Use of Garlic Processing By-Products to Remove Pollutants from Aqueous Media

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Abstract: The paper summarized the literature data on using ground peels, outer leaves, and garlic roots (Allium sativum L.) as sorption materials to remove various metal ions, dyes, and antibiotics from aqueous media. This paper provides brief information on the amount of waste generated from processing garlic, its chemical composition, and ways of reuse. It gives the adsorption processes parameters and the values of sorption parameters for the studied pollutants. It was shown that garlic residue sorption characteristics for various pollutants could be increased by chemical modification with various chemical reagents. It was determined that the Langmuir model more accurately describes the pollutant’s adsorption isotherms in most cases, and the kinetics of the process more accurately describes the pseudo-second-order model. It was shown that garlic peels and steam are good precursors for activated carbons production.

Keywords: garlic peel and steam; metal ions; dyes; antibiotics; adsorption; modification.

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1. Introduction

The pollution of the World Ocean by various substances is becoming more and more threatening. The source of pollutants entering water bodies is, as a rule, untreated and insufficiently treated wastewater. Various purification methods are used to extract pollutants from wastewater, including mechanical, physicochemical, chemical, and biological. Of all the variety of methods to remove pollutants, adsorption of the latter is a promising method because it allows the minimization of sewage impurities with different initial concentrations in treated water. However, the activated carbons used in practice are expensive; besides, their regeneration contributes to an increase in the cost of cleaning [1].

Currently, to reduce the costs of treatment, an innovative environmental protection trend is being intensively developed in the world community – the use of various industrial wastes as reagents to remove pollutants from water environments [2-11].

Of particular interest are cheap, annually renewable by-products of processing agricultural raw materials, including vegetables. The world literature provides information about the use of by-products of processing vegetables such as cabbage [12], carrots [13, 14],...
tomatoes [15-17], eggplants [18, 19], turnips [20], cucurbits [10] and others as sorption materials.

As shown in [21], onion (Allium cepa) processing waste has good sorption characteristics for dyes, metal ions, and other pollutants. In addition to onions, garlic (Lat. Allium sativum) is also a bulbous vegetable crop that is widely spread throughout the world. It is a perennial herbaceous plant, an Onion species of the Amaryllis (Amaryllidaceae) family of the Onion (Allioideae) subfamily. The bulb is complex and forms in its skins' axils from 2 to 50 ratoons, each covered with hard leathery skins. The bulb is rounded, somewhat flattened, oval-ribbed in the middle, of various colors. With the help of bulbs, garlic reproduces vegetatively. The leaves are solid, narrow, lance-elongated, grooved, with a keel on the lower side, centimeter wide, pointed to the end, whole-edged, erect or drooping, reach 30-100 cm in length. Each subsequent leaf sprouts from inside the previous one, thereby forming a false stem, more durable than onions [22].

The peduncle (flower-bearing stem, scape) is from 60 to 150 cm high, dressed with leaf sheaths almost to the half-height, before flowering twists at the end into a spiral and ends with an inflorescence in the form of an umbrella, which is covered with a film membrane before flowering. The inflorescence is a simple spherical umbrella consisting of sterile flowers, aerial propagating bulbs, and a dense blanket (wrapper). The flowers are on long pedicels, with a simple corollaceous perianth consisting of six white petals. The fruit is a capsule [22].

Garlic bulbs contain 35-42% dry substances, including 6.0-7.9 % proteins, 7.0-28 mg% vitamin C (in leaves - up to 80 mg%), 0.5 % sugars, 20-27 % polysaccharides. The taste and smell of garlic are due to the presence of essential oil (0.23-0.74 %), which contains allicin and other organic sulfide group compounds (phytoncides). Allicin is an essential oil of garlic, an organic substance that is the strongest antioxidant; that is, it removes free radicals from cells [22].

