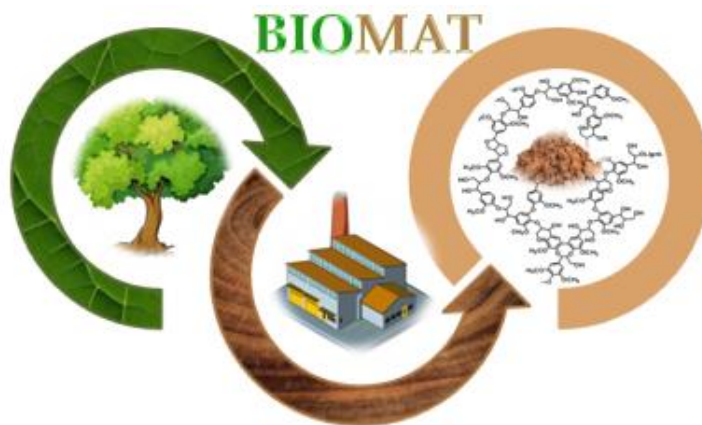


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Part 2

Obtaining polymeric materials with the addition of lignin, testing, and evaluation of their properties

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1. Synthesis of polymer microspheres with added lignin by the suspension polymerization method

Introduction

Polymers (gr. *poly* = "many", gr. *meros* = "parts") are a group of macromolecular compounds whose molecules are composed of repeating elements (units) called mers, bonded together in sufficient numbers to possess properties that do not change significantly because of the addition or removal of one or more mers. Polymer macromolecules can be formed by the joining (polymerization) of many molecules called monomers. The number of mers present in a macromolecule is the so-called degree of polymerization (Figure 1.1).

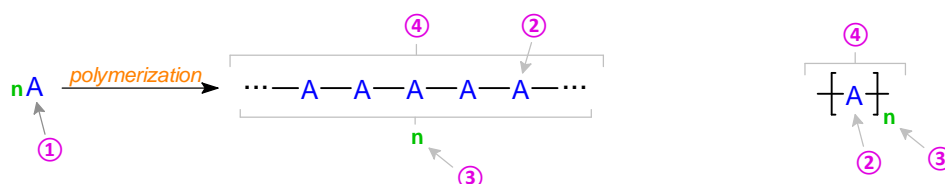


Figure 1.1. Scheme of formation and structure of polymer macromolecules: ① monomer, ② mer, ③ degree of polymerization, ④ polymer macromolecule.

Examples of the most popular polymers that are widely used are polyethylene, polystyrene, and polyvinyl chloride (Figure 1.2).

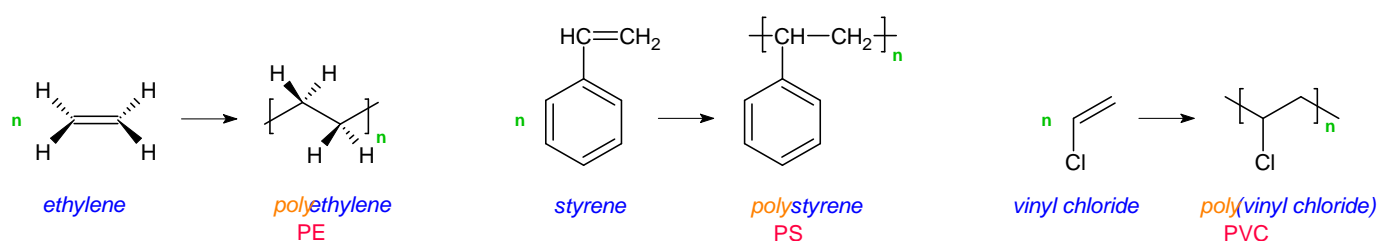


Figure 1.2. Chemical formulas of monomers and fragments of macromolecular structures for polyethylene, polystyrene, and poly (vinyl chloride).

In addition to the term *mer* or *structural unit*, one can also find the terms *constitutional*, *repeating*, or *monomeric unit* (Florjańczyk, Penczek, 1997).

Oligomers are macromolecules containing from 1000 to 10000 mers. Polymer macromolecules are composed of many thousands of atoms connected by first-order bonds (mainly covalent) with dissociation energies of 10^5 – 10^6 J/mol.

Physical interactions called second-order bonds occur between the chains of the same macromolecule and adjacent macromolecules. These interactions, classified as van der Waals forces, are characterized by dissociation energies on the order of 10^2 – 10^3 J/mol, which is significantly lower than the energy of covalent bonds in macromolecules.

In the case of polymers, the following interactions play a particularly important role:

- permanent dipole – permanent dipole,
- permanent dipole – induced dipole,
- induced dipole – induced dipole,
- dispersion forces.

Second-order bonds also include hydrogen bonds with dissociation energies of the order of 10^2 – 10^4 J/mol. These bonds play an important role in many polymers, including polyamides (Figure 1.3).

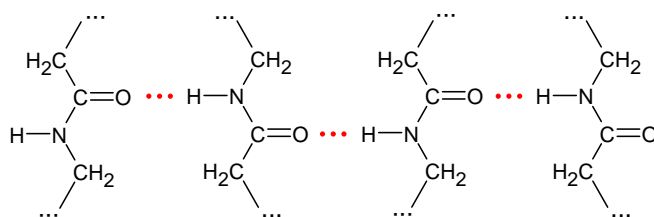


Figure 1.3. The structure of a polyamide fragment stabilized by the presence of hydrogen bonds.

Second-order bonds also determine the cohesion between polymer macromolecules and therefore have a significant impact on the mechanical properties of polymers (Rabek, 2008).

Polymer synthesis methods

There are many methods for obtaining polymers. The most important and most frequently used include (Oadian, 2004): bulk polymerization, solution polymerization, suspension polymerization, and emulsion polymerization (Table 1.1).

