Biointerface Research in Applied Chemistry
Platinum Open Access Journal (ISSN: 2069-5837)

Review
Volume 11, Issue 5, 2021, 12689 - 12705
https://doi.org/10.33263/BRIAC115.1268912705

Using Cucurbits By-Products as Reagents for Disposal of Pollutants from Water Environments (a Literature Review)

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Received: 16.12.2020; Revised: 16.01.2021; Accepted: 22.01.2021; Published: 31.01.2021

Abstract: The paper summarizes data from literature sources using the waste of processing cucurbits (pumpkin, watermelon, melon, cucumber) as a sorption material to remove various pollutants from water environments. It states that cucurbits' shells are effective sorption materials for extracting heavy metal ions and dyes. Seeds of large cucurbits fruits (pumpkin, watermelon, melon) and seed shells also showed good sorption performance for heavy metal ions and dyes. It was found that most of the pollutants adsorption isotherms on cucurbits by-products are most accurately described by the Langmuir model, less often by the Freundlich model, and occasionally by the Tyomkin or Dubinin-Radushkevich models. It was determined that the adsorption process kinetics most often follows the pseudo-second-order model, less often – the logistic model. To increase the adsorption characteristics of cucurbits fruit components for various pollutants, they were modified with various chemical reagents.

Keywords: cucurbits; by-products; water treatment; adsorption; heavy metal ions; dyes; modification.

1. Introduction

The world community is currently rapidly developing a new innovative environmental protection area – the use of industrial and agricultural waste as reagents for removing pollutants from water environments. By-products of agricultural raw materials are of particular importance. The latter are formed annually on a large scale, are renewable, very cheap, contain natural compounds and biopolymers with various functional groups, promoting their widespread use in various sectors of the national economy.

The world literature provides much information about the use of agricultural raw materials waste as coagulants and flocculants, sorption materials for various pollutants removal from water [1-14].

A fairly large role in human nutrition is played by cucurbits, usually those from the gourd family (Cucurbitaceae). The latter mainly include pumpkins, watermelons, melons, marrows, scallop squashes, cucumbers. When they are processed, various wastes are formed, usually the rind of fruits and seeds.

2. The Use of Pumpkin Fruit Waste as Sorption Materials for Removal of Metal Ions and Dyes from Aqueous Media

The most important of these crops for people are pumpkins (*Cucurbita*), i.e., herbaceous plant genus in the gourd family (*Cucurbitaceae*). The word "pumpkin" usually refers to the common pumpkin (*Cucurbita pepo*) and winter squash (*Cucurbita maxima*), which are widely spread and cultivated as food and fodder plants. Annual or perennial rough or hairy grasses that creep along the ground and cling with branched tendrils. The stems are covered with more or less large lobed leaves. The fruit is a pumpkin, normally with a hard outer layer (skin) and numerous flattened seeds framed by thick bloat [15].

Pumpkin is a fruit that has a high nutritional value due to its high content of carbohydrates, soluble fiber, protein, carotenoid compounds, vitamin A precursors, β-carotene, cryptoxanthin, and lutein [16]. Epy seeds are flat, oval, of various colors, and are used for food and medicinal purposes. Pumpkin seeds are rich in oil and nutrients. In particular, the composition of pumpkin seeds was determined in [17]: humidity - 4.06%, ash content - 3.80%, fiber - 2.91%, fat - 36.70%, protein - 34.56%, soluble protein - 18.1 %, sugar - 1.08%, and starch - 2.15%. Pumpkin seeds contain 48.92% of oils, of which 29.04% is oleic acid, 51.87% – linoleic acid, 11.64% – palmitic acid, and 7.0% – stearic acid [18].

Processing pumpkin fruits results in waste in the form of fruit rind and seeds. There are various ways to use the waste from processing cucurbits, including pumpkins, in the national economy [19]. The latter has also been studied as sorption materials for extracting various pollutants from natural and wastewater.

Muscat pumpkin (*Cucurbita moschata Duchesne ex Poir*) rind, dried and treated with 1 mol KOH solution, was studied as a sorption material for extracting Cu^{2+} ions from simulated solutions. It was found that the maximum sorption capacity for these ions is 78.13mg/g at an initial Cu^{2+} concentration of 80 mg/dm^3, a temperature of 298K, pH = 6.3, and a dosage of the sorption material of $0.5g/dm^3$. It was determined that the adsorption isotherms at 298-318K are most adequately described by the Freundlich equation, and the process kinetics is described by the logistic model [20].

Native and carboxylated common pumpkin rind was studied to extract Cd^{2+}, Hg^{2+}, Pb^{2+}, and Zn^{2+} ions [21]. At the initial concentration of these ions of $100mg/dm^3$, the dosage of the sorption material of $1.2g/dm^3$, pH = 7.5 and 1-hour contact, the degree of metal ions removal by native pumpkin rind was 67%, 52%, 85%, and 78%, respectively. For a carboxylated sample of pumpkin rind, these ions' removal rates were 73%, 60%, 65%, and 95%, respectively.

The dried and ground rind of muscat pumpkin was also studied to extract Lanaset Red G [22] and Reactive Red 120 [23] dyes from simulated solutions. It was found that the maximum sorption capacity for these dyes was 440.78 and 98.61mg/g, respectively. In both cases, the isotherms of dye adsorption in the temperature range of 298-328K are most accurately described by the Freundlich equations. The logistic model describes the process kinetics. Determination of thermodynamic parameters showed that both cases' adsorption process is physical, exothermic, and spontaneous.

