Fish Scales as a Biosorbent of Pollutants from Wastewaters and Natural Waters (a Literature Review)

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Abstract: We have reviewed literature data on the use of various fish scales as a sorption material for extracting various pollutants (heavy metal ions, dyes, antibiotics) from waste and natural waters. The parameters of sorption interaction that ensure the greatest degree of pollutant removal are given in this paper. It is shown that the sorption capacity of fish scales can be increased by modifying various chemical reagents. The isotherms of pollutant adsorption with fish scales were found to be, in most cases, most adequately described by the Langmuir model, less often by the Freundlich model, and the pseudo-second second-order model most often describes the process kinetics.

Keywords: fish scales; metal ions; dyes; antibiotics; adsorption; models of adsorption isotherms; thermodynamic parameters.

1. Introduction

In the last few decades, the world scientific community has been intensively studying industrial and agricultural waste as reagents for removal of pollutants of different nature from natural and wastewaters with a particular focus on ligno-and cellulose-containing waste from the processing of agricultural raw materials and wood biomass [1-10]. The latter are mainly used as sorption materials in native or modified form to adsorb pollutants of different origin from aqueous media (heavy metal ions, oil and petrochemical products, dyes, surfactants, pesticides, etc.).

Among the various biosorbents, chitin is the second most abundant natural biopolymer after cellulose. However, chitosan, with its molecular structure similar to cellulose, is more critical than chitin. Chitin and chitosan have also been extensively investigated as sorption materials for the extraction of various pollutants from aqueous media [11-14].

It should be noted that among natural biopolymers, a large share is taken by keratin in terms of content in the biosphere, which is part of the family of fibrillar proteins with mechanical strength, which among biological materials comes second only to chitin. Basically,

keratins build the horny derivatives of the epidermis - such structures as hair, nails, horns, animal hooves, birds' feathers, as well as scales of fish and reptiles [15].

The elemental composition of keratin is as follows, %: C – 50.3-52.5; H – 6.4-7.3; N – 16.2-17.7; O – 15.0-20.7; S – 0.7-5.0. The simplest formula corresponding to the elemental composition of keratin contains 39 carbon atoms ($C_{39}H_{65}N_{11}SO_{13}$). Keratin consists of 20 amino acids, 17 of which have the highest content: alanine, arginine, aspartic acid, valine, histidine, glycine, glutamic acid, isoleucine, leucine, lysine, methionine, proline, serine, threonine, tyrosine, cystine, and phenylalanine. Their amount varies widely in the macromolecule of keratin. The structure, composition, and structure of keratin are detailed in this paper [16].

It is shown that wool and wool waste effectively extract various pollutants from aqueous media [17, 18]. Keratin is also the building material of birds' feathers, which are studied as effective sorption materials for removal of metal ions, dyes, and petroleum products from natural and wastewaters [19, 20].

2. Fish Scales Structure and Composition

Fish scales are also a multi-tonnage fish processing waste. Information about the morphology, properties, and structure of fish scales on the example of arapaima scales are given in the review [21]. In fish, there are three main types of scales, which differ both in form and in material from which they are built: plakoid, ganoid, and bony. Bony scales are characteristic of most modern bony fish, phylogenetically is a modification of the ganoid scales. There are two types of bony scales: the cycloid scales with smooth hind edge and the ctenoid characterized by small teeth on their posterior margins (cteni). The cycloid scales [22] are characteristic mainly of lower fish (herring-, pike-like, etc.); the ctenoid scales can be found in highly organized fishes (perch-like, flatfishes). The size of the scales is closely related to the way the fish moves. The largest scales are found in slow-moving fish, most of which live in still waters (many carps). It was established that the scales structure is clearly divided into the thin outer highly mineralized hyalodentin layer and a thick internal basal plate [22]. The hyalodentin layer structure consists of pigments, hydroxyapatite crystals, and randomly oriented collagen fibers. The base plate of scales consists of a set of thin lamellae, each including densely packed bundles of collagen fibers of constant diameter. In such a way, collagen fibers are distributed in the base plate of scales like overlaid plywood. The collagen fiber bundles are packed quite densely. Scales' resistance to mechanical stress is very high due to this hierarchically organized structure. Fish scales are a source of protein (40-60%) and minerals (30-56%). Scales collagen accounts for 80-90% of all their proteins.