Bulk polymerization (in a block) has relatively limited industrial applications. This process occurs in a pure liquid monomer, without the addition of solvents. This type of polymerization is most often initiated using initiators, i.e., substances that decompose under specific conditions (e.g., elevated temperature or UV radiation) into reactive molecules (e.g., radicals). The process results in a uniform polymer block that retains the shape of the vessel in which the reaction was carried out. Bulk polymerization can be carried out in the following systems:

- homogeneous – when the monomer and the resulting polymer dissolve each other,
- heterogeneous – when the resulting polymer precipitates in the reaction medium.

A variant of bulk polymerization is block - precipitation polymerization, during which the resulting polymer does not dissolve in the monomer and precipitates as a precipitate.

Solution polymerization involves diluting the monomer with a suitable solvent or solvent mixture.

Solvent polymerization can be carried out in two ways:

- when the solvent used dissolves both the monomer and the polymer (*lacquer method*),
- when the solvent used dissolves only the monomer.

The most important advantages of this polymerization method are:

- the possibility of obtaining polymers with a relatively narrow molecular weight distribution,
- the possibility of direct use of polymer solutions to produce fibers, varnishes, and adhesives,
- the ability to control the temperature of the system, especially in the case of highly exothermic reactions.

Suspension polymerization (also known as *pearl polymerization* or *suspension polymerization*) is initiated by an initiator dissolved in a monomer dispersed in an aqueous solution of organic colloids or an aqueous suspension of inorganic salts. These stabilizers (fixatives), in the suspension, prevent agglomeration of suspension particles and influence the size of the resulting "pearls." This polymerization proceeds according to a mechanism typical of bulk polymerization, with the difference that in this case, each droplet of dispersed monomer constitutes a "microblock."

Factors influencing the course of suspension polymerization and the properties of the resulting polymer include the type/amount of polymerization initiator, the type/amount of suspension stabilizer, the mixing of the system, and the pH of the environment.

Some of the most used initiators are benzoyl peroxide (BPO) and azobisisobutyronitrile (AIBN). Increasing the initiator concentration in the system shortens the polymerization time but also reduces the product's porosity. Excessive shortening of the polymer chain lengths can result from excessively high polymerization temperature.

Very often, in addition to the main suspension stabilizer, additives are used to modify its performance or compensate for any deficiencies. These additives are called auxiliary suspension stabilizers. The essential feature of the main protective colloid must be its solubility or wettability in water, while the auxiliary stabilizer should dissolve better in the monomer. The most used protective colloids include poly(vinyl alcohol), cellulose and its derivatives: hydroxyethylcellulose, methylcellulose, carboxymethylcellulose and modified starch, gelatin, agar, pectins, etc. The protective colloid forms a thin layer around the monomer droplets, thereby stabilizing the suspension mechanically and electrostatically, which prevents coalescence of the dispersed phase.

To obtain porous polymers, an appropriate solvent system, usually a two-component one, must be used. One solvent is a good solvent for the polymer, while the other is a non-solvent. The structure and pore volume of the final copolymer depend on its type and volume ratio to the monomer. After

polymerization, the void-filling solvent is removed by extraction using a series of solvents, such as acetone, methanol, and toluene.


Emulsion polymerization – in this method, the monomer is dispersed in water using an emulsifying agent, usually a synthetic detergent. The detergent forms fine micelles that contain a small portion of the monomer, while the remainder is suspended in the water without the aid of a surfactant. Emulsion polymerization occurs primarily within clusters of surfactants. The monomers used for this type of polymerization must be highly pure and inhibitor-free. The following auxiliary agents are used in this method:

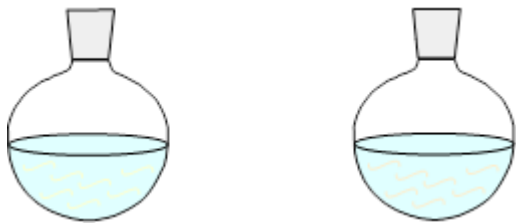
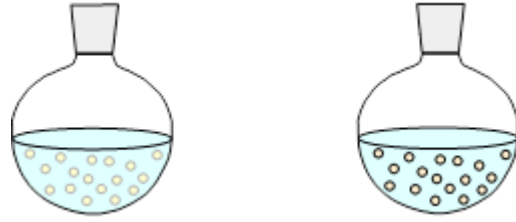
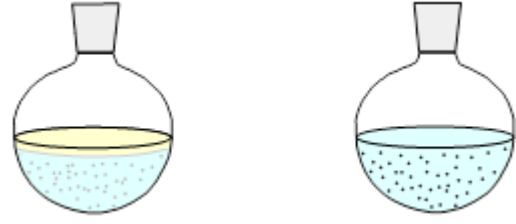
- emulsifiers,
- stabilizers emulsion,
- substance regulating,
- initiators (H_2O_2 , cumene hydroperoxide, persulfates, redox systems).

Emulsifiers are surface-active compounds that enable the formation of a stable emulsion of a monomer in water. Most of them consist of a hydrophilic part and a hydrophobic (alkyl) part. Emulsifiers used in emulsion polymerization include glycerol esters of fatty acids, quaternary ammonium salts, pyridinium salts, phosphonium salts, fatty acid salts, alkylsulfones, and alkylsulfates.

Buffer substances (acidic salts of carbonic acid, acetates, phosphates) are often added to the reaction mixture. This is to maintain a constant pH, as it affects emulsion stability and polymerization kinetics. Emulsion polymerization produces polymer emulsions intended to produce adhesives, emulsion paints, and impregnating agents. In emulsion polymerization, increasing the reaction rate does not significantly reduce the degree of polymerization, unlike in bulk polymerization. The products obtained from this reaction have high molecular weights. Due to the advantages mentioned above, this method is used on a large scale in industry. The main processes carried out using this method on an industrial scale include polymerization of vinyl acetate, vinyl chloride, isoprene, and acrylic acid esters.

