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Valorization of Rapeseed Waste Biomass in Sorption Processes for Wastewater Treatment

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Abstract

Circular economy provides an efficient framework for effective biomass valorization, through strategic use and processing of resources and waste reuse. Being the second largest energetic crop, rapeseed (RS) presents a high potential in this sense. However, good management of the large quantity of generated wastes from agro-industrial activities is required. The most common management strategies in this sense refer to the reuse of RS wastes (mainly stems and press-cake) for animal feed, compost, soil amendment and fertilizer. Valorization of RS wastes as adsorbent for wastewater treatment is attractive. Despite the fact that only few articles on this subject exist in literature, they are sufficient to reflect the potential of this adsorbent to remove both inorganic and organic compounds from aqueous phase. The rapeseed wastes were used in native form (for diluted effluents) or modified by chemical or thermal treatment (for concentrated effluents or large molecule contaminants). This chapter will provide a review on the RS wastes management strategies, highlighting the applications for removing contaminants from wastewater in single and multi-component systems, in static or continuous operation mode.

Keywords: rapeseed, canola, biomass, wastewater treatment, adsorption, biosorption, pollutants removal

1. Introduction

A sustainable growth of our society implies a continual and efficient (re)use of the available resources. At the European Union (EU) level, great efforts are made to move to a circular economy with an efficient use of resources and zero waste generation. In the latest report, member states view food, waste processing and mobility among the priority sectors in the circular economy strategies [1]. Waste from one part of the system may be a resource in other sector, matching demand and supply, while biofuels obtained from the high-growing biomass and biological wastes tackles the problem of renewable energy.

Rape or rapeseed (*Brassica napus* L. and its varieties) currently occupies the second place in the world production of oilseed and meal [2]. EU is the second major producer of rapeseed, after Canada. In Europe, the main oilseed culture consists of rapeseed, followed by sunflower seeds and soya beans. Romania is

among the top seven major producers, being responsible for almost 5.5% of the EU total RS production [3]. Crushing of oilseeds produces RS oil (for human consumption or biodiesel production) and RS meal. The latter represents almost 57% of the world total RS production [2]. Within the scope of this chapter, the terms “rape” or “rapeseed” will be used when referring to other common names or varieties, such as canola, colza, swede, swede rape, summer rape, winter rape, annual rape. Another mention is about the methods of oil extraction from rape seeds (RSs). This can be done by mechanical pressing, when RS meal is produced, with 8–20% residual oil content. The fat content could be further lowered by solvent extraction to 1–3%; then the solid waste obtained is RS cake [4]. Because we have found a great number of articles in literature where no distinction between RS meal (RSM) and RS cake (RSC) was made, we will be using these terms interchangeably here.

Valorization options for RS meal are based predominantly on the use as animal feed. Although a recognized feedstock for protein extraction, RS is still underutilized for production of commercially available protein products [5, 6]. Besides meal, other solid residues result from RS harvesting (stems and leaves). They are primarily used to obtain energy by combustion or fermentation [7] and soil amendment and fertilizer [8]. Currently at EU level, lignocellulosic and agricultural biomass (including rapeseed wastes) are the subject of some Bio-Based Industries Joint Undertaking projects [9].

An emerging valorization alternative consists of using RS wastes for the removal of pollutants from wastewater by adsorption. In order to lower the cost of activated carbon (AC) processes, abundant and readily available agricultural wastes were tested in native form or after a treatment as presented in various reviews [10–13]. The process is called *biosorption* when the waste is used in either its natural form or after some physical or chemical modification. At present, most of the work is done at laboratory scale. Although activated carbon process is an established technology at industrial scale, not many ventures can be encountered for the commercialization of biosorption [14].

This chapter aims to dive into the rapeseed waste management practices and strategies, specifically on the opportunity of valorization as a sorbent in wastewater treatment. Firstly, the sources of different rape waste biomass are identified and their valorization options are discussed from the circular economy perspective. The second part of the chapter will focus on the relation between adsorption and RS waste. After a short description of the adsorption process as a wastewater treatment technology, the characteristics that make RS a potentially suitable biosorbent are highlighted. Finally, an overview of the limited number of studies found in literature dealing with RS-based sorbents will be focusing on the types of pollutants and wastewater matrix investigated and the adsorption system configuration employed.

2. Rape waste biomass sources and management strategies

2.1 Sources

Rape is a multifunctional oily plant with yellow flowers and thin, long and branched stems. The many RS varieties are remarkable by extensive biomass, easiness in harvesting and adaptability to climatic change, their cultivation being estimated as one of the most sustainable oil crops [15]. The main applicability of the harvested component of the rape crop, the seeds, targets vegetable oils production (**Figure 1**). Rape seeds contain compounds of nutritional value (proteins and oil) and anti-nutrients, namely erucic acid and glucosinolates. The two varieties of *Brassica napus* seeds frequently cultivated - industrial rapeseed and canola- have

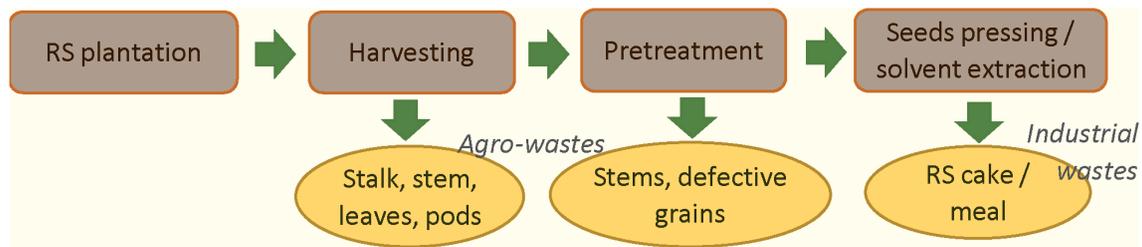


Figure 1.
Sources of wastes from the RS oil production process.

as distinguishing feature the erucic acid content in the corresponding oils. Unlike traditional varieties of rapeseed that give oils that contain 22–60% erucic acid, the cultivars of canola produce oils with low erucic [5].

The main sources of RS waste are agricultural activities and production of oil and biodiesel (**Figure 1**). Field residues, present after RS crop harvesting, consist of stems, stalks, leaves and seed pods. From the technological process before seed storing result impurities, broken and immature grains, stems, rotten grains etc. [16, 17]. The total RS biomass consists of 28–50% seeds, while the rest is crop residues, mainly stalks [18]. The agricultural wastes resulting in large amounts from the harvesting and postharvest of the seeds of rape are lignocellulosic materials: straws and stalks contain 15–36% cellulose, 18–25% hemicelluloses and 14–31.6% lignin [19, 20], while seeds husks contain: 13.7% cellulose, 19% hemicellulose and 25.5% lignin [21]. The processing of the rape seeds for vegetable oils yields press-cake or meal as industrial residue, which account for about 60% by weight of the input seeds [21, 22]. The RSC obtained by mechanical pressing of oleaginous seeds contains 30–40% proteins and 9.0–12.60% crude fibers [16, 23]. On the other hand, RSM resulted after the solvent extraction of the oil from the rape seeds has a content of about 37–40% proteins and 10–17.5% crude fibers [22, 24]. Authors [25] have determined the composition of deoiled canola meal (CM): 34.5% lignin, 33.5% hemicellulose and 30.2% cellulose. The RSC/RSM are currently important sources of organic matter and energy.

