill isotherm

The Hill equation suggests defining the binding of different adsorbates on homogeneous adsorbents. Adsorption, as assumed in this model, is a phenomenon that can adapt to the prevailing conditions with the possibility of binding the adsorbate in one place on the molecule [144].

6.1.8. Tóth isotherm

Tóth isotherm describes physical adsorption and corresponds to the asymmetric quasigaussian distribution of adsorption energy extended toward low adsorption energy. It might be considered as a special case of four – parameter isotherm GL, in which the parameter m describing the shape of function from the site of high energies equals $m = 1$.

This isotherm for low pressures might be approximated with the use of Henry isotherm, which is linear in logarithmic coordinates, for high pressures its course is

Table 5
Summary of kinetic equations

Reaction order	Equation	Constant
Zero-order	$-\frac{dC_t}{dt} = k_0$	k_0
First-order	$-\frac{dC_t}{dt} = k_1C_t$	k_1
Second-order	$-\frac{dC_t}{dt} = k_2C_t^2$	k_2
Pseudo-first-order	$\frac{dq_t}{dt} = k_{p1}\left(q_e - q_t\right)$	k_{p1}
Pseudo-second-order	$\frac{dq_t}{dt} = k_{p2}\left(q_e - q_t\right)^2$	k_{p2}

Table 6
Summary of adsorptions isotherms

Isotherm	Equation	Constant
Langmuir	$q_e = \frac{q_{\mathrm{calc}} \cdot b \cdot C_e}{1 + b \cdot C_e}$	b, q_{calc}
Langmuir 2	$q_e = \frac{q_{\mathrm{calc1}} \cdot b_1 \cdot C_e}{1 + b_1 \cdot C_e} + \frac{q_{\mathrm{calc2}} \cdot b_2 \cdot C_e}{1 + b_2 \cdot C_e}$	b_1, q_{calc1} b_2, q_{calc2}
Freundlich	$q_e = K_F C_e^{1/n}$	K_F, n
Redlich–Peterson	$q_e = \frac{K_R \cdot C_e}{1 + a_R \cdot C_e^g}$	K_R, a_R, g
Sips	$q_e = \frac{K_s \cdot C_e^{\beta_S}}{1 + a_s \cdot C_e^{\beta_S}}$	K_s, a_s, β_s
Dubinin-Radushkevich	$q_e = q_s \cdot \exp\left(-k_{\mathrm{DR}} \varepsilon^2\right)$ $E = \frac{1}{\sqrt{2 \cdot k_{\mathrm{DR}}}}$ $\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right)$	k_{DR}, ε, q_s
Temkin	$q_e = \left(\frac{RT}{b_T}\right) \cdot \ln\left(A_T \cdot C_e\right)$	A_T, b_T
Flory–Huggins	$\frac{\theta}{C_0} = K_{\mathrm{FH}} \left(1 - \theta\right)^{n_{\mathrm{FH}}}$	K_{FH}, θ, n_{FH}
Hill	$q_e = \frac{q_{S_H} \cdot C_e^{n_H}}{1 + K_H \cdot C_e^{n_H}}$	q_{SH}, n_H, B, n
Toth	$q_e = \frac{K_T \cdot C_e}{\left(a_T + C_e\right)^{\frac{1}{t}}}$	K_T, a_T
Koble–Corrigan	$q_e = \frac{A \cdot C_e^n}{1 + B \cdot C_e^n}$	A, B, n
Khan	$q_e = \frac{q_s \cdot b_K \cdot C_e}{\left(1 + b_K \cdot C_e\right)^{a_K}}$	a_K, b_K, q_s
Radke–Prausnitz	$q_e = \frac{a_{\mathrm{RP}} \cdot r_R \cdot C_e^{\beta_R}}{a_{\mathrm{RP}} + r_R \cdot C_e^{\beta_R - 1}}$	a_{RP}, r_R, β_R