Table 1.1. Characteristics of selected polymerization techniques.

Before polymerization	Technique polymerization	After polymerization
<u>Initiator</u> dissolved in <u>the monomer</u> .	<p style="text-align: center;">1. IN MASS</p> 	<u>Polymer</u> in the form of a uniform block.

<u>Initiator</u> , <u>monomer</u> and <u>surfactant</u> in solution.	<p style="text-align: center;">2. IN SOLUTION</p> 	<u>Polymer</u> dissolved in solution.
<u>Initiator</u> dissolved in monomer. <u>Monomer</u> in suspension form. <u>Surfactant</u> in continuous phase.	<p style="text-align: center;">3. SUSPENSION</p> 	<u>Polymer</u> in spherical form (microspheres).
<u>Initiator</u> dissolved in the continuous phase. <u>Monomer</u> as a separate phase forming micelles. <u>Surfactant</u> in micelles and in the continuous phase.	<p style="text-align: center;">4. EMULSION</p> 	<u>Polymer</u> in spherical form (microspheres).

Experimental part

The purpose of the experiment

The experiment aims to synthesize lignin-containing polymer microspheres using the suspension polymerization technique.

Equipment

Round-bottomed three-necked flask, 250 mL

Mechanical stirrer

Water jacket reflux condenser

Thermometer

Beakers, 50 mL

Glass baguette

Glass funnel

Heating jacket with a voltage regulator

Vacuum pressure filtration kit

Petri dish
Optical microscope
Balance

Reagents

Ethylene glycol dimethacrylate (EGDMA)
Vinyl acetate (VA)
Azobisisobutyronitrile (AIBN)
Kraft lignin (LIG)
Benzyl alcohol (BA)
Polyvinyl alcohol (PVA)
Distilled water

Performing the experiment

Preparing the reaction environment

Add 150 mL of water to a three-necked round-bottom flask. Fit the flask with a water-jacketed reflux condenser, a thermometer, and a mechanical stirrer. While stirring, heat the water to 80 °C, then add 1 g of PVA. Maintain the temperature at 80 °C and stir continuously until the PVA is completely dissolved.

Preparation of the reaction mixture

In a 50 mL beaker, prepare a mixture of 0.43 g of lignin in 10 mL of benzyl alcohol. Heat the contents of the beaker to 60 °C and then cool to room temperature. Add 10 g of EGDMA and 4.3 g of vinyl acetate (VA) to the lignin solution and mix thoroughly (relative molar ratio of monomers = 1:1). Immediately before starting the polymerization, add 0.143 g of AIBN (1 % wt. concerning the total mass of monomers) to the reaction mixture in the beaker.

Polymerization

After the initiator has completely dissolved in the reaction mixture, with the mechanical stirrer running continuously, pour the contents of the beaker into the round-bottom flask. Maintaining the temperature at 80°C and a constant stirrer speed, polymerize the system for 2 hours.

Product insulation

After polymerization is complete, filter the suspension obtained in the round-bottom flask under reduced pressure, and wash the polymer microspheres remaining on the filter thoroughly with hot water (until the foam in the filtrate disappears). Transfer the obtained polymer, i.e., poly(EGDMA-co-VA-co-LIG), to a Petri dish, dry, and weigh.

A diagram of the laboratory procedure for the synthesis of lignin-containing polymer microspheres is shown in Figure 1.4.

Interpretation of the results

- Calculate the reaction yield.
- Evaluate the morphology (e.g., shape, diameter) of the obtained poly(EGDMA-*co*-VA-*co*-LIG) microspheres based on microscopic observation of the sample.
- Optional: record the spectrum of poly(EGDMA-*co*-VA-*co*-LIG) by Fourier Transform Infrared Spectroscopy (FTIR) and analyze it.
- Investigate the sorption properties of poly(EGDMA-*co*-VA-*co*-LIG).
- To assess the effect of the presence of lignin on selected properties of the obtained product (including sorption properties), they should be compared with the properties of a reference material, i.e., a lignin-free copolymer obtained in a laboratory procedure identical to the one described except for the use of lignin.