The wide availability, low-cost, renewability, versatility, unique structure and interesting technological properties make these residual materials more than just wastes. Their resource potential for sustainable products with multi-faceted applications is still undervalued.

2.2 The circular economy approach and management of rape biomass

Circular economy can be described as an industrial system that is restorative or regenerative by intention and design, aiming for the elimination of waste through the superior design of materials, products, systems and business models [26]. The recovery of valuable by-products can contribute to circular economy transition by reducing waste generation, maximizing resources potential and also leading to cost reduction [27]. The management of RS wastes with the possibility of their reuse in different forms is presented in **Figure 2**. Rapeseed meal/cake, the main by-product of vegetable oil and biodiesel production, has a high potential for an integrated valorization scheme [28]. For example, RSM can be transformed into a hydrolysate and used with crude glycerol to produce poly (3-hydroxybutyrate) [29]. RSM contains bioactive constituents, such as phenolic sinapinic acid and protocatechuic acid, which can be used as functional food ingredients and for use in cosmetic and pharmaceutical applications [27, 30]. Its application for animal feed is limited however due to the presence of anti-nutritional compounds (e.g. glucosinolates, phytic acid, synapine, erucic acid, tannins) and high fiber contents. Treatment with ethanol reduces phenols and glucosinolates content, while increasing the protein

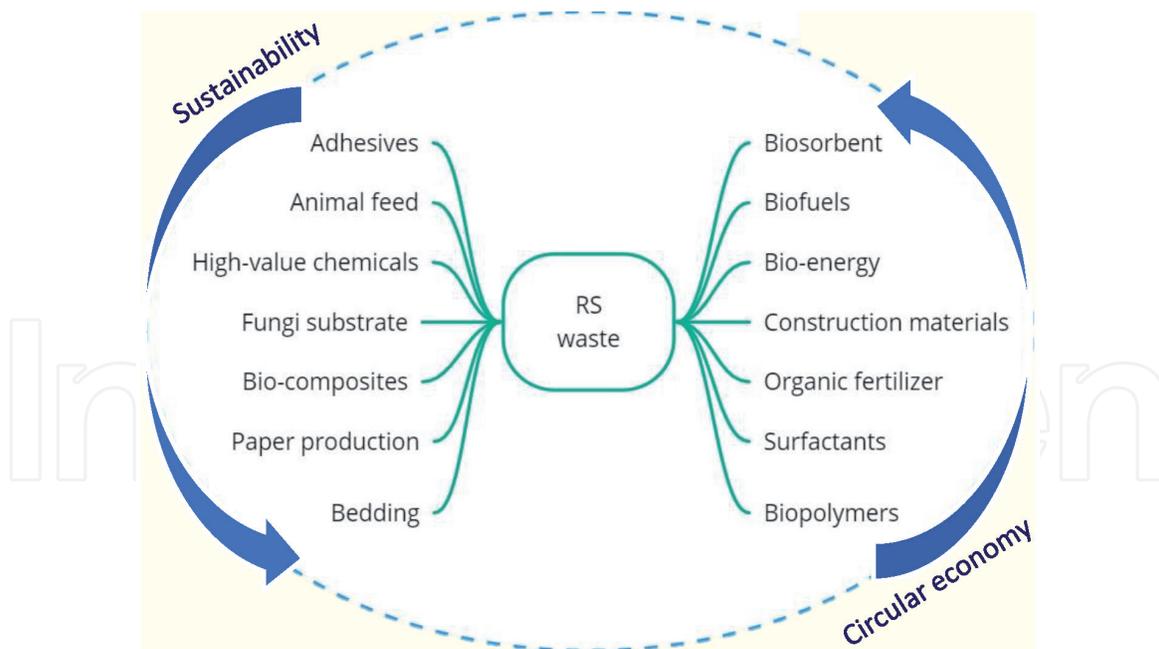


Figure 2.
Rape waste biomass as resourceful raw material in circular economy.

level, and makes possible RSM use as feed additive or as a source for production of protein-rich ingredients with specific value and functionality [31]. The biotransformation of RSM using bacteria increases its nutritional value and enriches it with a variety of additives, including polymers, bio-surfactants and enzymes [32]. RSM has proved to be a plant-derived alternative for development of bio-plastic materials [33] and new polyurethane composites [23].

The lignocellulosic biorefinery strategies integrate physical, chemical, thermo-physical, thermochemical or biological processes for the pretreatment and conversion of biomass into bio-based products [34]. In the case of RS, these processes are adapted to the characteristic content of cellulose, hemicellulose and lignin that are the main components responsible for biorefinery. The use of the whole plant of RS for production of biodiesel, bioethanol and methane into the frame of biorefinery concept resulted in a 3 times increase of the efficiency of energy recovery as compared to conventional process of biodiesel production [35–37]. RS straws, containing >50% of carbohydrates, are an interesting source of biomass for biorefineries, by conversion into bioenergy and high-value chemicals. It is also an attractive source of fermentable sugars for bioethanol production [19]. More than 50% of RS straw could be recovered as xylan, lignin and nanocellulose [38].

RS stalk and straw also present interest in pulping and papermaking industries [39–41]. The potential of RS straws as source of lignocellulosic fibers can also be valorized for the production of biocomposite materials [42, 43]. The beneficial effects of RS stalks use on the humus and nutrients content of some damaged soils have been pointed out [44, 45]. Polyphenols and proteins were extracted from rapeseed stems and leaves by pulse electric fields [46]. Another potential use for canola leaves is as annual forage for field-raised swine and poultry. RS leaves and hulls can be used in livestock (rabbits, swine, poultry, fish) feeding [17, 47], or substrate for fungi production [48]. RS shells can be used as precursors for activated carbon materials as cathode in lithium-sulfur batteries [49]. Other applications of RS wastes include the use as soil amendments for increasing crop growth, usually in biochar form [8, 50, 51].

Another interesting possibility of recycled-value added application of RS wastes involves their ability to act as efficient biosorbent for the removal of heavy metals

and organic pollutants from environmental aqueous media, which will be discussed in the second part of this chapter.