The adsorption of Acid Black 1 dye by dried native and modified by loading Ni^{2+} ions muscat pumpkin rind was studied. Modification with Ni^{2+} ions led to an increase in the rind sorption capacity towards the dye. It was determined that Acid Black 1 dye adsorption by these sorption materials increased with decreasing particle size, reagent dose, solution pH, and temperature, but increased with increasing contact time and initial dye concentration. It was found that rapid adsorption occurred in the first 5 minutes, and kinetic equilibrium was reached within 50 minutes. The maximum sorption capacity towards the studied dye for native and Ni^{2+}-modified pumpkin rind was 227.62mg/g and 228.49mg/g, respectively. The Freundlich equation most accurately described the adsorption isotherms, and the adsorption kinetics was described by the logistic model [24]. The activation energy values and thermodynamic parameters indicated that the adsorption process was physical, spontaneous, and exothermic.

Native and NaOH-modified shells of muscat pumpkin (*Cucurbita moschata Duchesne ex Poir*) seeds were studied to remove Cu^{2+} ions from simulated solutions. It was determined that the maximum sorption capacities were 14.96 and 14.32mg/g for native and modified pumpkin seed shells at an initial Cu^{2+} concentration of 553mg/g, pH = 7, solution temperature of 29^{o}C, and dosage of sorption materials of 40g/dm^{3}. It was determined that the Langmuir equation more accurately describes adsorption isotherms, and the adsorption kinetics follows the pseudo-second-order model. The calculated adsorption activation energies for the initial and the modified pumpkin seed shells (42.4 and 69.42kJ/mol, respectively) indicate chemisorption [25].

Methylene Blue dye adsorption by native shells of common pumpkin seeds (*Cucurbita pepo* L.) at 30^{o}C was studied. It was found that the maximum adsorption capacity for this dye is 141.92mg/g. The adsorption isotherm is most adequately described by the multilayer adsorption model (R2 = 0.999). The process kinetics is more accurately described by the pseudo-first-order model. The process mechanism study showed that the initial period is characterized by diffusion. In the future, diffusion into meso- and macropores of the sorption material is predominant [26].

Reactive Black 5 adsorption from simulated solutions by native shells of common pumpkin seeds was also studied. It was found that the maximum sorption capacity for the said dye is 9.18mg/g when the dosage of pumpkin shells is 1g/dm^{3}, pH = 2, and the contact time is 30 minutes at the initial pollutant concentration of 100mg/dm^{3}. The Langmuir equation describes the adsorption isotherm, and the process kinetics is described by a pseudo-second-order model [27].

Erythrosine B adsorption process was studied on native shells of pumpkin seeds. It was determined that this dye's maximum sorption capacity is 16.4mg/g at its initial concentration of 400mg/dm^{3}. The adsorption mechanism is defined by the diffusion of erythrosine molecules into the particles of pumpkin seed shells, depending on the pore size [28].

Methyl orange adsorption by ethanolamine- and hydrochloric acid-modified pumpkin seed shells was studied. The maximum sorption capacity was 200.3mg/g at 318K, pH=3, and T = 120 minutes. The Sips model most accurately describes the adsorption isotherms in the temperature range of 298-318 K, and the kinetics of the process follows the pseudo-second-order model [29]. The calculated thermodynamic parameters (ΔG^{o} = -2.761, -4.473, and -5.201kJ/mol at temperatures of 298, 308, and 318K, respectively, ΔH^{o} = 33.37kJ/mol, and ΔS^{0} = 123J/mol·K) indicate spontaneous endothermic physical adsorption.

2,4,6-trichlorophenol was removed from aqueous solutions using four sorption materials from agricultural raw material processing waste, including pumpkin seed shells [30]. The maximum sorption capacity of pumpkin seed shells was determined for the said reagent, 41.5mg/g. At an initial concentration of 2,4,6-trichlorophenol amounting to 0.025mmol/dm^{3}, pH = 6, and a solution temperature of 25^{o}C, the degree of pollutant removal ranged from 12 to 68% with an increase in the mass of pumpkin seed shells from 5 to 25g/dm^{3}. It was found that the adsorption isotherm is most accurately described by the Freundlich equation ($R^2 = 0.9939$), and the kinetics of the process follows the pseudo-second-order model.

Adsorption of suspended coal dust substances from wastewater was studied using pumpkin seed shells modified with phosphoric acid or ammonium chloride [31]. The adsorption isotherm is adequately described ($R^2 > 0.99$) by the Langmuir equation, and the process kinetics is described by the pseudo-second-order equation.

There are several reports on the use of biomass and seed shells of the so-called "fluted gourd" (*Telfairia occidentalis*), a plant from the Cucurbitaceae *family*, which is widely distributed in West Africa, as a sorption material. The fluted gourd fruits are very large - from 16 to 105 cm in length and an average of 9 cm in diameter, but inedible. There are up to 196 seeds in large gourds, the length of which is usually from 3.4 to 4.9 cm. Edible is the seeds of fluted gourds, which consist of 27% of raw protein and 53 % of fat [32].

The native and carboxylated rind of fluted gourd of various sizes was studied to extract Cd^{2+}, Hg^{2+}, Pb^{2+}, and Zn^{2+} ions [21]. At the initial concentration of these ions of 100mg/dm^3, the dosage of the sorption material of 1.2g/dm^3, pH = 7.5 and 1-hour contact, the degree of metal ions removal by native *Telfairia occidentalis* rind was 90%, 62%, 95%, and 82%, respectively. For a carboxylated sample of fluted gourd rind, these ions' removal rates were 63%, 42%, 78%, and 79%, respectively.