The review [23] indicates that fish scales make up 1 to 10% of the fish mass, and they are mainly used to produce fish meal (about 10% of all fish scales). It is shown that the best way to use fish scales is direct use as food or indirect use for the production of feed additives. The paper also describes some other ways of using fish scales: in various composite materials, as the main raw material for guanine production, an organic compound which is one of the purine bases (2-amino-hypoxanthine), for fish glue production due to the high collagen content, use in cosmetic, medical, pharmaceutical industry and, in functional foods production.

In medicine, fish collagen is used as various films, sponges, threads, bandages, patches, contact lenses, gels, ointments; preparations for the treatment of wounds, burns, trophic ulcers, pulpitis, hypertension, osteoarthritis, urorrhea; capsules and tablets with various fillers for oral administration; as culture media, a substitute for skin and bone tissue; as a component of

artificial blood vessels, an implant in cosmetic surgery; it was found to have an anti-cancer effect [23].

3. Metal Ions Extraction Using Fish Scales

Fish scales can be used as a sorption material for removal of pollutants from aquatic environments. In the world literature, there is information about the use of fish scales for the removal of metal ions from natural and wastewater [24-53]. Further, metal ions are listed in alphabetical order to simplify the description of the material.

Studies were made on adsorption of As(V) ions by carp scales (*Cyprinus carpio*) [25]. It was determined that the scales' surface area is $18.5 m^2/g$, pore volume $0.356 cm^3/g$, the average pore diameter 26.7nm. It was determined that the maximum sorption capacities determined by the Langmuir model were q_{max}=28.8-32.1mg/g at temperatures of 20-40°C. Sorption isotherms at these temperatures are most adequately described by the Langmuir model (R^2=0.984-0.992). The thermodynamic parameters of the process were as follows: ΔG^o=-40.3, -42.2 and -44.2kJ/mol at 293, 303, and 313K, respectively, ΔHo=17.6kJ/mol, ΔSo=197J/mol•K.

To increase the sorption capacity for arsenic ions, carp scales were modified by nanoparticles of Ce_2O_3. It was determined that the maximum sorption capacity at pH=4-6 was 78mg/g at the initial concentration of ions As(V) C_o=5.78mg/dm³, the adsorption isotherm is well described by the Freundlich model (R2=0.998) [26].

Studies were made on adsorption of As(III) and As(V) ions by cod scales (*Gadus Morhua*) under static conditions. The highest values of sorption capacity determined using the Langmuir equation were found to be achieved at pH=4 and are equal to q_{max}=26.67mg/g and 24.75mg/g for As(V) and As(III) ions, respectively [27]. The adsorption isotherms of these ions were determined to be most adequately described by the Langmuir model.

Studies were also made on adsorption of As(III) and As(V) ions by cod scales (*Gadus Morhua*) under dynamic conditions. For this purpose, simulated solutions containing As(III) and As(V) ions with an initial concentration of the last 0.45-84mg/dm³ with different pH values were passed through a cod scale layer weighing 61.54g at a rate of 2.0-2.75cm³/min. The characteristics at which the pollutants break through the layer of sorption material were determined by simulating the experiment using a two-dimensional mass transfer model. It was determined that such parameters as the porosity of the sorption material, selectivity, flow rate, and adsorption coefficient make a significant contribution to the change in the time intervals of the breakthrough [28]. It is indicated that such indicators as pH of the aqueous phase, the dosage of the adsorbent, also have a significant effect on the breakthrough. It was concluded that the said pollutants were extracted due to the physical adsorption and complexation with functional groups that are part of the biopolymers of the scales [29].

Carp scales (Cyprinus carpio) were also used for adsorption of Cd^{2+} ions under static conditions [25]. It was determined that the maximum sorption capacities determined by the Langmuir model were q_{max}=64.4-69.0mg/g at temperatures of 20-40°C. Sorption isotherms at these temperatures are most adequately described by the Langmuir model (R^2=0.992-0.996), and the kinetics of the process – by the pseudo-second-order model (R^2=0.998). The thermodynamic parameters of the process were as follows: ΔG^o=-40.7, -42.7 and -44.7kJ/mol at 293, 303, and 313K, respectively, ΔH^o=18.5kJ/mol, ΔS^o=202J/mol•K.