3. Adsorption on rape waste biomass

3.1 Adsorption/biosorption processes

Among the numerous wastewater treatment processes, adsorption distinguishes by efficiency, design simplicity and flexibility, operation easiness, insensitivity to toxic pollutants and economic feasibility [52]. Adsorption refers to the retention of a chemical species (adsorbate) on the surface of a solid substance (adsorbent) by means of physical and chemical interactions. The existence of weak van der Waals interactions determines the fast kinetics, low heat, monolayer or multilayer coverage, non-selectivity and reversibility of the physical adsorption. A chemisorption mechanism reaches equilibrium slower due to creation of covalent bonds, which causes a high activation energy, monolayer coverage and irreversibility. The adsorption of inorganic and organic pollutants from wastewater is most often the result of both types of mechanisms overlapping. The significance of adsorption for wastewater treatment is highlighted by the increasing range of materials used as adsorbents. The materials that can act as adsorbents are remarkable by the variety of structures and properties. They can be raw and modified materials of mineral, organic or biological origin, natural materials, synthetic materials, industrial and agricultural wastes and biomasses [53].

The “green” subcategory of adsorption, biosorption, can be defined as the low-cost and low-tech concentration of pollutants from aqueous media on the solid surface of a biological matrix (biosorbent), achieved through a passive mechanism [54]. As a physico-chemical process, biosorption works by a combination of different interactions ranging from hydrogen forces to covalent bonds through which the targeted toxic species is retained on the biosorptive materials surface. The key concepts of biosorption have been fully decrypted by means of a large number of laboratory studies addressing issues of fundamental research (**Table 1**).

Due to its quasi-perfect framing into the sustainable development coordinates, biosorption has received considerable acceptance in removing heavy metals and organic pollutants from wastewater [54, 55]. Besides the ecologic and economic advantages, biosorption is also challenging by its applicability over a wide array of operational conditions, adaptability to varied designs of systems, possibility of sequential or simultaneous removal of pollutants from large volumes of wastewaters. Biosorption is a propriety characteristic to a broad spectrum of natural or waste bio-origin materials that are cheap, abundant, ready available, renewable, recyclable and versatile [55]. The biosorption potential of biomass is mainly due to their surface functional groups (hydroxyl, carboxyl, amino, sulfhydryl, carbonyl, phosphate) able to cope with the pollutants’ toxicity. Due to the functional groups, these materials developed a wide range of uptake mechanisms (electrostatic interaction, ion exchange, precipitation, complexation, chelation, reduction) that ensure high pollutants removal efficiencies from aqueous media [13, 14, 56]. Various biological materials were tested for the development as biosorbents, including: microorganisms and algae, plant materials, agro-industrial wastes and other polysaccharides materials. These categories of green adsorbents have been almost exclusively investigated from the perspective of their application for removal of heavy metals and/or textile dyes from synthetic wastewaters. The promising results have opened the way to develop environmentally friendly technologies for removal – recovery – recycling of rare earths and precious metals [57, 58]. Biosorbents must

Targeted issues	Relevance
<i>Batch studies</i>	
Effect of experimental parameters: pH, initial pollutant concentration, biosorbent dose, contact time, temperature	Optimization of the biosorption process
Isotherm modeling: Langmuir, Freundlich, Dubinin-Radushkevich, Tempkin, Elovich etc.	Quantification of the interactions. Evaluation of the maximum biosorption capacity
Kinetics modeling: Lagergren (pseudo-first order), Ho (pseudo – second order); diffusion models - intraparticle, film	Determination of uptake rate. Insights into the mechanism of biosorption reactions
Thermodynamic parameters	Biosorption energy (heat)
<i>Fixed – bed column studies</i>	
Parameters process: initial concentration of adsorbate, pH, flow rate, bed height Breakthrough curve and its modeling	Valuable information for design of wastewater treatment for continuous operation in real conditions
<i>Desorption studies</i>	
Desorption agent Minimum number of reused cycles	Biosorbent regeneration and recyclability

Table 1.
Description of biosorption process and its characteristics.

exhibited high capacity and rate of biosorption, increased selectivity and multiple recyclability. Unlike algal biosorbents that have significant pollutant uptake capacity, fungi and some agricultural wastes show moderate capacity of biosorption [59]. Due to the adjustable surface chemistry of biomass, the essential features of biosorption materials can be significantly improved or tailored to practical applications by way of adequate chemical modification procedures [13, 14, 56, 60]. The stringent necessity for the near future is the transposition of biosorption processes performances to pilot and industrial scale.

3.2 Characteristics of rape waste

Rape waste biomass shows interesting properties that promote its biosorbent function for pollutants' removal, as another prospective way of waste reuse and recycling. The features of RS wastes are determined by factors correlated with the raw material (source, geographical region and environmental conditions), types of products and processes. RS wastes are vegetable materials with lignocellulosic composition of high degree of heterogeneity, as mentioned in Section 2.1. They have been assimilated with multi chromatographic systems carrying very different supports of polarity [61]. This heterogeneity is due to their complex structure and composition. For instance, the structure of the RSs encompasses three main structural components: (1) the embryo that in turn, is formed by cotyledon, hypocotyl and radicle; (2) the endosperm; (3) the coat of seed [62]. The seed flesh contains lipids (essentially residual oil) in the form of triacylglycerols and lipids associated with cell membranes, proteins (oleosins make up to 20% of total seed proteins) and fibers, composed from lignin and polysaccharides (cellulose, hemicellulose and pectin) [21]. The chemical composition of RS agro-wastes (stalk, straw, leaves) reveals a high content of carbon (457–465 mg/g) and nitrogen (1.9–6.7 mg/g), together with elements like Ca, Mg, K, Na and P [63, 64]. Deoiled CM contains

44.21% C, 6.3% H, 5.55% N and 0.37% S [25], while the following elemental analysis of RSC was reported: 77.82% C, 15.05% O, 5.48% N, 0.65% Ca, 0.48% S and 0.54% P [65].

The surface characteristics are of major importance for the biosorption potential of a material. One of them is the specific surface area assessed by Brunauer-Emmet-Teller (BET) method. For example, a BET area of $5.6 \text{ m}^2/\text{g}$ was determined for RSC by N_2 adsorption analysis at 77 K [66]. The surface area of RS waste from a local unit of biodiesel production has been evaluated at $107.32 \text{ m}^2/\text{g}$ by dynamic water vapor sorption [65]. A higher value was obtained for RS stalk - $43.21 \text{ m}^2/\text{g}$ [67].

The surface charge is expressed in terms of point of zero charge pH (pH_{PZC}), representing the pH value at which the surface of biosorbent is neutral from electric point of view. The pH_{PZC} of a RS waste has been reported as being 5 [68]. Thus, the surface of RS is positively charged at $\text{pH} < 5$ and favorable for anions biosorption. Meanwhile, for $\text{pH} > 5$, the surface of biosorbent is negatively charged and has affinity for cationic pollutants. More basic pH_{PZC} values were obtained for canola stalk (5.7) [69], canola stalk and leaves (6.1) [63] and canola hull (7.0) [70].