b, b_1, b_2 - Langmuir isotherm constant (L/mg); K_F – Freundlich isotherm constant (mg/g) (dm^3/g); n - related to adsorption capacity; K_R – Redlich–Peterson isotherm constant (L/g); a_R - Redlich–Peterson isotherm constant (1/mg); g - Redlich–Peterson isotherm exponent; a_S - Sips isotherm model constant (L/mg); K_s - Sips isotherm model constant (L/g); β_S - Sips isotherm model exponent; k_{DR} - Dubinin–Radushkevich isotherm constant (mol^2/kJ^2); ε - Dubinin–Radushkevich isotherm constant; E - mean free energy (kJ/mol); R - universal gas constant (8.314 J/mol K); T - temperature (K); A_T - Tempkin isotherm equilibrium binding constant (L/g); b_T – Tempkin isotherm constant; K_{FH} - Flory–Huggins isotherm equilibrium constant (L/g); n_{FH} – Flory–Huggins isotherm model exponent; θ - degree of surface coverage; K_H - Hill constant; n_H - Hill cooperativity coefficient of the binding interaction; q_{sH} - Hill isotherm maximum uptake saturation (mg/L); K_T – Toth isotherm constant (mg/g); a_T - Toth isotherm constant (L/mg); A - Koble–Corrigan isotherm constant (L^{n}mg^{1-n}/g); B - Koble–Corrigan isotherm constant (L/mg)^n, a_K - Khan isotherm model exponent; b_K - Khan isotherm model constant; a_{RP} - Radke–Prausnitz isotherm model constant; r_R - Radke–Prausnitz isotherm model constant; β_R - Radke–Prausnitz isotherm model exponent; C_e - equilibrium concentration (mg/L); C_0 - adsorbate initial concentration (mg/L); C_s - adsorbate monolayer saturation concentration (mg/L); q_e - amount of adsorbate in the adsorbent at equilibrium (mg/g); $q_{e,\mathrm{calc}}$ - calculated adsorbate concentration at equilibrium (mg/g); $q_{e,\mathrm{meas}}$ - measured adsorbate concentration at equilibrium(mg/g); q_s - theoretical isotherm saturation capacity (mg/g); Q_0 - maximum monolayer coverage capacities (mg/g).

close to Langmuir–Freundlich isotherm. After the formal change of pressure *p* to concentration *c*, the Tóth isotherm might be used for the description of adsorption from diluted solution (e.g., aqueous solution of organic substance). Multilayer adsorption may also be included [145].

6.1.9. Temkin isotherm

The Temkin isotherm is an experimental two parameter equation of the adsorption isotherm describing heterogenous solid body. The Temkin equation is not a monolayer isotherm (is not compatible with the Langmuir isotherm model). This isotherm presents continuous, endless (unlimited with minimal or maximal energy) energy distribution of adsorption sites. The assumption above (unlimited energy distribution) is not very realistic, as well as the constancy in probability density in all adsorption sites. The model ignores very low and very high concentrations [146].

The equations for adsorption isotherms and constants are presented in Table 6.

6.2. Multilayer adsorption isotherms

In 1938, Brunauer, Emmett, and Teller presented multilayer isotherm (BET) assuming buildup of further layers of adsorbate on a monolayer. The basic assumption of the BET theory is the possibility of use of Langmuir equation for the description of each adsorption layer. According to the theory the adsorbate particle falling into the occupied active site does not leave it, but creates short term adsorption complex [147].

In the model it is assumed, that the adsorbate particles adsorb in a localized way, what means that they cannot move across the surface because of strong adsorbate–adsorbent interactions. Thanks to the adsorbate–adsorbate interactions particles can adsorb "perpendicularly" on already adsorbed particles, etc. A model formulated this way usually predicts adsorption higher than observed experimentally. In general case, a 3-parameter equation is obtained (restriction of adsorption layer thickness to *n*-layers, e.g., through restrictions resulting from the pore sizes or the sizes of intergranular spaces). After the simplifying assumption, that the number of adsorption layers might not be limited by anything, a classical 2-parameter BET equation is obtained.

Despite the not very realistic assumptions, this model achieved remarkable success thanks to its simplicity, becoming the base of method for marking the surface of solid bodies.

Other models of multilayer adsorption are: Frenkel–Halsey–Hill (FHH) MacMillan–Teller (MET) (Table 7).

6.3. Flow models

In practice, for the prediction of breakdown curves, simplified adsorption dynamics models are being used [148–151].

The analytical solution of Thomas model is based on non-linear Langmuir isotherm as well as kinetics or pseudo-second order reaction [149,152,153]. The Borhart and Adams solution is based on the assumption of rectangular isotherm [154]. The Yoon and Nelson model assumes, that the probability of adsorption and desorption of each adsorbed particle is proportional, it assumes symmetry of breakdown curves in relation to stoichiometric point and does not require specific data considering adsorbate and adsorbent [148,153]. The Clark model is based on the conception of mass transfer in connection with the Freundlich isotherm as well as the piston fluid flow in adsorber with the omission of the phenomenon of axial dispersion [150]. The Wolborska model assumes, that adsorption in first period is controlled by the mechanism of diffusion in film [148]. The Yan model is based on Thomas equation and was developed as a modified dose-response model, in order to precisely predict

Table 7
Summary of multilayer adsorptions isotherms

Isotherm	Equation	Constant
Brunauer–Emmett–Teller BET	$q_e = \dfrac{q_s \cdot C_{\text{BET}} \cdot C_e}{\left(C_s - C_e\right) \cdot \left[1 + \left(C_{\text{BET}} - 1\right) \cdot \left(\dfrac{C_e}{C_s}\right)\right]}$	C_{BET}, q_s
Frenkel–Halsey–Hill FHH	$\ln\left(\dfrac{C_e}{C_s}\right) = -\dfrac{\alpha}{\text{RT}}\left(\dfrac{q_s}{q_e \cdot d}\right)^r$	α, q_s
MacMillan–Teller MET	$q_e = q_s \left[\dfrac{k \cdot C_e}{\ln\left(C_s - C_e\right)}\right]^{\frac{1}{3}}$	k, q_s