Studies were also made on adsorption of Cd^{2+} ions by glutaraldehyde cross-linked croaker (*Micropogonias furnieri*) scales collagen using IR spectroscopy, electron microscopy,

DSC and TGA, etc. It was determined that at the initial concentration of CD^{2+} ions $3.67 \cdot 10^{-4}$ mol/dm^3 in the solution, the maximum sorption capacity is $2.22 \cdot 10^{-5}$ mol/dm^3. It is determined that the adsorption kinetics is regulated by the pseudo-second-order model. ΔH^o values range from -12.55 to -117.0kJ/mol, depending on the initial concentration of cadmium ions and the solution temperature [30].

Studies were made on Co^{2+} and Pb^{2+} ions adsorption by cod (*Gadus Morhua*) and spangled emperor (*Lethrinus nebulosus*) scales in dynamic conditions [31]. The initial Co^{2+} ions concentrations were 50 and 100 ppm, Pb^{2+} ions - 470, and 1000 ppm. The experiments determined that the increase in the flow rate through the layer of sorption material results in an earlier breakthrough of pollutants into the filtrate. It was also found that the concentration of metal cations did not have a dominant effect on metal ions breakthrough. Sorption materials porosity was found to have a significant effect on sorption characteristics.

There are several reports on the study of adsorption of Cr6$^+$ ions by scales of different fish species [32-35]. In particular, the paper [31] considers adsorption of the said ions using Catla fish (*Catla catla*) scales under static conditions. It is found that the highest sorption capacity $q_{max=}$27.18 mg/g is achieved under the following conditions: C_o=15mg/dm^3, pH=1.0, scales dosage=0.05g/dm^3, mixing rate=200rpm. It is found that the sorption equilibrium is achieved within 180 min. It was determined that the adsorption isotherms are most adequately described by the Freundlich model, and the process kinetics is regulated by the pseudo-second-order model. The thermodynamic parameters of the process were as follows: ΔG^o=-13.62, -15.95 and -17.58kJ/mol at 293, 313 and 333K respectively, ΔH^o=15.10kJ/mol, ΔS^o=98J/mol•K [33]. It is indicated that the process is endothermic and occurs spontaneously; it is a chemisorption process.

Thermodynamic and calorimetric parameters of Cr^{6+} ions adsorption by croaker scales (*Micropogonias furnieri*) at 25°C were studied. It was found that enthalpies of Cr^{6+} ions sorption on croaker scales are highly exothermic (from -226.43 to -183.79kJ/mol) and the interaction energies decrease with increasing concentration of Cr(VI) ions in the solution. The solution microcalorimetry made us assume that interactions of scales with chromium ions occurs mainly due to the reaction of electrostatic interaction on the surface of the sorption material between positively charged collagen scales and negatively charged chromate ions [34].

Studies were made on adsorption of Cr^{6+} ions by glutaraldehyde cross-linked croaker (*Micropogonias furnieri*) scales collagen. It was determined that the maximum sorption capacity of the sorption material is 39.9mg/g for Cr^{6+} ions. Cr(VI) ions sorption by cross-linked croaker scales increases with increasing the initial pollutant concentration in the solution and decreases with increasing the solution temperature. Kinetic studies have shown that a multilinear exponential model is most suitable for describing the adsorption process. The values of the constant of Cr^{6+} ions diffusion to the sorption material increase, both with increasing the temperature and with the initial concentration of Cr(VI) ions in the solution [35].

Studies were made on Cu^{2+} ions adsorption by Nile tilapia (*Tilapia nilotica* Linnaeus) scales under static conditions [36]. The experiments were carried out at different ratios of biosorbent and copper ions at pH=4.05 with varying contact time (t=from 45 min to 8 days) and dosage of scales (M=from 0.2 to 7g). It is found that increasing the ratio scales: Cu^{2+} ions and contact time ensures the highest degree of sorbate extraction (97.18% at a biosorbent content of 5 g and its ratio to Cu^{2+} ions=10: 1 for 8 days) [36]. It was determined that the

isotherm of Cu^{2+} ions adsorption by Nile tilapia scales is most adequately described by the Langmuir model, and the kinetics of the process is subject to the pseudo-first-order model [37].