The morphological features of the biosorbents are usually studied by means of scanning electron microscopy (SEM). From **Figure 3a**, it may be observed that rapeseed waste has an uneven and porous structure that seems to be very adequate for the biosorption of pollutants [71, 72]. RS stalk, straw and hull present a rough surface, with regular tunnel-like structure (remains of cell wall) [70, 73–75]. The small pores on the surface had an average pore diameter of $1.09 \pm 0.13 \mu\text{m}$ [73].

The Fourier transform infrared spectroscopy (FTIR) features are valuable source of information related to the functional groups playing a key role in the biosorption process. FTIR studies revealed that the surface of RS waste contains valuable functional groups playing a key role in the biosorption process, such as amino, hydroxyl and carbonyl groups [65, 70–72, 76, 77]. The main peaks in the FTIR spectrum of RS waste are presented in **Figure 3b**.

Thermal stability and degradation behavior of RS have been assessed by thermogravimetric analysis (TGA). Thermal decomposition of RS biomass has been described as a three stages process: moisture evaporation (up to 120°C), hemicellulose decomposition ($200\text{--}250^\circ\text{C}$), degradation of cellulose and lignin ($300\text{--}450^\circ\text{C}$) [25, 68]. The high thermal stability indicated by the TGA suggests that the RS biosorbents yielding as wastes from the treatment of wastewaters could be reused for energy recovery purposes.

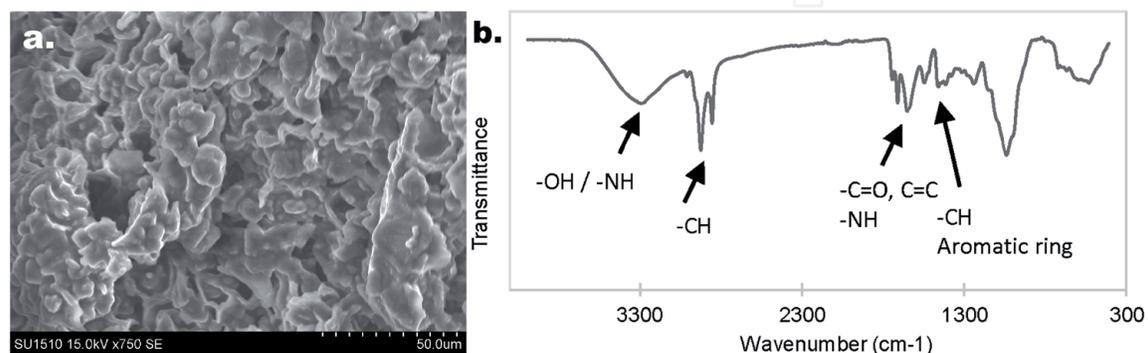


Figure 3.
SEM image (a) and FTIR spectra (b) of RS waste.

4. Pollutants removal and system configuration

4.1 Types of pollutants adsorbed and wastewater characteristics

A systematic adsorption investigation starts at laboratory scale, when the interaction between a single target pollutant and the adsorbent is studied. This fundamental set-up is called a mono-component system, consisting from a single pollutant-model (usually, its salt form) dissolved in high-grade purified water. The complexity of the system will grow with two or more target pollutants to be removed from the same aqueous media. The multi-component system study is necessary in order to see the possible effects (competitive or synergic) generated by the presence of another compound (possible interference) on the uptake by the adsorbent. The ultimate goal is to test the adsorbent in a real aqueous media, i.e. wastewater, which is a more complex system, containing many dissolved (and in many cases, not individually known) compounds.

To the authors' best knowledge, the first studies using RS biomass-based adsorbents, i.e. canola meal, were reported over two decades ago by Al-Asheh and Duvnjak [24, 78, 79]. After 2010 (**Figure 4a**), RS waste has again attracted attention in the research community, as a result of worldwide increased production of rape cultures and waste management regulatory pressures.

4.1.1 Mono-component systems: inorganics adsorption

Figure 4b presents the distribution of model pollutants reported in literature, by the number of RS-derived adsorbents investigated for the individual uptake of a certain pollutant (i.e., in mono-component system). Among inorganic compounds, the prevalence of heavy metals removal from wastewater is justified by their high occurrence, persistence in the environment and high toxicity. Numerous articles have reported the use of RS-based adsorbents for the abatement of Pb and Cd removal, followed by Cu, Ni and Zn (**Figure 4b**). It is interesting that most fractions of rape biomass were studied for Cu adsorption, in natural or modified state (**Table 2**): from sprouts to stalks and leaves resulted from harvesting and finally, to rapeseed press-cake. A quite similar variability can be observed for cadmium. An

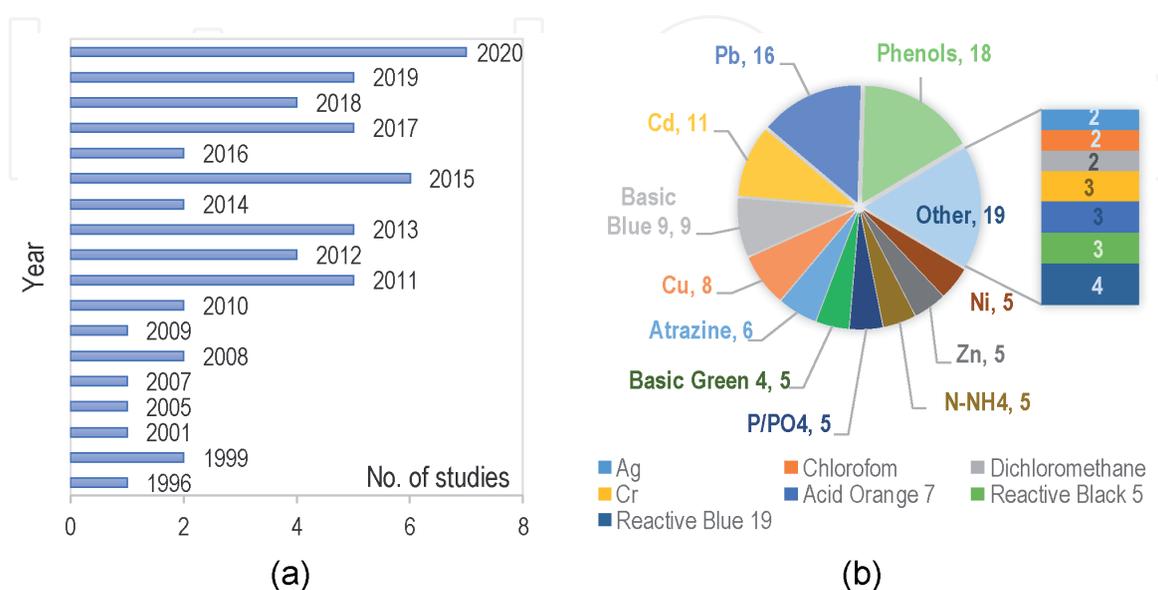


Figure 4. Distribution of adsorption studies using rapeseed biomass per years (a) and tested RS-based adsorbents (except the 22 cases of 1 adsorbent per pollutant) on different wastewater contaminants (b).