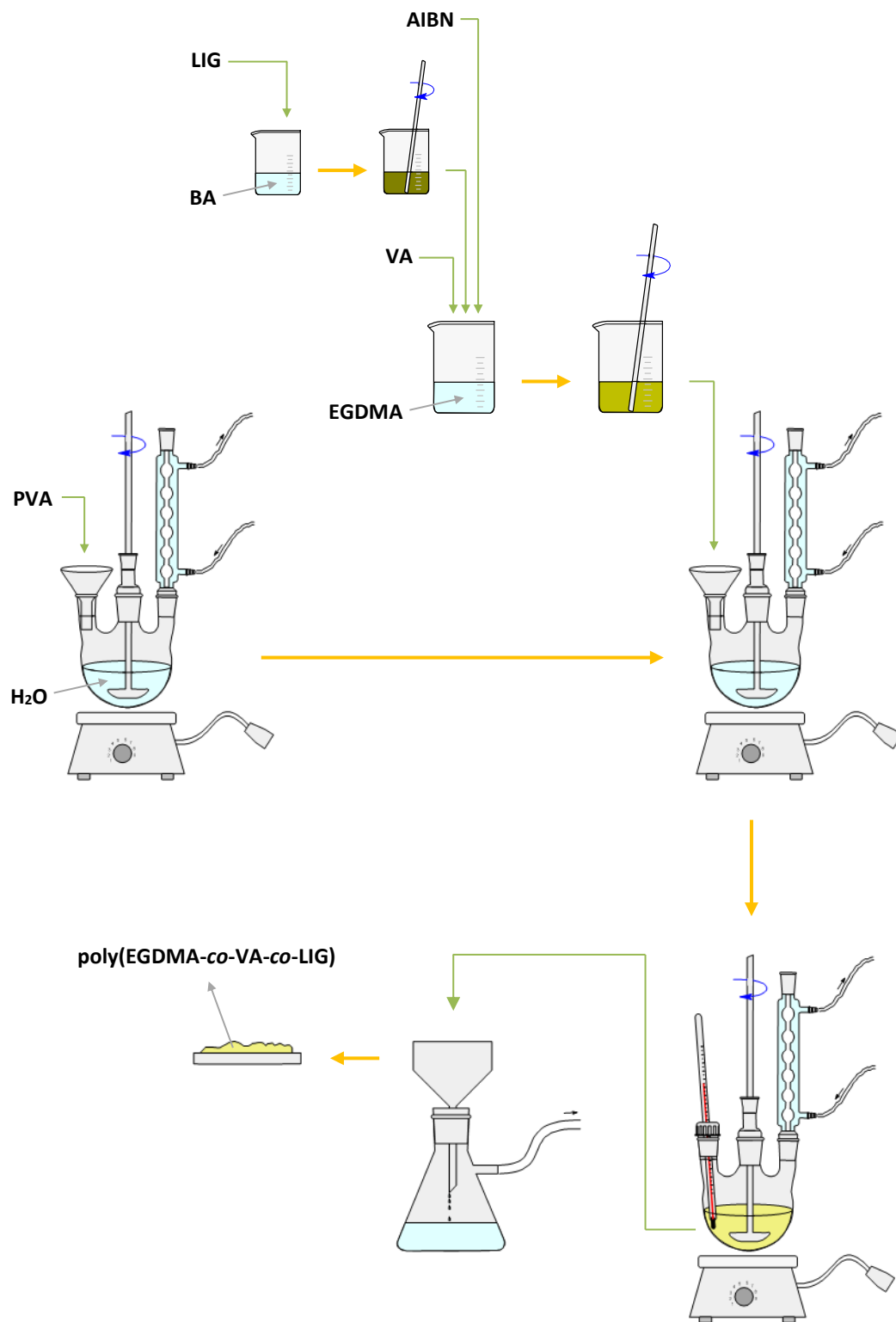


Figure 1.4. Schematic diagram of the laboratory procedure for the synthesis of lignin-containing polymer microspheres.

2. Application of polymer microspheres with lignin for the adsorption removal of toxic dyes

Introduction

A significant number of physical and chemical processes occur at the interface between contacting phases, such as solid and liquid phases. Understanding these phenomena is crucial to explaining the mechanisms of many reactions and technological processes.

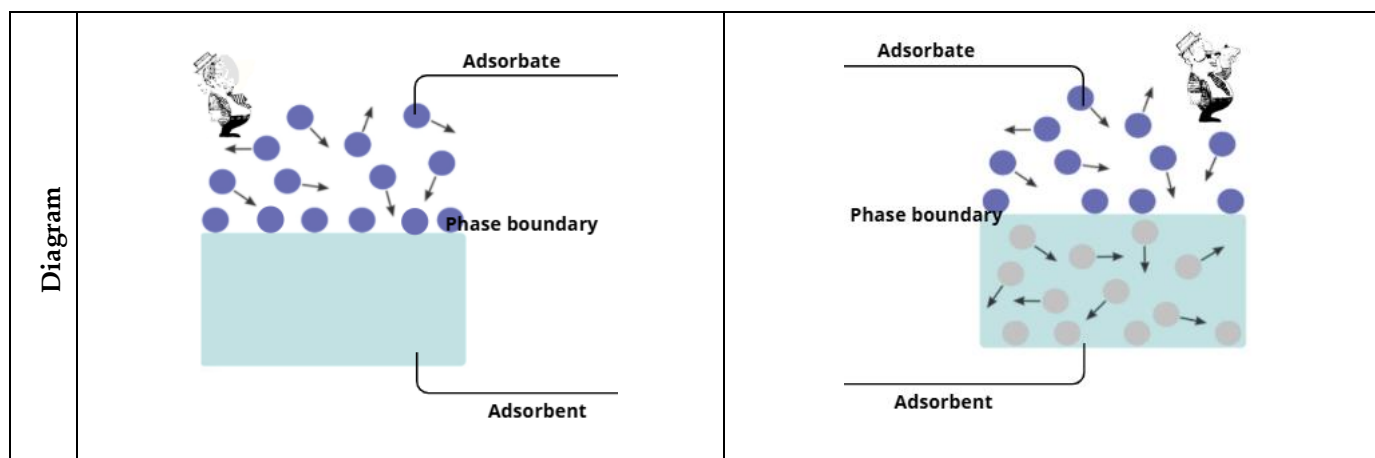
Adsorption is the process of accumulation of substances (molecules, atoms, or ions) at an interface or surface, leading to a change in the concentration of the substance at the boundary of two phases (Saleh, 2022). **Adsorption can occur at various phase boundaries:** solid–gas; solid–liquid; liquid–liquid; liquid–gas (Bielański, 2013). The substance on which compounds adsorb is called **the adsorbent**, and the adsorbing substance is called **the adsorbate** (Tien, 2019).

Adsorption and absorption

Due to the similarity in spelling, the terms adsorption and absorption are often used interchangeably by non-experts. However, **adsorption** should not be confused with **absorption**, as there are significant differences between them (Table 2.1).

Table 2.1. Comparison of adsorption and absorption (Chua et al., 2002; Nguyen et al., 2025; Tien, 2019; Zamljen et al., 2024; Zarzycki et al., 2013).