The scales of common bass (*Dicentrarchus labrax*) were also used as a biosorbent to extract Cu^{2+} ions from simulated solutions [38]. It was found that at the initial concentration of Cu^{2+} ions=200mg/dm³ and pH=3.0, T=45°C and a scales dosage of 1g/dm³, the maximum sorption capacity is 127.16mg/g. It is stated that the adsorption isotherm is most adequately described by the Langmuir model (R^2=0.9932), and the adsorption kinetics is best regulated by the pseudo-second-order model [38].

The paper [39] considers the adsorption of Cu^{2+} ions using Catla fish (*Catla catla*) scales under static conditions. It is found that the highest sorption capacity q_{max}=79.35mg/g is achieved under the following conditions: C_o=50mg/dm³, pH=5.5, scales dosage=10g/dm³, mixing rate=1500rpm. It is found that the sorption equilibrium is achieved within 180 min. It was determined that the adsorption isotherms are most adequately described by the Langmuir model, and the process kinetics is regulated by the pseudo-second-order model [39].

Studies were made on La^{3+} ions adsorption with unknown fish species scales used as biosorbent. It is noted that the maximum absorption of La(III) ions equal to 200.0mg/g occurs under the following conditions: pH=6.0, scales dosage=0.3g/dm³, initial concentration of metal ion=300mg/dm³, T=50°C, t=4 h. It was determined that the adsorption isotherm is more adequately described by the Langmuir model, and the adsorption kinetics is more accurately described by the pseudo-second-order model. The thermodynamic parameters of the process were as follows: ΔG^o=-24.17, -24.55 and -24.93kJ/mol at 293, 303 and 313K, respectively, ΔH^o=13.04kJ/mol, ΔS^o=38J/mol•K [40], indicates that the process is endothermic and spontaneous. FTIR analysis confirmed the participation of different functional groups in the composition of scale biopolymers in the chemisorption of La(III) ions.

Ni^{2+} ions were studied during adsorption under static conditions using tilapia (*Oreochromis niloticus*) scales as the sorption material. At the initial Ni^{2+} ions concentration=20 ppm, pH=9, the scales dosage=2g/dm³, mixing rate=125 rpm for 4 hours, the said ions removal degree amounted to 74.6%. The maximum sorption capacity under the above conditions was 1.49mg/g [41].

Studies were made on Pb^{2+} ions adsorption by crushed Rohu (*Labeo rohita*) scales under static conditions. It was determined that the scales' surface area was 76.32m²/g, and the maximum sorption capacity reached 196mg/g at pH=3.5, T=20°C, mixing speed 200 rpm for 24 hours. The adsorption isotherm is most accurately described by the Freundlich model (R^2=0.9447), and the adsorption kinetics is regulated by the pseudo-second-order model (R^2=1.0) [42]. It is shown that the scale biomass pretreatment using autoclaving, boiling, heating, treatment with HCl, H_3PO_4, and $Ca(OH)_2$ solutions resulted in an increase in sorption indices, while exposure to H_2SO_4, NaOH, and $Al(OH)_3$ solutions showed the reverse pattern.

Studies were also made on the influence of arsenic ions presence on Pb^{2+} ions adsorption by cod (*Gadus Morhua*) scales [43]. Initial concentrations of Pb^{2+} ions were 2.5, 10 and 40mg/dm³, AS^{3+} and As^{5+} - 350 and 1000µg/dm³. The experiments were carried out at different pH values. It was found that with an increase in arsenic ion concentration, the sorption capacity of cod scales for Pb^{2+} ions increases, and the greatest extraction of the said ion is observed at pH=11 [43].

The scales of Nile tilapia (*Oreochromis niloticus*) were studied for Se^{4+} ions adsorption under static conditions. It was determined that the highest sorption capacity was observed at pH=3-6 and increases with increasing the initial ion concentration and contact time. It is found

that the maximum sorption capacity of tilapia scales is low and equals to 2.12mg/g. The adsorption isotherm is more adequately described by the Freundlich model (R^2=0.913). The kinetics of the process is more accurately regulated by the intraparticle diffusion model [44].