Adsorbent	Efficiency	Adsorbent	Efficiency
Canola meal [24]	36.747 mg Cu/g*	RSC [68]	13.858 mg Zn/g*
Canola meal [78]	22.69 mg Zn/g*, 89.6% Cd, 67.2% Cu, 40.3% Ni, 92.3% Pb	Brassica straw [char, magnetic-gelatin] [85]	Cr*: 35.1971 mg/g char; 434.85 mg/g magnetic-gelatin char
RSC, husks, WS, ground seeds [21]	Cu*: 13.4 mg/g RSC; 36.6 mg/g husk; 8.6 mg/g WS; 10.7 mg Cu/g seeds	Canola stalk and leaves [75]	62.5 mg Fe/g*, 40.0 mg Mn/g*, 41.7 mg Zn/g*, 20.8 mg Ni/g*, 35.7 mg Cu/g*, 71.4 mg Cd/g*
RSM [71]	18.35–22.70 mg Pb/g*	Canola straw [char] [64]	30.50–37.49 mg Cu/g*
RS pellet cellulose [citric acid] [86]	40% Cu	RS oil cake [char] [87]	129.87 mg Pb/g*, 133.33 mg Ni/g*
RSM [77]	15.43 mg Cu/g*, 21.72 mg Cd/g*	Deoiled RSM [88]	97.09 mg Pb/g*
Brassica campestris waste stem [82]	40% Ni, 98% Pb, 91.8% Cr	Canola straw [char] [84]	Pb*: 84–108 mg/g char; 72–195 mg/g steam-AC
Canola straw [char] [83]	14.56 mg/g* Cr	Expired rapeseeds [89]	4.65–45.38 mg Hg/g
Canola residues [81]	90–99% Cd	Canola shoot [char] [80]	4.14 mg Cd/g, 15.52 mg Cu/g
RS pomace [sunflower husks, char] [90]	26.9 mg Ag/g*, 17.1 mg Cu/g*	RS stalk from 2 cultivars [NaOH, enzymatic hydrolysis] [67]	Cd*: 10.93–25.19 mg/g stalks; 18.15–27.40 mg/g fermentation residues

Notes: “[X]” indicates that the native biomass has undergone significant structure modification, while X can be the chemical agent used, the final adsorbent or other mixture component; char – carbonized material (e.g. biochar).
 *Langmuir maximum sorption capacity.

Table 2.
 Efficiency of RS-based adsorbents for heavy metals removal from liquid phase.

AC prepared from canola shoot showed maximum sorption capacities of 15.52 mg Cu/g and 4.14 mg Cd/g [80]. Similar efficiency for Cu adsorption was observed for RSM, i.e. 15.43 mg/g [77].

The sorptive potential of RS agro-wastes was commonly assessed (**Table 2**). In many cases, the residues were used after minimal pre-treatment, which usually involves the removal of impurities by several washings and drying for a certain period of time, at room temperature, in sunlight or in an oven. Washed and dried canola agro-residues from Iran were used for adsorption of cadmium ions from aqueous solution [81], whilst a mixture of stalk and leaves was used for the removal of several metals in the sequence of sorption capacities: Cd > Fe > Zn > Mn > Cu > Ni [75]. Untreated stalks have been investigated in the adsorption process of Cr, Cd, Ni and Pb [82]. Reference [67] used several cultivars of RS to assess the ethanol production after a mild alkali pretreatment (1% NaOH, 50°C). The solid residues obtained after yeast fermentation exhibited higher Cd adsorption capacities than the raw stalks (**Table 2**). In the last years, RS straw was used as feedstock for biochar production at laboratory scale [64, 83–85]. Although the adsorption capacities of these materials are usually higher than the precursors (**Table 2**), the feedstock particles size and preparation conditions vary.

According to **Table 2**, the most popular bio-material for heavy metals adsorption is RS meal (or cake, press-cake). This complex lignocellulosic material is comprised of a water-soluble fraction (e.g., phytic acid, proteins, glucosinolates etc.) and a solid fraction, formed from husks (hulls) and the flesh of seeds. Authors [21] made a systematic research regarding the component of RSC responsible for metal binding. By comparing the adsorption capacity of Cu for press-cake, husks, white sediment (WS, i.e. flesh of seeds) and ground seeds, under the same experimental conditions, they observed that husks are the most efficient fraction. Based on the removal efficiency, RSC presents higher affinity for Pb, followed by Cd, Cu and Ni [78]. The values of metal biosorption capacity reported in literature aren't higher than 40 mg/g. Meanwhile, the ACs obtained from RSM can easily achieve adsorption capacities of around 130 mg/g (**Table 2**), by creating a microporous structure and a high surface area.

Nutrients were also under investigation for adsorption on agricultural RS residues. Native and modified canola stalks and leaves were used for the removal of phosphorus from aqueous solutions [63]. According to Langmuir sorption capacity (q_L), sorbents efficiency followed the sequence: *native* (4.3 mg/g) < *modified by CaCl₂* (6.6 mg/g) < *modified by urea* (8.5 mg/g) < *modified by FeCl₃* (9.0 mg/g). A biochar prepared from RS leaves and stems was combined with Mg-Al layered double oxides and tested for the adsorption of phosphate from water [91]. The phosphate removal efficiency remained above 92% at a pH range of 2–10, for an initial pollutant concentration (C_i) of 50 mg/L, while q_L reached a value of 132.8 mg/g. Adsorption of ammonium nitrogen from diluted aqueous solutions was studied using natural mineral and organic adsorbents [76]. The authors observed that the canola agro-residues presented an adsorption capacity comparable to that of zeolite and bentonite. The organic spent adsorbent can be safely used afterwards as soil fertilizer. q_L of ammonium ion for several ACs from CM varied between 17.9 and 148.9 mg/g [92]. The low cost of the KOH treated AC was determined.

A single study was found with regards to the adsorption of fluoride using canola stalk treated with bicarbonate, reporting a removal efficiency of 79% for C_i of 10 mg F/L [93].

4.1.2 Mono-component systems: organics adsorption

To the authors' knowledge, adsorption/biosorption studies using rape-derived sorbents involved the following categories of organic compounds: textile dyes, phenolic compounds, organochloride compounds, pesticides and herbicides. Phenolic compounds and textile dyes were the organic pollutants with the highest interest for removal from aqueous phase by RS biomass (**Figure 4b**).