C_{BET} - BET adsorption isotherm relating to the energy of surface interaction (L/mg); d - interlayer spacing (m); $q_{s\text{H}}$ - Hill isotherm maximum uptake saturation (mg/L); r - inverse power of distance from the surface; R - universal gas constant (8.314 J/mol K); T - temperature (K); α - Frenkel–Halsey–Hill isotherm constant (Jmr/mol) with r is the sign of inverse power of distance from the surface; k - MacMillan–Teller (MET) isotherm constant; q_s - theoretical isotherm saturation capacity (mg/g); C_e - equilibrium concentration (mg/L); C_s - adsorbate monolayer saturation concentration (mg/L).

Table 8
Dynamic models

Dynamic models	Equation	Constant
Thomas model	$\frac{C}{C_0}=\frac{1}{1+\exp\left(k_{\mathrm{TH}}\cdot q_0\cdot m/Q-k_{\mathrm{TH}}\cdot C_0\cdot t\right)}$	k_{TH}, q_0
Yoon–Nelson model	$\frac{C}{C_0}=\frac{1}{1+\exp\left[k_{\mathrm{YN}}(t_{1/2}-t)\right]}$	k_{YN}, $t_{1/2}$
Adams–Bohart model	$\frac{C_t}{C_i}=\exp\left(k_{\mathrm{AB}}C_i t-k_{\mathrm{AB}}q_m\frac{Z}{w}\right)$	k_{BA}, q_m
Wolborska model	$\frac{C}{C_0}=\exp\left(\frac{\beta_L\cdot C_0\cdot t}{q_m}-\frac{\beta_L\cdot H}{w}\right)$	β_L, q_m
Yan model	$\frac{C}{C_0}=\frac{1}{1+\exp\left(k_{\mathrm{TH}}\cdot q_0\cdot m/Q-k_{\mathrm{TH}}\cdot C_0\cdot t\right)^{k_Y\cdot C_0/Q}}$	k_Y, q_0
Clark model	$\frac{C}{C_0}=\frac{1}{(1+A_C\cdot\exp\left(-r_C\cdot t\right)^{1/(r_c-t)}}$	A_C, r_C

k_{TH} – rate constant in Thomas model, (m^3/kg s); m – adsorbent mass, (g); k_{YN} – rate constant in Yoon and Nelson model, (1/s); $t_{1/2}$ – time to reach half of the adsorbent saturation (s); k_{BA} – rate constant in Bohart and Adams model, (m^3/kg s); β_L – mass transfer coefficient, H – height of bed in the column, (m); q_m – maximum volumetric sorption capacity, (kg/m^3); k_Y – rate constant in Yan model, (m^3/kg s); A_C – Clark model constant, (–); r_C – rate constant in Clark model, (1/s); Q – volumetric liquid flow rate, (m^3/s); q_0 – sorption capacity of the adsorbent (kg/kg); t – time, (s); w – linear velocity of liquid flow in the column, (m/s); (1/s); C_0, C – inlet and outlet concentration of adsorbate, (kg/m^3)

the concentration in the beginning and end part of the breakdown curve [149] (Table 8).

These models require the knowledge of parameters such as initial concentration of adsorbate, volumetric liquid flow rate, linear velocity of fluid in the column and mass, height, density, and porosity of the bed [148,153]. Despite restrictions, they are widely used for the predictions of breakdown curves, both for adsorption in the gas phase and in liquid phase.

7. Summary

The adsorbents based on chitosan might soon replace the currently used adsorbents, for example, active carbons. However, in order to do that, they should not require much treatment, and need to be profitable, accessible, environmentally friendly, and most importantly, effective.

In order to achieve high sorption capacity of chitosan adsorbents, the modification of the chitosan particle is necessary. There are many ways of chitin and chitosan modification. The change in the properties of chitosan sorbent might be obtained through the reaction of crosslinking – covalent or ionic (the connecting of macroparticle chains with each other), grafting (insertion of additional functional groups), or impregnation which leads to the creation of chitosan materials of higher sorption capability, better mechanical properties or allows to carry out the process of adsorption in wider range of pH.

For the description of experimental data, many adsorption isotherms, taking into account various parameters of the process, are used. Most of the experimental results are described with Langmuir, Freundlich, or BET models but there are many more adsorption isotherms, which might be better suited to the varying conditions of the process of adsorption.

Based on carried out research, it can be stated, that the chitosan might meet up most of these expectations due to its special features such as low cost, high sorption capability and selectivity, versatility, environment friendliness, and biodegradability.

Chitin and chitosan might be attractive adsorbents for the removal of contamination from water and wastewater in the process of adsorption because of high supply, low cost, high sorption capability, and simplicity of modification as well as environmental friendliness and easiness of regeneration.

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