Sorption	Adsorption	Absorption
	accumulation of substances on the surface of another phase	absorption of a substance into another phase
Examples	<ul style="list-style-type: none"> - adsorption of dyes on the surface of activated carbon (purification of solutions) - adsorption of water vapor by silica gel (packaged desiccants) - absorption of gases by activated carbon (gas masks) - hydrogen adsorption on the platinum surface in hydrogenation reactions (heterogeneous catalysis) 	<ul style="list-style-type: none"> - dissolving gases in liquids (food industry, e.g., CO₂ in water) - absorption of water by the sponge (the liquid penetrates the porous material) - absorption of oxygen by hemoglobin in the blood (medicine) - absorption of water vapor by hygroscopic salts, e.g., CaCl₂ (delivery), concentrated acids, e.g., H₂SO₄ or bases, e.g., NaOH (chemical processes requiring anhydrous conditions, drying of air and technical gases, storage of moisture-sensitive products)



Unlike adsorption, which occurs on a surface, absorption involves the absorption of adsorbate particles by the entire volume of a liquid or solid (Bieleński, 2013). Gas absorption is a process in which a gaseous mixture is brought into contact with a liquid to dissolve one or more of the mixture's components in the liquid. Absorption is therefore a volumetric phenomenon, and the degree of separation is limited by the solubility of the gases involved. When it is difficult to determine which of the two phenomena is being addressed, we briefly refer to it as **sorption** (Tien, 2019; Zarzycki et al., 2013). Adsorption plays the most important role in analytical chemistry, where the adsorbent is a solid, and the adsorbate is a substance dissolved in the solution.

Types of adsorptions

Depending on the type of interactions between the molecules of the adsorbed body (adsorbate) and the surface of the adsorbing body (adsorbent), we distinguish **physical adsorption** (*physisorption*) and **chemical adsorption** (*chemisorption*) (Table 2.2).

Table 2.2. Comparison of physical and chemical adsorption (Aljamali i in., 2021; Bielański, 2013).

	Physical adsorption (physisorption)	Chemical adsorption (chemisorption)
Interactions	is determined by relatively weak intermolecular forces, van der Waals interactions	is determined by much stronger interactions – chemical bonds are formed between the adsorbate and the adsorbent
Adsorbent	the adsorbate can form multiple adsorption layers on the surface	the adsorbate can form a single adsorption layer (monolayer) on the surface
Reversibility of the process	it is reversible – the adsorbed substance can be easily removed (desorbed) from the surface	it is rather irreversible – the adsorbed substance is generally difficult to remove from the surface of the adsorbent, or its removal requires the use of specific treatments
Temperature	an increase in temperature causes desorption	an increase in temperature increases the rate

		of adsorption
Heat of adsorption	it is usually low and falls within the range of 5 to 40 kJ/mol of adsorbate	it is high, comparable to the heat of a chemical reaction, and ranges from 80 to 400 kJ/mol

Adsorption at the solid-solution interface

Adsorption at the solid-solution interface is a more complex process compared to gas adsorption. In this case, both solute and solvent molecules are adsorbed. As concentrations change, the solution components displace each other from the surface layer, which is the most characteristic feature of the adsorption process from solutions. The magnitude of adsorption is determined by both the interaction between the adsorbent and each of the solution components and the interaction between the solution component molecules. A solute adsorbs more strongly the less soluble it is in each solvent. The amount of adsorbed solvent also depends on its ability to wet the adsorbent. For example, water does not wet activated carbon well, and therefore, activated carbon adsorbs primarily the solute from an aqueous solution. Adsorption of weak electrolytes is like that of nonelectrolytes. In the case of adsorption of strong electrolytes, phenomena related to the interaction of the electrical charges of ions play a significant role. Only ions of the same sign adsorb on the surface of a solid, causing an accumulation of electric charge on the adsorbent surface, which violates the principle of electroneutrality. The system, therefore, tends to spontaneously compensate for this charge. This can be achieved in two ways. One possibility is the accumulation of ions of the opposite sign (e.g., negative) on the layer of adsorbed ions (i.e., positive). This type of adsorption is called **specific adsorption**. The second method is for the adsorbent to release an equivalent number of other ions of the same type into the solution. This type of adsorption, called **ion-exchange adsorption**, occurs on commonly used natural and synthetic zeolites or synthetic organic resins, so-called **ion-exchange resins** (Bielański, 2013).

The concept of adsorption is related to the concept of adsorption capacity. **Adsorption capacity** is the amount of a substance adsorbed per unit mass or volume of adsorbent under specific conditions, typically expressed in mg of adsorbate per g of adsorbent (mg/g) or in volumetric units, e.g., g/cm³ or mol/L. This value reflects the adsorbent's ability to bind contaminant molecules from the liquid (or gas) phase and is one of the basic parameters characterizing adsorbent effectiveness. It is typically measured under equilibrium conditions (so-called equilibrium capacity) or at a specified phase contact time (instantaneous capacity).

Adsorption in a solid-liquid system is one of the most frequently used processes for the separation and removal of environmental pollutants, including organic substances, e.g. dyes, from aqueous solutions and wastewater, due to its effectiveness, not only due to its advantages, but also to the wide range of available adsorbents of various types (activated carbon, nano-adsorbents, metal oxides, metal-organic frameworks, polymers and bio-adsorbents, etc., Figure 2.1.) (Dutta et al., 2021). The process is based on the sorption of solution components onto a solid surface due to their affinity for the adsorbent surface,

which may be due to their hydrophobic nature. The affinity of a substance for an adsorbent surface is a measure of the ability and strength with which adsorbate molecules interact and bind to the adsorbent surface during the adsorption process. The higher the affinity, the stronger and more durable the adsorbate's binding to the surface, leading to more effective substance retention. The sorption efficiency of organic substances also depends on their solubility in solution – the lower the solubility of the compound, the better the sorption, and the solubility of these compounds, in turn, depends on the length of the hydrocarbon chain – the longer the hydrocarbon chain of the molecule, the lower the solubility. Therefore, the longer the hydrocarbon chain, the higher the sorption efficiency (Adamczak et al., 2017).