Various dyestuffs, including acid, basic, direct and reactive, were used as model pollutants in the adsorption experiments. From **Table 3**, higher sorption capacities for cationic dyes (13.22–836.2 mg/g) were observed, when compared to those for anionic dyes (2.01–11.81 mg/g). This is mainly because of the different treatments (chemical or thermal) applied to the rape biomass. Among the various dyes, malachite green (MG) and methylene blue (MB) are preferred as model contaminants. Extensive research was done using stalk adsorbents, in different forms: native, chemically treated, biochar or activated form (**Table 3**).

Other studies involving RS meal adsorbents (**Table 3**) deal with the removal of chloroform and dichloromethane, atrazine, phenolic compounds and dyes. In addition, there is a study from Canada reporting acyclovir adsorption on powdered AC prepared from deoiled CM with a removal efficiency of 39.5% at $C_i = 400$ mg/L [25]. RS cake was used many times as precursor for AC production, which was then used

Adsorbent	Efficiency	Adsorbent	Efficiency
Defatted seeds [94]	68.6% chloroform, 70.4% dichloromethane, 78.6% trichloroethylene	Defatted seeds [95]	71.9% chloroform, 69% dichloromethane, 46.8% benzene
RSM [magnetic NPs, polypyrrole] [96]	MG [*] : 836.2 mg/g RS-magnetic NPs, 93.3 mg/g RS-polypyrrole	Waste of RS after microbial culture medium [48]	17.857 mg MG/g [*]
RS straw-based compost [97]	2.15 mg Reactive Yellow 84/g [*] , 4.78 mg Reactive Black 5/g [*] , 26.41 mg Basic Green 4/g [*] , 27.19 mg Basic Violet 10/g [*]	Laccase immobilized with RS press cake [98]	74% Amaranth, 81% Acid Orange 7, 50% Acid Blue 113, 83% Trypan Blue, 57% Sunset Yellow FCF
RSC [61]	58.2% atrazine	RS [AC] [99]	70–95% phenol
RSC [alginate] [100]	Atrazine: 70% for beads form; 96% for rods form	Canola stalk [101]	6.73 mg Methylene blue/g ^{**}
RS meal [72]	11.81 mg Reactive Blue 19/g [*]	RSC [AC] [102]	332 mg phenol/g, 482 mg p-chlorophenol/g
RS stalk [AC] [103]	0.079 mg bromopropylate/g [*] ; 90–100%	RSC [AC] [104]	Phenol: 88 mg/g steam-AC, 68 mg/g CO ₂ -AC
Canola hull [70]	67.56 mg Basic Blue 41/g [*] , 49.01 mg Basic Red 46/g [*] , 25.0 mg Basic Violet 16/g [*]	Canola hull [105]	63% Reactive Red 198, 70% Reactive Blue 19, 80% Direct Red 79, 81% Direct Red 80
Swede rape straw native, [oxalic acid] [73]	MB [*] : 143 mg/g native, 432 mg/g modified	Swede rape straw native, [tartaric acid] [74]	MB [*] : 128.2 mg/g native, 246.4 mg/g modified
Canola straw [char] [106]	102 mg Methyl violet/g	Canola stalk [char] [107]	93.4 mg MB/g
Canola stalk [69]	32.8 mg Remazol Black B/g [*]	Canola residue [108]	Acid Orange 7
Canola stalk [20]	25.06 mg Acid Orange 7/g [*] , 32.79 mg Remazol Black 5/g	Swede rape hull [microwave] [109]	272 mg MB/g [*]
RSM [110]	78 mg MG/g [*] , 122 mg MB/g [*]	Canola stalk [AC] [111]	135.8 mg 2,4-dichlorophenoxyacetic acid/g

Notes: “[X]” indicates that the native biomass has undergone significant structure modification, while X can be the chemical agent used, the final adsorbent or other mixture component; char – carbonized material (e.g. biochar).
^{*}Langmuir sorption capacity.
^{**}Sips sorption capacity.

Table 3.
 Efficiency of RS-based adsorbents for organics removal from liquid phase.

for phenolic compounds abatement (Table 3). Moreover, pesticides of moderately to highly hydrophobic nature, like atrazine, have shown fairly good removal efficiencies when RS cake was used (yet, mainly due to the absorption in the oil droplets that remain trapped in the matrix after seed pressing) [61]. Higher efficiencies than powdered AC were obtained for volatile organic compounds, where some intracellular fat particles named spherosomes are responsible for their uptake [94, 95].

4.1.3 Multi-component systems

There are few studies involving RS sorbents that report simultaneous adsorption experiments. Firstly, Al-Asheh et al. [24, 78] investigated the single, binary, ternary and quaternary adsorption of some heavy metals using CM. They observed the same succession in single system and mixture based on the molar sorption capacities for: $Zn > Cu > Cd$ [24]. In a later study, the same authors noticed Ni was strongly inhibited by the presence of Cu and Pb in the same solution [78]. In binary and tertiary metal systems, inhibition of Pb was manifested by Cu, Cd and/or Ni, whereas Cd uptake was higher in binary mixture with Ni or Pb. Copper biosorption was restricted by Pb only in binary mixtures, while in any other combination with Cd and Ni, it was promoted. In all cases, copper exhibited the highest molar biosorption capacity, followed by Cd, Ni and then Pb in mono-, bi- and tri-component systems. In a quaternary mixture, the following order (molar basis) was obtained: $Cu > Cd > Pb > Ni$.

The efficiency of canola residues (stalk and leaves) in the competitive biosorption of Cd, Cu, Ni, Zn, Fe and Mn was investigated by means of equilibrium isotherms [75]. The authors mention that: “The sorption isotherm of heavy metals in single and competitive systems were studied using batch technique. Sorbents were allowed to equilibrate with solutions at different initial metal concentrations (0, 5, 10, 30, 50, 100, 150, 200, and 300 mg/L).” However, it is not clearly stated for competitive systems if the mentioned initial concentrations are for each metal (and the highest total C_i would be 300 mg/L times 6 metals = 2400 mg/L) or the values are cumulated (the highest C_i of each metal would be 300 mg/L divided by 6 metals = 50 mg/L). In any case, the biosorption capacities of all metals have decreased in multi-component systems with more than 67% as compared to the individual biosorption (**Table 2**), in the following order of metal sorption: $Ni (6.6 \text{ mg/g}) < Zn (9.4 \text{ mg/g}) < Fe (10.7 \text{ mg/g}) < Mn (10.2 \text{ mg/g}) < Cu (11.6 \text{ mg/g}) < Cd (14.7 \text{ mg/g})$.