A bulb of fresh garlic has the following composition (per 100 g): water 58-59 g, proteins – 6.2-6.6 g, fats – 0.5 g, carbohydrates – 33.0 g and vitamins, β – carotene – 5 g., thiamin (In1) – 0.2 mg, Riboflavin (In2) – 0.1 mg, Niacin (In3) – 0.7 mg, Pantothenic acid (as In5) - 0.6 mg, pyridoxine (In6) - 1.2 mg, folacin (In9) – 3 μg, ascorbic acid (S) – 31 mg [22].

In addition to the above, the following compounds were identified in fresh garlic: pyruvic acid, salicin, sitosterol, caffeic acid, chlorogenic acid, diallyl disulfide, ferulic acid, geraniol, kaempferol· linalool, oleanolic acid, coumaric acid, chlorogluclinol, phytic acid, quercetin, rutin, allyl cysteine, saponins, stigmasterol, etc. [22].

The largest producer of garlic is China – 21,197,131 tons were grown in 2016. Also, India (1,400,000 tons) and Bangladesh (381,851 tons) are among the three countries leading in garlic production.

Garlic processing by-products include skins, outer leaves, tops, and bottoms. Currently, these materials are disposed of in landfills or used as soil amendments, which result in negative environmental impacts and phytotoxicity to plants, respectively. These materials need to be economically and environmentally managed [23].

They can be used for the production of valuable products [24] such as cellulose [25-27], tannins [28], oligosaccharides [29], allicin [30], inulin [31]. It is proposed to use garlic processing by-products as a substrate for growing mushrooms [32], as a feed additive to improve the quality of laying hens’ eggs [33]. Extracts from skins and outer leaves were studied as reagents for reducing corrosion [34], emulsifier [35], antioxidants [36, 37], etc.
One of the areas of using garlic processing by-products is their use as sorption materials to remove various pollutants from aqueous media.

2. Removal of Metal Ions with Garlic Processing By-Products

The presence of compounds containing various functional groupings in the composition of garlic skins and outer leaves, as mentioned above, may contribute to the effective extraction of metal ions [24, 38].

In particular, the adsorption of Cd\(^{2+}\) ions from simulated solutions with an initial concentration of 5, 10, and 20 mg/g of garlic skin was studied. The highest sorption capacity was determined to be 4.78, 9.43, and 19.64 mg/g at the above-mentioned starting concentrations, respectively, at a dosage of 1 g/dm\(^3\), a contact period of 1 hour, and a temperature of 288 °C. It was discovered that the Langmuir model best describes the adsorption isotherms, while the pseudo-second-order model best describes the process kinetics [57].

For the aim of wastewater treatment, the biosorption of Cr(VI) by the garlic stem in a batch-type reactor was researched in depth. To maximize Cr(VI) removal from aqueous solutions and equilibrium isotherms and kinetic data, the effects of initial Cr(VI) concentration, time, and pH were explored. From a solution containing 3000 ppm of Cr, the garlic stem adsorption capacity was reported to be 103.09 mg/g of adsorbent (VI). It can be concluded that the Langmuir adsorption isotherm was more appropriate for explaining equilibrium than the Freundlich adsorption isotherm. Gibbs' free energy was spontaneous for all interactions, and the adsorption process had exothermic enthalpy values [40].

The effects of various experimental conditions on the removal of Cu\(^{2+}\) ions from aqueous solution by garlic skin were investigated. The point of zero charges for garlic skin was between 4.55 to 4.75. The adsorption capacity of the garlic stem was found to be 66.7 mg/g at pH = 5.3 and T = 303K. The pseudo-second-order kinetic model fitted the batch data adequately. The rate constant garlic scale in the absence of diffusional resistance was estimated to be 0.075 mg/g/min respectively at 303 K. The thermodynamic studies showed that the Cu\(^{2+}\) ions adsorption on the garlic skin was spontaneous and endothermic [41].

Garlic skin treated with 2 N HCl solution was studied to remove Mn(VII) ions from simulated solutions. It was determined that at the initial Mn(VII) ions concentration of 20-100 ppm, pH = 5-6, the sorbent dosage of 1-5 g/dm\(^3\), and the interaction time of 3 hours, the degree of manganese ions removal was 100% [42].