Fluted gourd (*Telfairia occidentalis*) biomass modified with sulfonyl acetic acid was studied as a sorption material for removing Cd^{2+}, Pb^{2+} Zn^{2+} ions from simulated solutions. It was found that the native biomass of fluted gourd powder has an area of 33m^2/g; after modification, the sample area increased to 90m^2/g [33]. It was found that the best sorption parameters are achieved at pH = 4, solution temperature 40 °C, and the contact time more than 30 minutes. The maximum sorption capacities for Cd^{2+}, Pb^{2+}, and Zn^{2+} ions were determined using the Langmuir equation for native fluted gourd biomass: 9.79, 9.54, and 13.33mg/g, respectively, and for modified *Telfairia occidentalis* biomass: 11.34, 9.26, and 17.18mg/g, respectively. The calculated thermodynamic parameters indicate exothermic physical adsorption.

Adsorption of divalent metal ions (Hg, Rh, Pt, and Pd) by fluted gourd biomass was studied. It was determined that the maximum sorption capacity for these metals was 9.89mg/g, 9.81mg/g, 10.59mg/g, and 6.84mg/g, respectively, and correlates with the size of the ions of these metals [34]. This statement is confirmed by experiments on adsorption of Al^{3+}, Co^{2+}, and Ag^{+} ions by the biomass of fluted gourd. The maximum sorption capacity for these ions was 16.98mg/g, 10.34mg/g, and 8.03mg/g, respectively, and correlated with the size of metal ions. A decrease in the size of the metal ion ($Al^{3+} = 0.52$ A; $Co^{2+} = 0.78$ A and $Ag^{+} = 1.26$ A) resulted in an increase of sorption parameters [34]. It was determined that the metal ion adsorption isotherms are well described ($R^2 > 0.99$) by the Langmuir equation [33, 34] and the Freundlich equation [35].

Besides, native and 2-mercaptoethanoic acid-modified *Telfairia occidentalis* biomass was studied as a sorption material for removing Ni^{2+} ions from simulated solutions. It was found that the native biomass maximum sorption capacity for Ni^{2+} ions was 12.69mg/g. That of biomass treated with 0.5 and 1.0 N solutions of 2-mercaptoethanoic acids was 40.0 and 42.19mg/g, respectively [36]. It was found that at the initial Ni^{2+} ions concentration of 50mg/dm^3 in the solution, the highest removal rate of the latter was achieved at pH = 4-5. 5, a temperature of 30 °C and 10 minutes of contact. The calculated thermodynamic parameters show that the process is physical and exothermic.

The removal of Congo red, Bromocresol green, and Indigo carmine dyes was studied using dried biomass of fruits of edible chayote (*Sechium edule,* an edible plant from the *Sechium* genus, the gourd family (*Cucurbitaceae*)) and fig-leaved gourd (*Cucurbita ficifolia*) in a dosage of 10 to 30g/dm^3. It was determined that chayote fruits' biomass contributes to the complete discoloration in solutions after 24 hours of contact. The process kinetics follows the pseudo-second-order model [37].

3. The Use of Watermelon Fruit Waste as Sorption Materials for Removal of Metal Ions and Dyes from Aqueous Media

A bit more publications are devoted to studying the use of watermelon fruit waste as effective sorption materials. Watermelon (*Citrullus lanatus*) is an annual herbaceous plant, a watermelon (*Citrullus*) species of the gourd family (*Cucurbitaceae*). The fruit is a pumpkin, spherical, oval, flattened, or cylindrical; the rind color is from white and yellow to dark green with stripes and spots; the flesh is pink, red, crimson, rarely white and yellow [38]. The watermelon fruit pulp contains 5.5 to 13% of easily digestible sugars (glucose, fructose, and sucrose). By the time of maturation, glucose and fructose predominate, sucrose accumulates during the storage of watermelon. The pulp contains pectins – 0.68%, proteins – 0.7%; calcium – 14mg/% (mg per 100 g), magnesium – 224mg/%, sodium – 16mg/%, potassium – 64mg/%, phosphorus – 7mg/%; vitamins – thiamine, riboflavin, folic acid, carotene – 0.1-0.7mg/%, ascorbic acid – 0.7-20mg/% [38].

People use watermelon pulp mainly for food. Its main waste is the rind. The latter does not contain amino acids and includes some vitamins: retinol (vitamin A) - 51.5mg/100g, ascorbic acid (vitamin C) - 7.23mg/100g, as well as vitamins B_1, B_2, B_3 and B_6 in the amount of 0.03, 0.02, 0.04 and 0.04mg/100g, respectively [38] . Watermelon rind also contains elements ranging from 4mg/kg of copper to 1,297mg/kg of phosphorus [39]. Watermelon rind is widely used in various industries [19].

One of the watermelon rind applications uses it as a sorption material to remove various pollutants from water environments [40-68].

Heavy metal ions. The presence of biopolymers with different functional groups in watermelon rind, e.g., C(O)OH in pectin, -OH in cellulose, $-NH_2$ in proteins, etc., should contribute to metal ions removal. The sorption characteristics and the conditions for conducting experiments to study the removal of metal ions using native and modified watermelon rind are shown below (Table 1).

Table 1. Experiment conditions and metal ions adsorption characteristics of the native and modified watermelon rind.