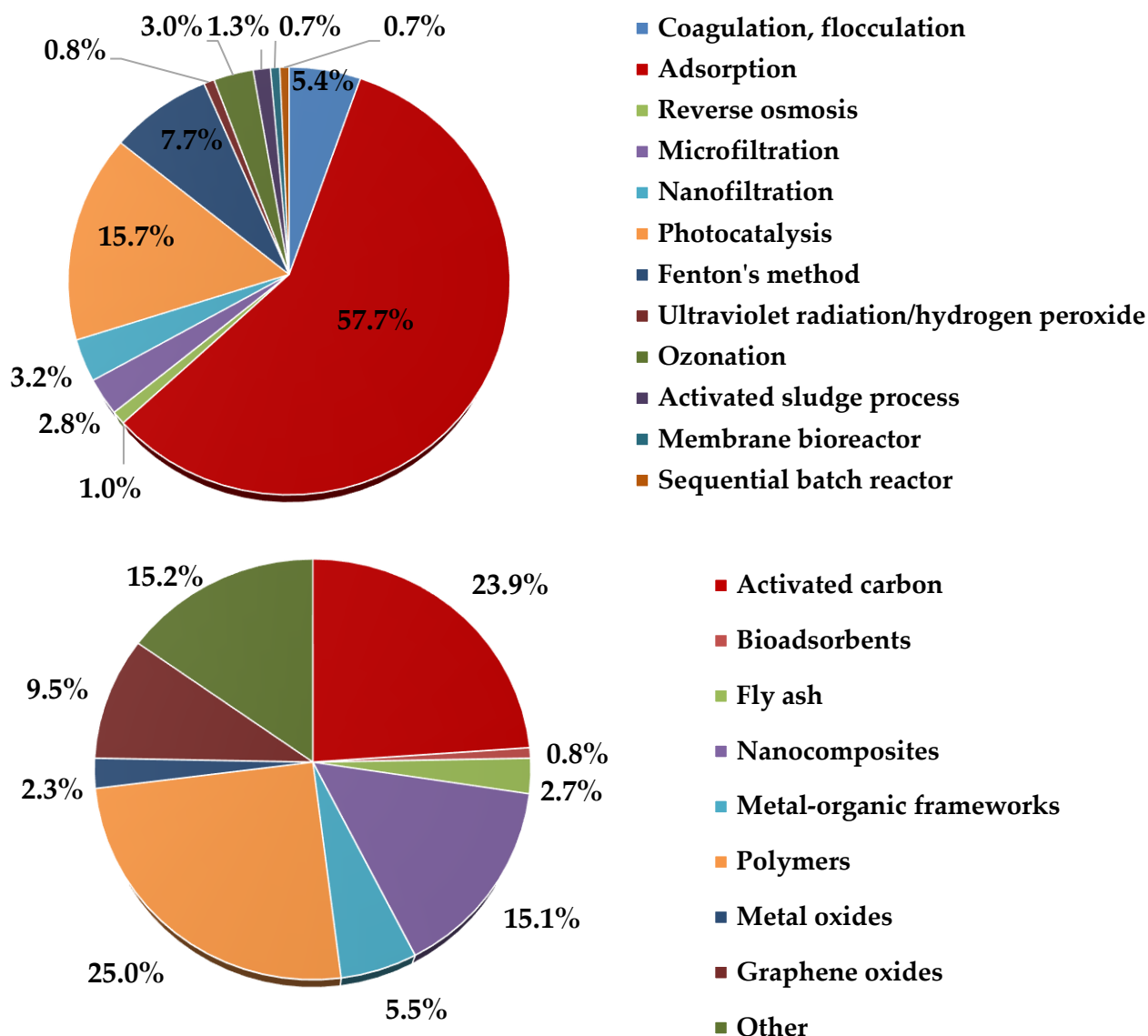


Figure 2.1. The widespread use of physicochemical and biological techniques and particular types of adsorbents for the removal of dyes from aqueous solutions and wastewater.

Factors influencing the adsorption process

The adsorption process and its effectiveness are determined by many factors related to the properties of both the adsorbent and the adsorbate, as well as the environmental and experimental conditions of the process and temperature (Aljamali et al., 2021). Individual factors that may affect the adsorption process are shown in Figure 2.2.

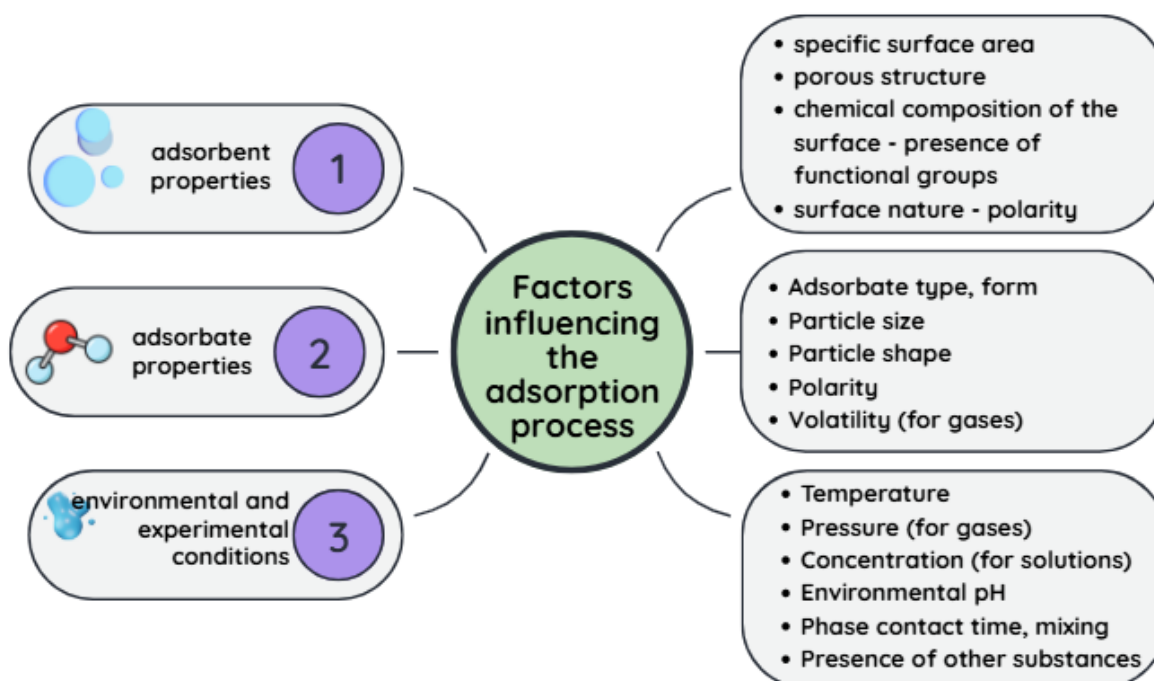


Figure 2.2. Factors influencing adsorption efficiency.