Native and mercerized garlic skin was used to remove Pb\(^{2+}\) ions from simulated solutions. It was found that at pH = 3-7, CPb = 10 μg/sm\(^3\); contact time 15 min, the dosage of adsorbent 10 mg the maximum sorption capacity of native garlic peel was 51.73mg/g, modified – 109.05 [43].

Garlic peel (GP) was changed by cation exchange loading with Fe(III), Ti(IV), and Ce(III) ions, which could successfully adsorb tungstate ions under mildly acidic conditions. For Ti-GP, hY=1-4 for Fe-GP, and pH=3 for Ce-GP, the best initial pH for maximum adsorption of W(VI) ions was determined to be pH=1-3, hY=1-4 for Fe-GP, and pH=3 for Ce-GP, respectively. The maximum adsorption capacity of Fe-GP, Ti-GP, and Ce-GP at pH=2.5 was determined to be 91.5 mg/g, 83 mg/g, and 84 mg/g tungsten, respectively. Anions such as chloride, sulfate, and carbonate had minimal effect on tungsten adsorption, whereas fluoride and phosphate significantly impeded it. The breakthrough points for Ce-GP, Ti-GP, and Fe-GP
were 180 minutes, 200 minutes, and 270 minutes, respectively, according to column adsorption [44].

The above information on the sorption capacity of garlic processing by-products has incomparable indicators since the experiments were carried out under different conditions. In this regard, information on sorption characteristics for metal ions conducted under the same conditions is of interest. Thus, the adsorption of Cu$^{2+}$ and Pb$^{2+}$ ions on garlic stalks were studied. The efficiency of the adsorbent was investigated using the batch adsorption approach under various experimental settings by altering parameters such as pH, starting concentration, and contact time. The results reveal that Pb$^{2+}$ ions have the highest adsorption capability when the pH is 2.03, the adsorption temperature is 35 °C, the adsorption period is 90 minutes, and the amount of garlic stem is 1.0 g. The maximal adsorption capacity of Pb$^{2+}$ ions on the garlic stem is 28.42 mg/g, with a 94.74 percent absorption rate. Cu$^{2+}$ ions have the greatest adsorption at the same temperature when the pH is 4.05, the adsorption time is 120 minutes, and the amount of garlic stem is 1.0. Cu$^{2+}$ ions have maximum adsorption of 20.90 mg/g and a 69.75 percent adsorption rate [45].

The viability of garlic peel (GP) to remove Pb$^{2+}$, Cu$^{2+}$, and Ni$^{2+}$ ions was evaluated. Batch experiments were carried out to investigate the effects of pH, temperature, time, and on the adsorption of a single heavy metal ion by GP, the initial metal ion concentration. Competitive adsorption of the binary mixture (Pb$^{2+}$/Cu$^{2+}$ ions and Pb$^{2+}$/Ni$^{2+}$ ions) by GP was also investigated. The results showed that the adsorption process could attain an equilibrium within 20 min, and kinetics was found to fit the pseudo-second-order equation. GP had a remarkably higher adsorption affinity for Pb2+ ions than Cu2+ ions and Ni2+ ions with the maximum adsorption capacity of 209 mg/g. The adsorption efficiency and uptake capacity of one metal ion were reduced by the presence of the other metal ion. The adsorption mechanism was supposed to be ion exchange between Ca$^{2+}$ ions of GP with heavy metal ions in the solution [46].

At various adsorbent/metal ion ratios, garlic wastes from the market and food canning processes were employed to adsorb Pb$^{2+}$, Sn$^{2+}$, Fe$^{2+}$, Hg$^{2+}$, As$^{3+}$, and Cd$^{2+}$ from multi-component systems. The effects of pH, contact time, temperature, and the concentration of adsorbent and adsorbate on the decontamination of effluents in a batch adsorption approach were investigated in order to improve the conditions for use on a commercial scale. The experiment was carried out at 50°C, and the results revealed that efficiencies are pH-dependent. A second-order model was used to compute the kinetic parameters, which took 30 minutes to reach equilibrium. It is found that the maximum sorption capacity for the said metal ions can be ranked as follows: Pb$^{2+}$ (10.47 mg/g) > Fe$^{2+}$ (8.46 mg/g) > Sn$^{2+}$ (7.13 mg/g) > Hg$^{2+}$ (5.12 mg/g) > As$^{3+}$ (2.30 mg/g) > Cd$^{2+}$ (1.47 mg/g). Desorption indicates a maximum 71% recovery of metal ions, making the remediation process cost-effective and reusable [47].