Metal ion	Experiment conditions	Adsorption characteristics	Note	Source
As^{3+}	$D_{sorp} < 0.2$mm, $C_0 = 4$ mg/dm^3, pH = 7.2-8.2, t = 60 min, DS = 1g/dm^3, modified with xanthate and citric acid	A = ~ 4 mg/g, removal rate – 99%	the Langmuir model, pseudo-second order kinetics	[40]
As^{5+}	$D_{sorp} < 0.2$mm, $C_0 = 4$mg/dm^3, pH = 4.5-5.3, t = 60 min, DS = 1g/dm^3, modified with xanthate and citric acid	A = ~ 4mg/g, removal rate – 98%	the Langmuir model, pseudo-second order kinetics	[40]
Cd^{2+}	C_0 = 50-200ppm, pH = 2-8, 50rpm, t = 5-120 min, DS = 0.5-5.0g/dm^3	A_{max} = 63.29mg/g	the Langmuir model (R^2 = 0.995), pseudo-second order kinetics (R^2 = 1.0)	[41]
Cr^{3+}	C_0 = 50-300ppm, pH = 2-8, 150rpm, t = 30 min, DS = 0.5-5.0g/dm^3	A_{max} = 172.6mg/g, maximum removal rate – 90.8% (pH = 3, C_0 = 50 ppm, DS = 1.5g/dm^3)	the Langmuir model (R^2 = 0.9989), pseudo-second order kinetics; ΔG^o = -	

Metal ion	**Experiment conditions**	**Adsorption characteristics**	**Note**	**Source**
			3.330, -2.234, and -2.165kJ/mol (303, 313, and 323 K), ΔH° = -3.741kJ/mol, ΔS° = -582J/mol·K	[42]
Cu^{2+}	C_0 = 10mg/dm^3; pH = 6.48; DS = 1g/dm^3; t = 10h; 125rpm; T = 20 °C	A_{max} = 5.73mg/g		[43]
Cu^{2+}	C_0 = 5-20mg/dm^3, DS = 0,5-2g/dm^3, pH = 2-10, t = 1-4h	A_{max} = 9.54mg/g	the Freundlich model	[44]
Cu^{2+}	C_0 = 10mg/dm^3, DS = 0.02-2g/dm^3, T = 26 °C, 150rpm, t = 1-200 min,	A_{max} = 111.1mg/g	the Langmuir model, pseudo-second order kinetics; ΔG° = -4.584, -4.916, and -5.249kJ/mol (303, 313 and 323 K), ΔH° = -5.494kJ/mol, ΔS° = 33.26J/mol·K	[45]
Cu^{2+}	C_0 = 10-40mg/dm^3, DS = 0,2-2g/dm^3, T = 30 °C, t = 1-60 min, pH = 2-8, 60-130W ultrasound treatment.	A_{max} = 31.25mg/g(CA $(OH)_2$ modification), A_{max} = 27.03mg/g (citric acid modification).	the Langmuir model, pseudo-second-order kinetics.	[46]
Ni^{2+}	C_0 = 10-60мг/dm^3, pH = 2-10, DS = 1-5g/dm^3, t = 2-120 min, T = 30 °C,	S = 150.6m2/g, $A_{\text{мах}}$ $^{= 38.98}$мг/г	the Langmuir model, pseudo-second order kinetics, Dumwald–Wagner diffusion model (R^2 = 0.9795).	[47]
NH_4^+	C_0 = 1-50мг/dm^3, pH = 5-7, DS = 10-40g/dm^3, t = 1-40min, KOH, NaOH, H_2SO_4 (20mmol/dm^3) solutions modification	$A_{\text{мах}}$ = 1.24mg/g (native watermelon rind), 1.21mg/g (KOH), 1.21 (NaOH), 1.23 (H_2SO_4).		[48]
NH_4^+	C_0 = 1-50mg/dm^3, pH = 7, KOH, NaOH, H_2SO_4 (20mmol/dm^3) solutions modification	$A_{\text{мах}}$ = 1.22mg/g (native watermelon rind), 1.21mg/g (KOH), 1.19 (NaOH), 1.19 (H_2SO_4).	the Langmuir model (R^2 = 1.0 in all cases), pseudo-second order kinetics (R^2 = 1.0 in all cases)	[49]
Zn^{2+}	C_0 = 100ppm/dm^3, pH = 6, T = 60 °C, 150 rpm, DS = 4g/dm^3, modification with citric acid solutions, H_2SO_4, $Ca(OH)_2$, NaOH	$A_{\text{мах}}$ = 13.10mg/g (Untreated), 5.08mg/g (Citric Acid), 3.78mg/g (H_2SO_4), 22.55mg/g (NaOH), 17.55mg/g ($Ca(OH)_2$)		[50]
Zn^{2+}	C_0 = 400mg/dm^3, pH = 8, DS = 1.5mg/dm^3, t = 30min			[51]

C_0 is the initial concentration of pollutants in solutions, DS is the dosage of the sorption material, T is the experiment temperature, t is the adsorption time, and A_{max} is the maximum adsorption capacity.

As follows from the data shown in Table 1, experiments on metal ions and ammonium nitrogen adsorption were carried out under various conditions. This circumstance contributed to the fact that the resulting adsorption parameters have a wide range of values. In all studies, the adsorption isotherms of native and modified watermelon rind are most accurately described by the Langmuir equation. The process kinetics follows the pseudo-second-order model.

Experiments were done in which adsorption of two or three metal ions by watermelon rind was studied under the same conditions. For example, Co^{2+} and Ni^{2+} ions adsorption by dried watermelon rind was studied under equal conditions – with the initial metal ions concentration of 50mg/dm^3, pH = 5, contact time 3 minutes, and the sorption material dosage of 2.0 and 2.5 g/dm^3, respectively. It was found that the maximum sorption capacity for Co^{2+} ions was 23.3mg/g, and for Ni^{2+} ions - 35.3mg/g [52].