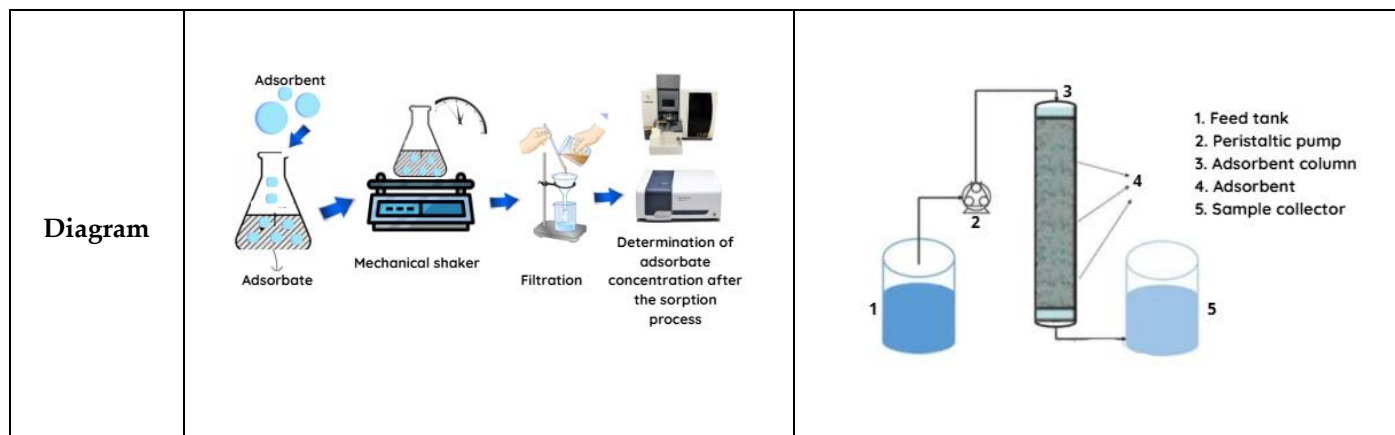
Adsorption techniques

The process of dye adsorption on solid adsorbents of various types can be carried out using the static method (*batch method*) and dynamic, also called the column method (*dynamic method*). A comparison of the above-mentioned methods is presented in Table 2.3.

During sorption in a static system, a certain equilibrium is established between the adsorbate in the solid phase and the solution. This equilibrium is consistent with the mass action equations or the Freundlich and Langmuir adsorption isotherm equations, or related relationships. The adsorption process in a column system involves passing a solution containing the contaminants (adsorbate) through a column filled with an adsorption material (adsorbent), where the contaminants are retained on the surface or in the pores of this material. In the column technique, three basic methods are used to separate the substances of interest: the front method, the elution method, and the displacement method.

Table 2.3. Comparison of static and dynamic methods (Patel, 2022; Pathirana et al., 2022; Sazali et al., 2020; Tien, 2019).

Principle methods	Static method	Dynamic method
	It involves contacting the adsorbent with a solution or gas containing the adsorbate under rest conditions (no flow).	It involves passing a solution or gas containing the adsorbate through an adsorbent layer continuously.
Procedure	A known amount of adsorbent and a solution with a specific concentration of the substance are introduced into a vessel (e.g., flask, vial) to bring the phases into contact. The system is left at a constant temperature for the appropriate time until the adsorption equilibrium is achieved. Typically, the contents of the reaction vessels are mixed to accelerate the reaction, e.g., using a mechanical shaker. After a specified time, the phases are separated by filtration. The final concentration of the adsorbate in the solution is then determined using analytical or physicochemical methods. The amount of adsorbed substance is calculated from the difference in concentrations before and after adsorption. The relationship between the concentration of the adsorbed substance and the time of phase contact or its concentration in the solution at equilibrium is then graphically presented.	The adsorbent is placed in a column, and a solution (or gas) containing a known concentration of adsorbate is passed at a specific rate through a stationary layer of solid adsorbent. During the process, the concentration of the substance at the column outlet (known as the breakthrough curve) is monitored, determining its concentration in the collected effluent. Once the column breakthrough point is reached, the process is not interrupted but continued until the adsorbate concentration in the effluent reaches its initial concentration (the concentration of the solution entering the column). Equalization of the concentrations indicates complete depletion of the adsorbent capacity. Based on the changes in the effluent concentration, the amount of adsorbed substance and the bed efficiency are calculated.
Process control	Less controlled mass exchange.	Better control over flow and mass transfer
Scale	Laboratory tests. Small samples.	Industrial processes. Larger quantities.
Application	Studies on adsorption kinetics and isotherms. Preliminary assessment of the adsorption capacity of various adsorbents and the adsorption mechanism.	Determination of adsorbent capacity, breakthrough curves, and bed operating conditions. Simulation and design of industrial processes.
Duration	Specified contact time, e.g., 24 hours.	Continuous process, duration depends on the flow rate.
Cost and equipment	Simple, cheap apparatus (flasks, shaker).	More complex equipment (adsorption columns, pumps, detectors).