Studies were made on the ability of Nile tilapia (*Oreochromis niloticus*) scales as a biosorbent to remove Zn^{2+} ions from wastewater of the automotive industry. The maximum sorption capacity is 16.92mg/g, and the adsorption isotherm is well described by the Langmuir model and the process kinetics by the Elovich model [45].

The sorption characteristics for Zn^{2+} ions were compared to those for Fe^{3+} ions in adsorption by Mozambique tilapia (*Oreochromis mossambicus*) scales. Table 1 shows the conditions under which the maximum values of the sorption capacity for these metal ions and the conditions of the process are achieved [46]. It was determined that the scale adsorption isotherms for Zn^{2+} and Fe^{3+} ions are most accurately described by the Langmuir model, and the process kinetics is more adequately described by the pseudo-second-order model (R^2=0.999 and R^2=0.998, respectively) [47]. IR spectroscopy showed chemisorption of these metal ions with functional biopolymer groups that are part of the scales.

Table 1. Results on ions sorption of Zn^{2+} and Fe^{3+} in the found optimal conditions [46].

Ion	pH	Dosage of scale, g	Touch time, h.	The initial concentration of metal ions	Process efficiency	Sorption capacity, mg/g
Zn^{2+}	6.0	0.02	3	10.0	93.52	46.76
Fe^{3+}	4.5	0.8	3	300.0	65.9	15.2

The sorption indices in adsorption of Zn^{2+} ions were compared to those for Pb^{2+} ions by Mozambique tilapia scales [48]. It was found that the highest sorption capacity for Pb^{2+} ions equal to 26.9mg/g is achieved at pH=5.5, the sorption material dosage=0.001g, and the initial metal ion concentration=0.3mg/g [49].

The paper considers the removal of the above-mentioned metal ions (Fe^{3+}, Pb^{2+}, Zn^{2+}) by Nile tilapia (*Oreochromis niloticus*) scales from wastewater [50]. IR spectroscopy, scanning electron microscopy, x-ray diffraction analysis showed chemisorption [51].

The scales of this fish were also used for adsorption of Cu^{2+}, Fe^{3+}, and Mn^{4+} ions from the Owabi and the Wewe (Ghana) rivers. The study determined that the sorption capacity for Cu, Mn, Fe ions adsorbed from the Owabi river was 685.70 ± 16.51, 247.06 ± 50.46 and 892.90 ± 96.29, respectively; from the Wewe river, it was 501.60 ± 77.78, 300.89 ± 54.61 and 413.04 ± 9.92mg/kg, respectively [52].

Studies were made on adsorption of 4 heavy metal ions (Cu^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}) by Nile tilapia (*Oreochromis niloticus*) scales. The highest sorption capacity was found for Cu^{2+} ions-58mg/g [53], and the sorption characteristics of metal ions are arranged in a row: $Cu^{2+} > Pb^{2+} > Co^{2+} > Ni^{2+}$. Low-vacuum scanning electron microscopy and elemental analysis show that the ion exchange reaction is the main mechanism of metal ions adsorption by fish scales.

In addition to metal cations, Catla fish (*Catla catla*) scales were used to extract fluoride ions. It was determined that at the initial concentration of fluoride ions in a solution, equal to 8.5mg/dm^3, the highest sorption indices (17.84mg/g) were achieved at pH=9.93, sorption material dosage=22.6g/dm^3, and sorbate contact time=179.7 min [54]. It was determined that the adsorption isotherms at different temperatures are more adequately described by the Langmuir model, and the process kinetics is regulated by the pseudo-second-order model.

4. Fish Scales as a Dye Sorption Material

In addition to heavy metal ions, studies were made on adsorption of various dyes by scales of various fish species [55-70]. In particular, these included adsorption of Remazol yellow, Remazol blue, and Remazol red by striped leporinus (Leporinus elongates) scales. It was determined that the maximum sorption capacity for these dyes is low and at 30°C equals to 3.10; 5.19 and 5.41mg/g, respectively. The thermodynamic parameters of the process were as follows: the ΔHo values range from 83.3 to 199.7kJ/mol, ΔGo from 17.9 to 22.5kJ/mol, ΔSo from 219.2 to 599.4J/mol•K [55].