The maximum sorption capacity of dried watermelon rind treated with 0.1 mol HCl solution for Cu^{2+} and Pb^{2+} ions was 39.2mg/g and 116.2mg/g, respectively [53]. In another study, it was found that under comparable experimental conditions, the maximum sorption capacity for Pb^{2+} ions was 1.4mg/g. For Zn^{2+} ions, it was 23.3mg/g [54] with a degree of purification of 77.3% and 90.3%, respectively [55].

A study was also made of the process of adsorption of Cu^{2+}, Zn^{2+}, and Pb^{2+}ions by native dried watermelon rind. At the initial concentration of all metal ions in a 10mg/dm^3 solution, the efficiency of removal of these ions is as follows: Pb > Cu > Zn. The maximum sorption capacity calculated from the adsorption isotherms using the Langmuir equation was 98.06, 6.28, and 6.85 mg / g, respectively [56]. Watermelon rind treated with 5% HNO_3 solution was used to extract heavy metal ions from aqueous solutions. At an initial Zn^{2+} 2.5mg/dm^3, Fe^{3+} 0.9mg/dm^3, and Pb^{2+} 0.09mg/dm^3 concentration, the final concentrations were 0.36mg/dm^3 (recovery rate 85.6%), 0.35mg/dm^3 (61.1%), and 0.04mg/dm^3 (55.6%), respectively [57].

Watermelon rinds have also been studied as a biosorbent for removing dyes from aqueous media. Information about the experimental conditions and the results on the adsorption of various dyes by watermelon rind are shown in Table 2.

Table 2. Experiment conditions and dyes adsorption characteristics of the native and modified watermelon rind.

Dye	**Experiment conditions**	**Adsorption characteristics**	**Note**	**Source**
Methylene blue	C_0 = 50-400mg/dm^3, pH = 3-10, t = 0-180min, DS = 0.2-2.0g/dm^3, 125rpm	A_{max} = 188.68mg/g	the Langmuir and Tyomkin models, pseudo-second order kinetics; ΔG^o = -5.811, -5.796, and -5.781kJ/mol (303, 313 and 323 K), ΔH^o = -6.267kJ/mol, ΔS^o = -1503J/mol·K	[58,59]
Brilliant green	Orthophosphoric acid modification	A_{Max} = 92.6mg/g (native rind), A_{Max} = 188.6mg/g (modified)	the Langmuir model, pseudo-second order kinetics	[60]
Congo Red	C_0 = 5-300mg/dm^3, pH = 2-12, t = 5-240min, DS = 2-10g/dm^3, T = 25 °C, 300rpm	A_{max} = 24.75mg/g	the Langmuir model (R^2 = 0.9998)	[61]
Methyl orange	C_0 = 300mg/dm^3, pH = 2-12, t = 5-240min, DS = 2 g/dm^3, T = 303-333 K, 150rpm	A_{max} = 24.86mg/g	pseudo-second order kinetics	[62]
Remazol Brilliant Blue	C_0 = 25-150mg/dm^3, pH = 2-10, t = 24h, DS = 0.5-1.5g/dm^3, T = 25 °C, 100rpm	A_{max} = 29.4mg/g	The Freundlich equations (R^2 = 0.945), pseudo-second order kinetics (R^2 = 0.99)	[63]
Alizarin Red-S	C_0 = 5-40ppm, pH = 1-10, t = 5-80min, DS = 0.5-1.5g/dm^3, T = 20-70 °C, 100rpm	The maximum dye removal efficiency is 94.0 %. A_{max} = 79.6mg/g	the Tyomkin model (R^2 = 0.987), pseudo-second-order kinetics (R^2 = 0.903). ΔG^o = -15.40kJ/mol	[64]
Emerald green		A_{max} = 2.1mg/g	ΔG^o = -2.785kJ/mol	[65]
Methyl Orange, Rhodamine B	C_0 = 10-310mg/dm^3, pH = 2-12, t = 5-120min h, DS = 1-20g/dm^3, T = 25 °C, 300rpm. Treatment with sulfuric acid and annealing at 300°C for 3 hours.	Dye removal rate ~ 100%	pseudo-second order kinetics	[66]
Basic red 2, Orange G	C_0 = 140mg/dm^3, pH = 2-11, t = 180min h, DS = 0.35-25g/dm^3, T = 293-318K, 150rpm.	A_{Max} = 73,53mg/g (Basic red 2), A_{Max} = 68.14mg/g (Orange G)	Both isotherms are described by the Langmuir model; the kinetics is most accurately described by the model of Fractal-like. ΔG^o = -23.62 – -21.23kJ/mol (293-318 K), ΔH^o = 0.09kJ/mol, ΔS^o = -50.04J/mol·K (Basic red 2); ΔG^o = -22.39 – -24.73kJ/mol (293-318 K),	[67]

Dye	Experiment conditions	Adsorption characteristics	Note	Source
			ΔH° = -0.94kJ/mol, ΔS° = 5.127J/mol·K (Orange G)	
Fluorescein, Eosin	C_0 = 50mg/dm^3, pH = 1-7, t = 30min h, DS = 4-40g/dm^3, T = 30 °C, 100rpm. Treatment with 0.1N NaOH and 0.1N HNO_3	The maximum Fuorescein removal rate is 64.83% (native), 81.96% (HNO_3), 86.33% (NaOH); Eosin removal rate is -64.74% (native), 76.01% - (HNO_3), 79.41% (NaOH)	The adsorption isotherms are described by the Langmuir (Fuorescein) and Freundlich (Eosin) models. Pseudo-second order kinetics. ΔH° = -0.048kJ/mol, ΔS° = 59j/mol·K (Fuorescein); ΔH° = -0.051kJ/mol, ΔS° = 34j/mol·K (Eosin)	[68]
Methylene Blue, Crystal violet, Rhodamine B		A_{Max} = 489.8mg/g (Methylene Blue), 104.76mg/g (Crystal Violet), 86.6mg/g (Rhodamine B)		[69]