To the authors’ knowledge, the only article reporting simultaneous biosorption of pollutants of different type, i.e. Pb and Reactive blue 19 (Rb19) dye, is reference [112]. In the absence of a rigorous experimental framework for multi-component biosorption study, the authors have tried multiple strategies to study the biosorption of binary system using RS meal. These involved: (i) influence of Pb:Rb19 molar ratio (range of 0.8–6.0), (ii) equilibrium studies by varying the initial concentration of one pollutant (15–150 mg/L), while maintaining a fixed C_i (50 mg/L) of the second contaminant, (iii) kinetics modeling at various pollutant molar ratios, and (iv) selectivity tests. The biosorption profile of the binary system was found to be versatile. At low C_i , dye biosorption was promoted by the presence of metal ions. However, at high C_i of dye, lead uptake was inhibited.

Studies on sorption processes with rape biomass involving real effluents were reported by few authors [71, 80, 94, 98, 111]. Heavy metals have been successfully removed from industrial effluents: Cu from smelting wastewater in Canada using CM [78], Pb from spiked industrial wastewater in Romania (94% efficiency in biosorption column with RS meal) [71] and Cd (20% reduction) and Cu (95% removal) from acid mine water in Australia by using biochar obtained from canola shoot [80]. Dichloromethane was removed (90%) from chemical wastewater on defatted seeds from oil extraction in Japan, while total elimination of an herbicide from drainage water from sugarcane fields in Iran using canola stalk-based AC was obtained [111].

4.2 Batch and dynamic process operation

Current research regarding adsorption as a wastewater treatment technology is focused on trials of a large and diverse range of materials that could become

suitable adsorbents for different pollutants. This could be easily done at laboratory scale by using batch testing. The batch operation is also favored for obtaining fundamental information about the adsorption process, like the adsorption capacity in optimum working conditions. A summary of the best adsorption conditions by using RS biomass is presented in **Table 4**. Among the factors influencing the sorption process, solution acidity affects the pollutant speciation, the charge of functional groups on the sorbents surface and the ions competition for the binding sites. As **Table 4** shows, metals usually adsorb at acidic pH (precipitation of metal hydroxides at $\text{pH} > 6$ is also avoided). Organic contaminants, like volatile compounds or phenols, mostly favor neutral to alkaline conditions. On the other hand, pH values of 6–8 are optimal for cationic dyes, while acidic medium is best for anionic dyes. The amount of available sorption sites is directly dependent on the amount of adsorbent used and its granulometry. Native biosorbents, which have low specific area, impose the use of a higher dose, whereas a lower dosage is necessary for chemically modified or pyrolysed adsorbents. However, a too high dose may lead to particle agglomeration and low access to the sorbent. The rapidity with which the sorption equilibrium is reached depends on the contact time and agitation speed. The average time when using RS adsorbents was reported to be a few hours (**Table 4**). Temperature influences the sorption capacity and biosorbent structural stability. An endothermic process is favored at high temperatures, involving heating costs and a possible biosorbent structural damage. However, many studies have reported high adsorption capacities close to room temperature (**Table 4**), which is important for practical reasons.

The biosorption equilibrium can be modeled by using equilibrium and kinetics experimental data. The most frequently used isotherms are Langmuir and Freundlich. The wide applicability of Langmuir isotherm model in case of heavy metals on native RS biosorbents and dyestuffs (**Table 4**) indicates the monolayer uptake on a homogenous surface without interaction between adsorbed molecules [48]. When using ACs, the metals sorption conformed to the assumptions of the Freundlich model – multilayer uptake occurring on a heterogeneous surface [85]. Phenol and organochloride compounds adsorption also follow the Freundlich model. In some cases, Freundlich and Langmuir models were both good models to describe the system at equilibrium conditions, indicating the complexity of the process. Kinetics of adsorption using RS biomass widely conforms to the pseudo-second order model (**Table 4**), implying that the rate-limiting step is a chemical sorption between the adsorbent and pollutant [73].

Because it is inconvenient to have a one-time use sorbent, regeneration of the spent sorbent by means of desorption is necessary. The eluents used for desorption of metal and dyes can be either acids, alkalis or some other chemical compounds (**Table 4**). The observed trend is that the pH can act like a switch for the selective desorption of pollutants (acidic medium for metals, basic medium for dyes). After desorption, the recovered rape-based adsorbent can be re-used in a new sorption process. The number of cycles of sorption–desorption indicate the reusability adsorbent potential (**Table 4**). Some sorbents, including untreated RS meal, maintain a decent sorption efficiency after several cycles of adsorption–desorption. After 3 cycles, the drop in efficiency was between <5% and 22.5% [48, 88]. Some studies reported up to 5–6 cycles of biosorbent reuse, and the decrease in the removal efficiency was found between 16.2% and 43% [85, 111]. Another practical aspect of the type of eluent used is the indication about the sorption mechanism. For example, a pH-dependent desorption suggests the involvement of electrostatic interactions in the sorption process. Or if water is a successful eluent, then the pollutant uptake is predominantly based on physisorption [21]. Several researchers have made efforts to elucidate the main sorption mechanism(s) (**Table 4**). Nevertheless, the adsorption

Ref.	Optimum parameters	Best fit model	Desorption	Proposed mechanism
[95]	pH 7, dose 10 g/L, 6 h	F	- Chloroform, dichloromethane, benzene	Uptake by spherosomes
[21]	pH 5, dose 10 g/L, 1 h, 120rpm	L	HCl 0.1 M; 102.6% Cu	Proton & Ca exchange, chemisorption
[99]	pH 7.5, dose 1 g/L, 7 days, 25°C	F	- Phenol	π - π dispersion interaction, electrostatic interaction
[113]	pH 2.5, dose 1 (RR198, RB19) - 2 (DR79, DR80) g/L, 60 min, 200 rpm	T; PSO	H ₂ SO ₄ ; 88% RR198, 86% RB19, 91% DR79, and 95% DR80 at pH 12	Electrostatic interaction
[64]	pH 4.5-5, dose 8 g/L, 25°C, 2 h	L	NaNO ₃ 1 M; 45.7% Cu @ pH 3.5	Electrostatic interaction, formation of surface complexes
[20]	pH 2.5, dose 7.5 g/L, 25°C, 120min, 100 rpm	L; PSO	- Acid orange 7, Remazol black 5	Electrostatic attraction, chemisorption
[74]	pH 8, dose 1 g/L, 40-60 min	L; PSO	HCl 0.01 M; 91.01% MB	Electrostatic attraction, chemisorption, particle diffusion
[73]	pH 8, dose 1 g/L, 60-180 min	L; PSO	HCl 0.01 M; 68.6% MB for SRS and 12.4% for SRSOA	Electrostatic attraction, chemisorption, diffusion
[48]	pH 6.5, dose 2.5 g/L, 180 min, 120 rpm	L; PSO; endothermal	NaOH 0.1 M; 94.5% MG; 95% of MG uptake capacity in the next adsorption cycle was achieved	Electrostatic attraction
[83]	pH 4, dose 4 g/L, 25°C, 2 h	F, L	- Cr	Formation of surface complexes, hydrolysis reactions
[96]	pH 6, dose 1 g/L, 25°C, 120 min (RM-MNs) - 150 min (RM-PPy)	S; SD (RM-MNs), ANN (RM-PPy); endothermal	NaCl 0.05 M at pH 3; MG: 93% (RM-MNs) - 71% (RM-PPy); 3 reuse cycles with 22.5% decrease of dye removal for RM-MNs and 11.2% for RM-PPy	Electrostatic interactions; more complex mechanism for RM-PPy
[71]	pH 5.2, dose 10 g/L, 20 °C, 3 h	L; PSO; endothermal	- Pb	Electrostatic interaction, complexation reaction, ion-exchange
[88]	pH 5.5, dose 8 g/L, 22 °C, 30 min	L; PSO	HNO ₃ 0.1 M; 98.2% Pb; min. 3 reuse cycles with <5% decrease of biosorption efficiency	Ion-exchange