In addition to metal cations and metalloids, garlic processing by-products were studied as sorption materials to remove anions from aqueous media. Thus, a low-cost and effective biosorbent made from garlic peel was proposed for recovering phosphorus selectively from acid leach liquid under acidic conditions at pH=1–2. To determine the best adsorption parameters for the model solutions, various batch experiments were conducted under various conditions, including altering pH, contact time, adsorbent doses, and metal ion concentration. The ideal pH for phosphate ion adsorption was about pH=1.5, reaching adsorption equilibrium after 240 minutes. The maximum adsorption capacity for phosphate ions was 1.40 mmol/g and 0.81 mmol/g, respectively, at equilibrium pH=1.5 and pH=6.5. A NaOH solution effectively
eluted the adsorbed phosphate ions, and the eluted solution contained mainly Na₃PO₄ and NaOH. The garlic peel adsorbent was particularly successful in recovering phosphorus from iron ore leach liquor, and the adsorption efficiency could retain 85 percent of the original adsorption capability even after five cycles of adsorption and desorption. [48].

The efficacy of Zr(IV)-loaded garlic peel in removing fluoride ions from a continuous fixed-bed column was investigated in order to provide direction for the column reactor's design and operation. On the fluoorine adsorption performance, the impacts of Zr(IV) ion loading concentration, beginning pH, initial fluoride concentration, flow rate, and bed depth were investigated. The experimental data were found to correspond well with the Thomas and bed depth service time models. Through a 0.5 g Zr(IV)-GP column, 1.2 dm³ clean groundwater was created to meet China's national standard (1.0 mg/dm³), implying that 1 kg Zr(IV)-GP adsorbent can provide 2.4 m³ cleaning water. The Zr(IV)-GP column may be regenerated by eluting adsorbed fluoride ions with 1M NaOH, and at least three cycles were performed to detect a slight decrease in adsorption performance. The adsorbent is affordable; a kilogram of adsorbent costs less than $0.50. [49].

3. Removal of Dyes and other Organic Compounds with Garlic Processing By-Products

Studies have been conducted on the removal of dyes from aqueous solutions with garlic processing by-products. Thus, in a batch method, the ability of garlic peel (GP), an agricultural waste, to remove methylene blue (MB) from an aqueous solution was assessed. Contact period, starting concentration (25–200 mg/dm³), pH (4–12), and temperature were all factors in the experiments (303, 313, and 323 K). The data matched the Freundlich isotherm well. At 303, 313, and 323 K, the maximal monolayer adsorption capacities were found to be 82.64, 123.45, and 142.86 mg/g, respectively. Pseudo-first-order and pseudo-second-order models were used to assess the kinetic data. The findings suggested that garlic peel could be utilized as an alternative to more expensive adsorbents for color removal. [50].

The efficacy of garlic straw (GS) was investigated in this study as a novel adsorbent to eliminate dye molecules. With an adsorbent dosage of 0.04 g per 10 sm³ and an initial dye concentration of 100 mg/dm³, more than 85% removal efficiency was achieved in less than 200 minutes. At pH=7 and T=303 K, the highest sorption capacity was reported to be 256.41 mg/g. The data on kinetic sorption was found to be consistent with pseudo-second-order kinetics. Calculations of various thermodynamic parameters (ΔG= −1.532, −1.609 and −1.737 kJ/mol at 303, 313 and 323 K, ΔH=50.367 kJ/mol, ΔS = 109.71 J/mol•K), show that the sorption process is endothermic and spontaneous. Desorption studies on regenerating garlic straw revealed that it has a greater desorption capacity following sorption MB with HCl at pH=2. [51].