Wastewater containing dyes was treated with a composite material made from dried watermelon rind and chitosan. The wastewater had a pH value of 8.54, COD – 455mg/dm/dm^3. It was found that the optimal dosage of the composite sorption material was 8g/dm^3; with pH =2, the efficiency of dye removal was ~ 100% [70].

Watermelon processing by-products also include seeds. The latter has also been studied as sorption materials for removing heavy metal ions and dyes from aqueous media. There are reports of Cd^{2+} ion removal by watermelon seed husks. It was found that at an initial concentration of metal ion 10 mg/dm^3, the sorption material completely removes the pollutant; if the initial concentration is increased to 60mg/dm^3, the degree of Cd^{2+} ion removal is 40.9%. The highest degree of removal at this concentration (47.7%) is achieved at pH =3 and the amount of watermelon seed husk of 2.5g/dm^3 [71].

The adsorption of Cu^{2+} and Pb^{2+} ions from aqueous solutions using watermelon seed husks was studied. The study involved the determination of the influence of pH (2-6), biosorbent dose (0.1–1.0 g), initial metal ion concentration (10-500mg/dm^3), contact time (5-270min), and temperature (293-333K) on the adsorption characteristics. It was found that the Langmuir model most accurately describes the adsorption isotherm, and the kinetics of the process corresponds to the pseudo-second-order model [72]. The adsorption of these two metal ions on the husks of watermelon seeds was found to be a spontaneous and endothermic process.

Watermelon seed husks were studied to remove the Methylene Blue dye from simulated solutions. It was found that the highest removal rate (87.28 %) of the dye at its initial concentration of 100mg/dm^3 is achieved within 120 minutes of contact at a dosage of the sorption material of 1.5g/dm^3 and pH = 10. It was found that the adsorption isotherm is most adequately described by the Freundlich model [73].

Watermelon seeds themselves have also been studied as a sorption material for Pb^{2+} ions removal from various water samples (fresh, artesian, sea). Pb^{2+}ions concentration was 5mg/dm^3. It was shown that the removal rate of these ions was 93.6-96.8%, depending on the type of water. It was found that the maximum sorption capacity of watermelon seeds for Pb^{2+} ions is 9.64mg/g at pH = 6. Thermodynamic parameters (ΔG° = -20.96kJ/mol (333K), ΔH° = 18.51j/mol, and ΔS° = 63.0j/mol·K) indicate a spontaneous endothermic process [74].

The Reactive Yellow 145 dye adsorption process by crushed watermelon seeds pre-treated with hexane in the Soxhlet apparatus was studied. From the Langmuir equation, it was found that the maximum sorption capacity of watermelon seeds for the above dye can be 115mg/g. Actually, it was slightly more than 83mg/g. It was found that the Freundlich equation more accurately describes adsorption isotherm, and the process kinetics follows the pseudo-second-order model [75].

Urban wastewater was treated using watermelon seeds as a coagulant and biofilter media. It was noted that the use of the latter allows reducing the values of BOD by 91%, COD by 79%, the content of nitrate ions by 26.3%, and nitrite ions by 95% [76]. It is stated that the use of a coagulative composition consisting of 80% crushed watermelon seeds and 20 % alum can remove the turbidity and color of river water by 100% [77].

4. The Use of Melon Fruit Waste as Materials to Absorb Pollutants from Water Media

There is literature about using biomass and by-products of melon (*Cucumis melo*), a Cucumis plant in the *gourd* family, a cucurbit, https://ru.wikipedia.org/wiki/%D0%9E%D0%B3%D1%83%D1%80%D0%B5%D1%86_(%D1%80%D0%BE%D0%B4)as a sorption material. It is an annual herbaceous plant with creeping rounded-faceted stems with tendrils. Leaves are large, alternate, without stipules, round-ovate or palmate-lobed, on long petioles. Flowers are bisexual, pale yellow. The fruit is a pumpkin of a spherical or cylindrical shape with a strong leathery exocarp, juicy mesocarp, and endocarp; it may be of various colors and shapes, with white or greenish flesh [78].

The by-products of melon fruits processing are rind and seeds, which can be used to produce various biologically active agents, as a substrate for solid-phase fermentation, etc. [19, 79].

Besides, the dried melon rind was studied as a sorption material to remove pollutants from aqueous media. In particular, the melon rind was used to remove Cd^{2+} ions from the water phase. The results indicate an increase in the absorption of Cd^{2+} ions at an increase in the initial concentration of Cd^{2+} ions, the solution pH, and the contact time. The maximum sorption capacity was found to be 81.97mg/g. It was found that the Langmuir model provides the best correlation of the experimental data, and the pseudo-second-order model is the most applicable for describing the kinetics of Cd^{2+} ion adsorption by melon rind [80].

Cu^{2+} ions were removed in the dynamic mode of adsorption using dried melon rind as the sorption material. Initial concentrations of Cu^{2+} ions ranged from 20 to 200mg/dm^{3,} and the height of the sorption material layer was 0.5-1.25m. It was found that an increase in the melon rind layer and a decrease in Cu^{2+} ion concentration resulted in increased channeling time [81].