Application of adsorption

Adsorption is currently widely used in many fields (Ahmed Alsharif, 2025; Dąbrowski, 2001; Suprakas et al., 2020), including:

- **environmental protection:** water treatment processes, wastewater and air purification, industrial emissions control - reduction of harmful gases, e.g., SO_2 , CO_2 in exhaust gases, e.g. catalytic converters of car exhaust gases,
- **chemical and technological industry:** catalysis – catalysts for chemical reactions, e.g. esterification, hydration, condensation or catalyst supports – porous bodies with a developed surface (e.g. Al_2O_3 , SiO_2), separation and purification of substances – e.g. adsorption chromatography, recovery of valuable metals, e.g. in hydrometallurgy of precious metals, separation of strong acids from their salts, NaCl from HCl , FeCl_2 from HCl , separation of nitrogen from air in oxygen concentrators, drying of gases and liquids, e.g. silica gel, molecular sieves, concentrated H_2SO_4 ,
- **medicine and pharmacy:** poisoning - removal of toxins from the gastrointestinal tract, hemoperfusion - removal of toxins from the blood using adsorbents, controlled drug release, antibiotic purification,
- **food and cosmetics industry:** removal of dyes and impurities – e.g. decolorization of sugar, edible oils, decolorization and stabilization of juices, removal of undesirable substances from plant extracts, dairy: to control the content of calcium and sodium ions, wine: for deacidification of wines, stabilization of products using adsorbents as anti-caking agents, e.g. cosmetics, moisture absorbers, skin cleansing, e.g. adsorption masks and peels (adsorption of sebum, heavy metals, toxins, etc.), odor removal, pH control,
- **specialist applications:** adsorption heat pumps and refrigerators – using the adsorption phenomenon for heat exchange, storing gases in porous materials, e.g. hydrogen, methane, gas masks and filters – adsorption of toxic substances and odors.

Experimental part

The purpose of the experiment

The experiment aims to carry out the adsorption removal of the toxic dye basic yellow 2 from an aqueous solution using a polymeric adsorbent with the addition of lignin poly(EGDMA-*co*-VA-*co*-LIG) and to determine its sorption capacity concerning the above-mentioned dye.

Equipment

Weighing vessel
Spatula
Wash bottle
Volumetric flasks, 25 – 250 mL
Measuring cylinders, 25 mL
Conical flasks with silicone stoppers, 100 mL
Graduated beakers, 10 – 100 mL
Automatic variable volume measuring pipettes, 0.01 mL – 25 mL
Funnels
Filters
Test tubes
Test tube racks
Quartz cuvettes
Analytical balance
pH meter
Mechanical shaker
UV-vis spectrophotometer

Reagents

Basic yellow 2
1 M NaOH solution
1 M HCl solution
Distilled water

Performing the experiment

Preparation of basic yellow 2 stock solution and working solutions

In a weighing vessel, weigh 1250 mg of basic yellow 2 using an analytical balance. Then quantitatively transfer the dye to a 250 mL volumetric flask and prepare its solution in distilled water to obtain a dye concentration of 5000 mg/L. From the stock solution of basic yellow 2, a sample should be taken using a volumetric pipette, transferring the appropriate amount of the dye into 25 mL volumetric flasks. The

concentration of basic yellow 2 in the working solutions (C_0) should be 10, 50, 100, 200, 300, 400, 500, 600, 700, 800, 1000 mg/L. Using a pH meter, adjust the pH of the basic yellow 2 working solutions to a value within the range of 8-9. Top up to the mark with distilled water and mix well.

Weighing polymer adsorbents with lignin addition

Weigh 0.02 g of adsorbent using an analytical balance in 100 mL conical flasks.

Prepare 11 weighed portions of adsorbent.

Adsorption of basic yellow 2 by the static method

Add 20 mL of basic yellow 2 solutions at concentrations ranging from 10 to 1000 mg/L, measured using graduated cylinders, to conical flasks containing 0.02 g of adsorbent. Seal the flasks tightly with silicone stoppers and place them on a mechanical shaker rotating at 150 cycles/min. Shake the flask contents for 24 h at room temperature. After the specified time, separate the dye solutions from the adsorbent by filtration. Save the dye solutions after the sorption process for spectrophotometric determinations.

Carry out dye adsorption tests in a similar manner on a reference material, i.e., a lignin-free copolymer.

Determination of the concentration of basic yellow 2 by the spectrophotometric method

The dye concentration in the solutions after the sorption process (C_e) was measured spectrophotometrically. Absorbance (Abs) measurements were made relative to water, which served as a reference, in 1 cm thick quartz cuvette, at a maximum wavelength of 431 nm. The dye content was determined from the standard curve equation by establishing the relationship between absorbance and dye concentration under measurement conditions at the maximum wavelength. The standard curve equation is as follows: $\text{Abs} = 0.1222 \cdot C_e + 0.014$. After the sorption process, basic yellow 2 solutions were diluted appropriately in 10 mL volumetric flasks, considering the assay ranges from 1 to 20 mg/L. Perform absorbance measurements twice and calculate the mean absorbance value. Determine the basic yellow 2 concentration in the solutions after the sorption process by transforming the calibration curve formula and considering the sample dilution.

Interpretation of results

Based on the obtained data, calculate the sorption capacity of the adsorbent (q_e , mg/g) with the addition of lignin, poly(EGDMA-co-VA-co-LIG), relative to basic yellow 2, using the following formula:

$$q_e = \frac{(C_0 - C_e)}{m} \cdot V$$

where: C_0 , C_e – dye concentration before and after the sorption process in the aqueous phase (mg/L), V – solution volume (L), m – adsorbent mass (g).

Plot the relationship between q_e and C_e for poly(EGDMA-co-VA-co-LIG) on a graph. Evaluate the tested adsorbent in terms of its effectiveness and applicability for the above-mentioned purpose and compare its effectiveness with a reference adsorbent without lignin and other lignin-containing adsorbents based on a literature review.

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