Studies were made on adsorption of acid blue 121 dye by common bass (Dicentrarchus labrax) [56] scales and determined the optimal process conditions: pH=2, temperature=30°C, initial dye concentration – 300mg/dm3 and the scales dosage of=1g/dm3. The maximum sorption capacity determined by the Langmuir equation was 300.7mg/g. Based on the thermodynamic process parameters, the adsorption process was concluded to be spontaneous and exothermic [56, 57].

The above sorption material was studied to remove acid blue 324 dye. The experiments were carried out under the conditions given above, except that the initial dye concentration was 200mg/dm3. It was determined that the value of the maximum sorption capacity at 25°C, determined by the Langmuir model, was 192mg/g [58]. The thermodynamic parameters of the process were as follows: ΔGo=-7.49, -5.27 and -4.25kJ/mol at 298, 303 and 313K, respectively, ΔHo=- 55.5kJ/mol, ΔSo=-161.9J/mol•K, indicating that the process occurs due to external as well as intraparticle diffusion [58].

The scales of common bass (Dicentrarchus labrax) were also used to extract Methylene blue dye. The experiments were carried out at an initial dye concentration of 0.5 and 5.0mmol/dm3 at 25-55°C. The maximum sorption capacity was 2.1mmol/g (0.672mg/g) at 35°C. The adsorption isotherms are more accurately described by the Langmuir model [59].

A much larger sorption capacity (68.72mg/g) was determined with Methylene blue dye adsorption by carp (Cyprinus carpio) scales, modified magnetite nanoparticles (Fe3O4). The scales were determined to have an area of 0.65m2/g, after magnetite treatment – 4.62m2/g. It is found that the maximum sorption capacity was 66.7mg/g. The adsorption isotherms at different temperatures are most adequately described by the Sips model and the process kinetics – by the pseudo-second-order model. The thermodynamic parameters of the process were as follows: ΔGo=-7.3055, -6.1153 and -5.2634kJ/mol at 303, 313 and 323K respectively, ΔHo=-38.299kJ/mol, ΔSo=-102.462J/mol•K, E=-0.466kJ/mol [60].

Carp scales have also been studied to determine the optimal medium for adsorption and desorption of Methylene orange dye. A comparative study of dye adsorption at different pH values shows that the equilibrium time was achieved earlier in case of a solution with a neutral pH value than in case of an acidic solution. At the same time, it was found that the fibers of fish scales were resistant to adsorbed dye molecules release at a lower pH than in a neutral medium [61].

Rohu (*Labeo rohita*) scales were used to remove Malachite green dye with varying parameters of the aquatic environment. It was determined that at the initial dye concentration of 50mg/dm3, pH=8, the scales dosage=2g/dm3, T=20-40°C, and the contact time of 3h, the maximum sorption capacity determined using the Langmuir equation was 31.3-38.5mg/g. It was determined that the adsorption isotherms are regulated by the Langmuir model (R2=0.999), and the process kinetics corresponds to the pseudo-second-order model [62].

Also, Rohu scales were studied as a sorption material for removal of Brilliant red dye under static conditions. It was found that at the initial dye concentration of $7 \cdot 10^{-5}$ mol/dm3, the highest degree of the pollutant removal was observed at pH=7.2 at 30-minute contact. It was found that the adsorption isotherms at 30-50°C are most accurately described by the Langmuir model, and the calculated adsorption energy value equal to -34.92kJ/mol indicates that the process is exothermic [63].

Nile tilapia (*Oreochromis niloticus*) scales were characterized as a sorption material [64] and investigated with varying process parameters in the presence of NaCl and surfactants to extract Reactive blue 5G dye from simulated solutions. It was found that the maximum sorption capacity of tilapia scales was 272.4mg/g [65], the addition of WK Profiber PLM 28 surfactant increased the above parameter to 291mg/g, and the presence of NaCl in the solution - to 299mg/g [66].