The dried melon rind was used to remove Fe^{2+}, Mn^{2+}, and Pb^{2+} ions from groundwater with varying parameters: pH value, biosorbent dosage, initial metal ion concentration contact time. It was found that adsorption was most effective at pH = 7 for Fe^{2+} ions and pH = 6.5 for Mn^{2+} and Pb^{2+} ions at a biosorbent dosage of 0.5g/dm^3 and a contact time of 45 minutes. Under these conditions, it was found that up to 90.73%, 91.47%, and 90.94% of the named ions are removed, respectively. It was found that the Langmuir model more accurately describes the adsorption isotherms, and the kinetics of the process corresponds to the pseudo-second-order model. The maximum adsorption capacity found from the Langmuir equation was 5.35mg/g, 2.75mg/g, and 0.083mg/g for Fe^{2+}, Mn^{2+}, and Pb^{2+} ions, respectively [82-84].

Melon rind was studied to remove the Methylene Blue dye under static conditions. The maximum sorption capacity was found to be 333mg/g [91]. Experiments described in [86] determined that the Methylene Blue dye's maximum sorption capacity is 46.4mg/g. This value was determined at an initial dye concentration of 500 mg/dm^3. It was determined that in both works, the adsorption isotherm is adequately described by the Langmuir model. The kinetics of the process corresponds to the pseudo-second-order model [85, 86]. Experiments were also performed under dynamic conditions with varying initial dye concentrations and flow rates. It was found that high layer height, low flow rate, and high initial dye concentration are the best conditions for maximum dye adsorption. It was determined that graphic dependencies are well described by the models of Bohart–Adams, Clark, Yoon, and Nelson [87].

Melon processing by-products also include seeds. Experiments were performed on the adsorption of Pb^{2+} ions by crushed native *Cucumis melo* seeds. It was found that an increase in the dosage of the biosorbent provides an increase in the degree of pollutant removal. It was determined that the Langmuir model more accurately describes the adsorption isotherm with a maximum biosorption capacity of the monolayer of $3.64 \cdot 10^{-4}$mol/g, and the kinetics of the process corresponds to the pseudo-second-order model. The calculated thermodynamic parameters indicate that Pb^{2+} ions biosorption on melon rind biomass is a spontaneous and endothermic process [88].

Melon seed husks have also been studied as a sorption material. In particular, it was shown that melon seed husks could be used to remove Methylene Blue from model solutions with an initial concentration of 30mg/dm^3. It was found that at pH =7, the dosage of melon seed husk 1.5g/dm^3 after 150 minutes of contact, the dye removal efficiency was 91.6%. It was determined that the adsorption isotherm and the kinetic parameters of the process best corresponded to the Tyomkin isotherm and the pseudo-first-order kinetic model [89].

The world literature provides several publications on the use of muskmelon components, aka cantaloupe (*Cucumis melo* var. *cantalupensis*), a plant in the gourd family (*Cucurbitaceae*), a melon type. Cantaloupe fruits are covered with a striped rind. The length of the fruit is 15-25 cm. Its tender orange pulp is juicy, dense, sweet, and fragrant. Inside, there is a voluminous seed cavity with many oval flat grains [90].

Native dried and polyvinyl alcohol-modified cantaloupe rind was studied, in particular, for the adsorption of Cd^{2+} ions with an initial concentration of 50mg/dm^3 from simulated solutions. It was found that the efficiency of removing these ions was 71 and 79%, respectively, with 15g/dm^3 sorption materials and 100 minutes contact time. It was found that the Langmuir model well describes the adsorption isotherm, and the kinetics of the process is well described by the pseudo-second-order model. Based on the process's calculated thermodynamic parameters, it was determined that the adsorption process is endothermic and spontaneous [91].

Cantaloupe rind modified with $Ca(OH)_2$ suspension was also studied for the ability to remove Pb^{2+} ions from simulated solutions. It was found that the maximum adsorption capacity for Pb^{2+} ions was 0.81mol/kg at an initial concentration of 1mol/dm^3. As in the previous case, adsorption isotherm is well described by the Langmuir model, and the kinetics equation is well described by the pseudo-second-order model [92].

Cantaloupe seed husks were used to remove the butachlor pesticide from aqueous solutions. It was determined that the highest sorption capacity for butachlor was 142.8mg/kg at pH = 3. The adsorption isotherm is well described by the Freundlich model ($R^2 = 0.9977$), and the pseudo-second-order model describes the process kinetics. Based on the calculated thermodynamic parameters of the process ($\Delta G^o = -0.646$ — -3.989kJ/mol (308-343 K), ΔH^o - 20.91J/mol, $\Delta S^o = -68.0$J/mol·K), the adsorption process is exothermic and spontaneous [93].

5. The Use of Cucumber Rind as Sorption Materials for Removal of Metal Ions and Dyes from Aqueous Media

The gourd family includes cucumbers (Cucurbita), which are widely distributed around the globe. Cucumber or ridge cucumber (*Cucumis sativus*) is an annual herbaceous plant, a Cucumber (*Cucumis*) species in the gourd family (*Cucurbitaceae*), a vegetable crop. The stem is creeping, rough ends in tendrils, which it can catch on the support, stretching out for 1-2 m. Leaves are heart-shaped, five-lobed. The fruit is multi-seeded, juicy, emerald-green, pimply. The fruit's structure is characteristic of the gourd family and is defined in Botanics as a pumpkin. It can be in different shapes and sizes (depending on the variety) [94].