Three chemical modification procedures were used to modify garlic peel: oxidation with H₂O₂, acid oxidation with HNO₃/C₆H₅O₇, and alkaline saponification with NaOH, respectively. Unmodified garlic peels and as-synthesized chemically modified garlic peels were thoroughly investigated and tested as biosorbents to eliminate Rhodamine B (RhB). Results showed that acid oxidation could increase surface area and acidic oxygen groups, which were beneficial for the adsorption of toxic dyes. Notably, HNO₃-GP turned out to be the most efficient among the five studied garlic peels, the adsorption capacity of which was 3.5 times of unmodified-GP when the initial Rhodamine B concentration was 15mg/dm³. It was found that the kinetics of the process follows the pseudo-second-order model (R² = 0.9999),
and the adsorption isotherms at different temperatures are most accurately described by the Tyomkin model. The adsorption of Rhodamine B was pH-dependent, and 95.8 ± 1.1% of the adsorbed dye could be eluted by 0.1 mol/dm3 NaOH [52].

In the next work, the efficiency and performance of garlic peel adsorbent for the removal of Direct Red 12B dye from wastewater were investigated. The pseudo-second-order kinetic model was shown to fit better with a high correlation coefficient, and the equilibrium data fitted well with the Langmuir model. More than 99% removal efficiency was obtained within 25 min at an adsorbent dose of 0.2 g per 50 sm3 for an initial dye concentration of 50 mg/dm3. The maximum sorption capacity calculated from the Langmuir model equation was 38mg/g. Calculation of various thermodynamic parameters (ΔG= -95.39, -111.2, -130.16 and -160.91 kJ/mol at 298, 308, 318 and 328K, respectively, ΔH=54.45 kJ/mol, ΔS = 213.621 J/mol•K) of the on-going adsorption process indicate feasibility and endothermic nature of Direct Red 12B dye adsorption [53].

In previous research, the ability of agricultural waste garlic root to remove Malachite green (MG) from aqueous solutions was assessed. [54]. The adsorption kinetics followed the pseudo-second-order equation (R2>0.99), and the equilibrium data fit well into the Langmuir model (R2>0.99). With the addition of 1 and 2 g/dm3 garlic root, the highest adsorption capacities of Malachite green dye onto the adsorbent were 172.41 and 232.56 mg/g, respectively. The treated Malachite green dye solutions were less harmful than the parent solutions in the acute toxicity test. These findings show that garlic root could be a low-cost adsorbent for color removal in industrial effluent. [54].

Several publications are devoted to the study of adsorption of phenol by garlic biomass processing by-products under static [55] and dynamic [56] conditions. In the course of experiments under static conditions, The following was discovered to be the ideal conditions for maximal phenol elimination from an aqueous solution containing garlic peel of 50 mg/ dm³ pH=2, 2.1 g/ dm³ adsorbent dosage, 7-hour contact period, and 135 rpm agitation Batch adsorption studies were carried out under these optimal circumstances to investigate the effects of starting concentration and temperature on phenol elimination. The sorption process was discovered to be both spontaneous and exothermic. The pseudo-second-order kinetic model is used to explain the adsorption kinetics of phenol elimination by GP. The study's findings revealed that more than 80% of the phenol could be removed. [55]. According to the investigations, the procedure of removing phenol from aqueous systems using garlic peel powder may be successfully adapted to the field because it can be done in a continuous mode. Furthermore, low flow rates were found to maintain performance for longer within breakthrough limits with a greater specific rate of adsorption, increasing the efficiency of garlic peel use. [56]. It is found that the process was most accurately (R2 = 0.9886) described by the Yoon–Nelson model.