Ref.	Optimum parameters	Best fit model	Desorption	Proposed mechanism
[91]	pH 2, dose 2.5 g/L, 30 min, 200 rpm	L, F; PSO	- Phosphate	“Memory effect,” electrostatic attraction, surface complexation, anion exchange
[111]	pH 2, dose 0.33 g/L, 25°C, 45–60 min, 120 rpm	PSO, IPD	Acetone; 83.79% 2,4-dichlorophenoxyacetic acid adsorption efficiency after 5 cycles	Aromatic ring interaction
[85]	pH 1, dose 1 g/L, 25°C, 12 h, 160 rpm	F; PSO; endothermal	NaOH 1 M; Cr: 57% sorption capacity after 6 cycles	Electrostatic interaction, redox reaction, surface complexation

Notes: Adsorbents corresponding to each reference can be found in **Tables 2 and 3**; L (Langmuir), F (Freundlich), L-F (Langmuir–Freundlich), S (Sips), T (Templekin) isotherm models; PFO (pseudo-first order), PSO (pseudo-second order), IPD (intraparticle diffusion), SD (surface diffusion) kinetics models; ANN – artificial neural network.

Table 4.
 Optimum conditions of adsorption/desorption for pollutant uptake on RS-based adsorbents.

mechanism is characterized by a high degree of complexity, especially when natural lignocellulosic biosorbents are involved.

In a single biosorption run, it is quite often that the sorbent does not reach the maximum sorption capacity (e.g., given by the Langmuir isotherm model) for a certain pollutant. Nevertheless, there will not be any further noticeable uptake of the respective pollutant even if the contact time is prolonged. Then, the spent sorbent is not sent to regeneration, but instead to a new sorption run involving a different target pollutant. And then in a third run of adsorption and so on. This concept is called an alternating or sequencing sorption. The main idea is to load the biosorbent as much as possible before its disposal, which could be practical for a low capacity biosorbent. This concept was studied by Morosan et al. [65, 114] using RS meal as adsorbent and they have achieved 4 sequential adsorptions. The research was done considering two directions: (a) the biosorption of Rb19 dye followed by lead ions - RS-Rb19/Pb biosorption system, and (b) the biosorption of Pb followed by Rb19 dye - RS-Pb/Rb19 system. The authors observed that: (i); Pb uptake at higher concentrations is impeded by the presence of Rb19 on RS; (ii) dye sorption is favored by Pb presence; (iii) for the system RS-Rb19/Pb, pollutant desorption is selective, as a function of pH (**Table 4**); (iv) desorption was <7% in case of RS-Pb/Rb19 system. The experimental data suggests that the succession of pollutant biosorption matters. However, the biosorbent reuse in a new sorption cycle in order to determine the pollutants' uptake was not done.

At larger scale, continuous sorption processes are preferred. However, we have found only two studies using RS adsorbents in column tests. Amiri et al. [111], using a fixed-bed column (30 cm length, 2.5 cm inlet diameter) filled with canola stalk-derived AC (height of 20 cm) to adsorb 2,4-dichlorophenoxyacetic acid, obtained maximum sorption capacities comparable with the batch data. The intraparticle diffusion coefficient from batch experiments was used for column modeling. Lead uptake in a fixed-bed column with RS meal (bed height 6 cm) was reported [71]. A faster column saturation was observed at higher pollutant concentration, while the maximum sorption capacities were higher than the one provided by Langmuir

model. The authors also tested an industrial wastewater containing lead ions in column configuration.

Considering the adsorbent's life cycle, when its regeneration is not economical anymore or it's not possible due to a previous chemisorption mechanism, the sorbent must be disposed of in such a manner that secondary pollution is avoided. In this sense, several authors proposed that exhausted RS meal could be used as a substrate for microbial colonization [48, 61]. Other practices involved biochar production from dye-loaded rape straw (modified with oxalic acid) [73], soil fertilizer [76] and using depleted biochars as biofuel [106]. To avoid leaching, a metal contaminated CM biochar was stabilized using phosphate binders [115]. Recovery of heavy metals from RS biomass can be done by electrochemical methods [116].

5. Conclusions

The wastes derived from rapeseed cultivation and production of oil and biodiesel are of interest in the context of circular economy. According to the reviewed literature, there exists valorization options for each rapeseed waste (stems, stalks, leaves, hulls, meal/cake). Major applications of these wastes include the use as cover crop for agricultural residues (stems and leaves) and animal feed for rapeseed meal. Rapeseed wastes contain valuable constituents and nutrients, making them of relevant nutritional and economic importance. Protein, pectin and polyphenols can be extracted from stems, leaves and meal. Besides the use of animal feed, the RS meal has great potential for obtaining high-value products for human consumption.

A less popular valorization option is the use of rapeseed waste as adsorbents for wastewater treatment. The literature survey presented in this chapter has revealed the existence of sufficient RS-derived adsorbents that have a stable structure and proved significant organic and inorganic removal efficiencies. However, many studies were done in batch operation, at laboratory scale. Very few researchers reported the use of fixed-bed column and/or real wastewater containing the target pollutants. Practical application of RS waste can sometimes be difficult. For example, RS meal forms a slurry when in sufficient contact time with water, which leads to difficult separation of phases or column clogging. This problem can be tackled by mixing the biosorbent with some inert material (e.g., ceramic rings) or immobilization in a matrix (e.g. alginate). The use of stalks or husks is another solution, due to their lower protein content. In any case, chemical or thermal modification of natural RS waste can be also an alternative, especially when a higher sorption capacity is desired. Regeneration of the adsorbent and its subsequent use in a new sorption cycle is also possible. The exhausted adsorbent can be valorized as substrate for microbial growth, biochar or biofuel production.

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