One hundred nine compounds were found in the rind, seeds, and pulp of cucumbers. Research has shown that cucumber rind and seeds contain rich nutrients, such as aromatic compounds, β-tocopherol, squalene, zingiberene, cathine, linoleic acid, and others [95]. Such saccharides as rhamnose, arabinose, xylose, mannose, and glucose were also found [96].

Biomass and by-products from cucumber processing have also been studied as sorption materials for removing pollutants from aquatic environments. For example, a dried rind of cucumbers was studied to remove Cd^{2+} ions from water media under static and dynamic conditions [97-100]. It was determined that the maximum sorption capacity for Cd^{2+} ions is 0.998mmol/g [97], and adsorption proceeds for functional –OH groups that are part of biopolymers and other compounds.

In [98], Cd2+ ions adsorption by cucumber rind under static conditions was also studied. It was found that at an initial concentration of 10mg/dm^3, pH = 5, temperature 25 $^{\circ}$C, and sorption material dosage of 2g/dm^3, the maximum efficiency of Cd^{2+} ions removal was 90.2%. It was found that the Freundlich model more accurately describes the adsorption isotherm, and the kinetics of the process corresponds to the pseudo-second-order model. The calculated thermodynamic parameters of the process revealed that the adsorption process is exothermic and spontaneous.

Cd^{2+} ions removal by crushed cucumber rind under dynamic conditions was also studied. It was determined that at the initial concentration of cadmium ions of 50mg/dm^3, the liquid flow rate through an 8cm layer of sorption material was 20cm^3/min, the efficiency of pollutant removal was 78.03%, with the maximum sorption capacity of 107.76mg/g [99].

To increase cucumber rind adsorption capacity for Cd^{2+} ions, the rind was treated with HCl solution. At an initial Cd^{2+} ions concentration of 20mg/dm^3, the maximum adsorption capacity increased from 3.6mg/g [98] to 58.1mg/g at 298 K [100]. It was found that the adsorption isotherm, in this case, is more accurately described by the Langmuir model with the same process parameters.

The work also included studying Pb^{2+} ions adsorption by dried cucumber rind under static conditions. It was found that the maximum adsorption capacity for lead ions is 28.25mg/g at the initial concentration of the latter in a solution of 25mg/dm^3 and a temperature of 30°C. It was found that the adsorption isotherm is most accurately described by the Langmuir model and the kinetics of the process by the pseudo-second-order model. It was determined that adsorption is spontaneous and exothermic [101]. At the same time, [102] states that the maximum adsorption capacity of cucumber rind for Pb^{2+} ions is 133.6mg/g at a temperature of 30°C, pH =5, and a contact time of 60 minutes.

Cucumber rind has also been studied as a sorption material for removing Cu^{2+} and Pb^{2+} ions [103]. It was determined that the maximum adsorption capacity for these ions is 88.5 and

147.1mg/g, respectively. These parameters were achieved at an initial ion concentration of 100mg/dm^3 (Cu^{2+}) and 150mg/dm^3 (Pb^{2+}), pH = 5, and a contact time of 60 and 85 minutes, respectively.

Dried cucumber rind has also been studied to extract various dyes from aqueous media [104-109]. In particular, it was determined that the maximum adsorption capacity of cucumber rind for the Crystal Violet dye is 149.25mg/g; the Langmuir model describes the adsorption isotherm, and the kinetics of the process corresponds to the pseudo-second-order model [105]. In [106], it was determined from the Langmuir equation that the maximum sorption capacity of cucumber rind for the above dye is 34.24mg/g. At the initial Crystal Violet concentration of 25 mg/dm^3, pH = 7, and the rind dosage of 4g/dm^3, the degree of dye removal was 92.15%.

The study also involved the removal of the Acid Red 1 dye by dried cucumber rind. With the initial dye concentration of 100mg/dm^3, the rind dosage of 12.5g/dm^3 and pH = 2, the maximum sorption capacity was 3.21mg/g [107]. It was determined that the adsorption isotherm is more accurately described ($R^2 = 0.984$) by the Dubinin-Radushkevich model.

Methylene blue and Orange G's sorption capacity was determined and compared of banana, cucumber, and tomato skins. It was found that the maximum adsorption capacity of cucumber rind for Methylene blue was 179.9mg/g, which is lower than that of banana skin and higher than that of tomato skin. For Orange G, this indicator is 40.5mg/g and exceeds the values of other sorption materials studied [108].

Crushed and dried cucumber rind was studied as a sorption material for removing Crystal Violet and Rhodamine B dyes. It was determined that the maximum sorption capacity for these dyes, determined by the Langmuir model equation, was 33.22mg/g and 40.82mg/g, respectively. It was found that the adsorption isotherms are most accurately described by the Langmuir model and the kinetics of the process by the pseudo-second-order model [109].

Information about the use of marrows and scallop squashes biomass and by-products as sorption materials for removing pollutants from water media is not found in the literature.

6. Conclusions

As can be seen from the above, we analyzed and summarized the information on using cucurbits by-products. It was determined that dried rind of pumpkins, watermelons, melons, and cucumbers have good sorption properties concerning heavy metal ions and various dyes. Most of the adsorption isotherms are most accurately described by the Langmuir model, less often by the Freundlich model. It was determined that the adsorption process kinetics most often follows the pseudo-second-order model. To improve the adsorption characteristics for various pollutants, adsorption materials were modified with various chemicals.

Funding

This research received no external funding.

Acknowledgments

This research has no acknowledgment.

Conflicts of Interest

The authors declare no conflict of interest.

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