Garlic peel has also proven itself as a good sorption material for removing antibiotics from aqueous media. Thus, the adsorption characteristics of garlic peel (GP) and HN O₃ modified garlic peel (HN O₃–GP) for quinolone antibiotics were compared in [57]. Comparisons of GP and HN O₃–GP characterizations demonstrated that increasing the surface acidic functional group of HN O₃–GP resulted in a considerable increase in adsorption capacity (about 10 times of GP). Furthermore, the adsorption behaviors of GP and HN O₃–GP for quinolone antibiotics were examined, including adsorption kinetics, isotherm, and thermodynamic investigations, with the results demonstrating that HN O₃–GP has a higher affinity for quinolones. [57].
Terbium, europium, and terbium/europium-loaded garlic peels (Tb-GP, Eu-GP, and Tb/Eu-GP) were successfully produced and tested as biosorbents for enrofloxacin (ENR) extraction from aqueous solutions. It was shown that Tb/Eu-GP (769 mg/g) had a much higher enrofloxacin adsorption capacity than unloaded GP (29.8 mg/g) and was superior to Tb-GP (580 mg/g) and Eu-GP (421 mg/g). Tb/Eu-GP was also found to be highly effective at pH values ranging from 6.0 to 8.0. Furthermore, ultrapure water containing 5% ammonia was able to elute 98.11.5 percent of the absorbed ENR from Tb/Eu-GP, and the reusability and regeneration tests indicated Tb/Eu-long-term GP's viability. [58].

4. Production of Activated Carbons from Garlic Processing Waste

One of the areas of using garlic processing by-products is the carbonation of the latter to produce activated carbons [59, 60]. Under comprehensive batch tests, nanoporous activated garlic stem carbon (AGSC) was produced from garlic stem waste and used to remove As(III) from synthetic water. The adsorption of As(III) onto AGSC was investigated using batch adsorption studies. The ideal conditions of pH 6, adsorbent dose 5 g/L, equilibrium period 150 min, beginning As(III) concentration 400 g/L, and temperature 298 K resulted in maximum removal of 93.3 percent of As(III). AGSC has a maximum adsorption capacity of 192.30 g/g for the elimination of As(III). In comparison to Freundlich's isotherm, both Langmuir and Temkin's isotherm models suit the experimental data well. According to kinetics, the adsorption of As(III) was more suited for pseudo-second-order than pseudo-first-order and Elovich models. Weber-Morris and Boyd's mass transfer models could be used to characterize the mass transfer mechanism. As(III), adsorption onto AGSC was exothermic and spontaneous, as evidenced by the negative enthalpy and free energy change. [61].

Using KOH as an activator, a garlic skin-derived porous biomass carbon (GSP-BC) material with an ultra-high specific surface area was created. The GSP-BC has a surface area of 3686 m2/g, an average pore diameter of 2.43 nm, and a total pore volume of 1.96 cm3/g, respectively. The GSP-BC has a remarkable adsorption capacity of 1911.8 mg/g (TCH) for tetracycline hydrochloride. The effects of critical variables such as starting concentration (300–800 mg/dm3), contact time, solution pH (3–10), ionic strength, and temperature (290–313 K) were studied in detail. The pseudo-second-order and Freundlich models, respectively, suit the experimental data of adsorption kinetics and isotherms well. Furthermore, the adsorption was endothermic and spontaneous. [62].

5. Conclusions

In paper summarized the literature data on using ground peels, outer leaves, and roots of garlic (Allium sativum L.) as sorption materials to remove various metal ions, such as As3+, Cd2+, Cr(VI), Cu2+, Fe2+, Hg2+, Mn(VII), Ni2+, Pb2+, Sn2+ and W(VI), dyes, and antibiotics from aqueous media. This paper provides brief information on the amount of waste generated from processing garlic, its chemical composition, and ways of reuse. It gives the adsorption processes parameters and the values of sorption parameters for the studied pollutants. It was shown that garlic residue sorption characteristics for various pollutants could be increased by chemical modification with various chemical reagents. It was determined that the Langmuir model more accurately describes the pollutant's adsorption isotherms in most cases, and the kinetics of the process more accurately describes the pseudo-second-order model. It was shown that garlic peels and steam are good precursors for activated carbons production.
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