It was determined that the best conditions for Congo red adsorption with an initial concentration of 14mg/dm3 by grass carp (Ctenopharyngodon idella) scales occurred at pH =7 and a temperature of 25°C, a sorption material dosage of 0.2g/dm3 cm. It was determined that adsorption proceeded with the endothermic effect, was spontaneous and irreversible [67]. Acid blue 113 dye adsorption by a mixture of scales of four-fingered threadfin (Eleutheronema tetradactylum), red grouper (Epinephelus moara), and black-spotted snapper (Lutjanus johnii) [68] was studied with varied process parameters: T=30-50oC, pH=5-10, t=10-180min. It is found that the maximum sorption capacity calculated according to the Langmuir equation was 151-157.3mg/g. The adsorption isotherms built at different temperatures are most adequately described by the Langmuir model and the process kinetics – by the pseudo-second-order model.

Studies were made on Indigo carmine dye adsorption by fish scales pretreated with NaOH solution at pH=9 for 4 hours under dynamic conditions. The dye solution at a concentration of 10-20mg/dm3 was passed through a column with a 3-6cm layer. It was determined that depending on the conditions of the experiment; the maximum sorption capacity was 8-13mg/g. It was determined that the Adams-Bogart, Thomas, Jan, and Yun-Nelson models describe the process with low accuracy [69].

Carbonized Rohu (*Labeo rohita*) scales were used to remove Reactive orange 16 dye from aqueous solutions. It is shown that carbonation dramatically increases the surface area (213m2/g by the BET method) and the total pore volume (0.215cm3/g). Studies were made on the effect of the initial dye concentration (25-400mg/dm3), the solution pH (3-13), and the temperature (30-50°C) on the adsorption efficiency of carbonized Rohu scales. It was found that the sorption capacity was 105.8, 107.2, and 114.2mg/g at 30, 40, and 50°C, respectively. The adsorption isotherms were best regulated by the Freundlich model and adsorption kinetics graphs – by pseudo-second-order models [70].

5. Organic Compounds Extraction Using Fish Scales

There are several publications devoted to the removal of organic compounds from aqueous solutions by fish scales. In particular, studies were made of tetracycline adsorption from aqueous solutions by giant gourami (Osphronemus gouramy) scales collagen. It was shown that at the initial tetracycline concentration of 236µg/cm3, the lowest concentration of the latter is achieved after 1 hour of contact – 160µg/cm3 [71].

Silver sea trout (*Cynoscion acoupa*) scales treated with glutaraldehyde and amines, was investigated for doxycycline removal from water bodies. Studies were made to determine the

influence of various parameters on the sorption capacity, which was 3.2·10-6mol/g at an initial doxycycline concentration of 2.5·10-5mol/dm3. It was determined that the best results of antibiotic desorption were obtained at pH=4.0 [72]. It is found that the process kinetics at 25-45°C was most adequately described by the pseudo-first-order model.

Glutaraldehyde and chitosan gel-treated croaker (Micropogonias furnieri) scales were studied for the ability to remove dichlorophenol-2,6-indophenol. The structure of the resulting material was investigated by various physical and chemical methods. It was found that the sorption energy was 1.46, 3.6, and 2.3J/mol at dichlorophenol-2,6-indophenol concentrations in solutions of 1·10-5, 1·10-4, and 1·10-3mol/dm3. The ΔH values ranged from -536.7 to -50.9kJ/mol, indicating the occurrence of chemisorption interaction [73].

The crushed saddled seabream scales were used in conjunction with aluminum sulfate as a coagulant for the humic acid deposition from an aqueous solution. The optimal conditions were determined in the course of experiment planning. It was found that the highest degree of humic substances deposition at the initial concentration of the latter=10mg/dm3 was observed at an aluminum sulfate dosage=1.03mg/dm3, fish scales=1.13mg/dm3 at pH=5 [74].

6. Conclusions

In general, we have summarized the information on the use of fish scales of different species as a sorption material for the removal of different pollutants from aquatic environments. It is shown that the sorption capacity of fish scales can be increase by modifying various chemical reagents. The isotherms of pollutant adsorption with fish scales were found to be, in most cases, most adequately described by the Langmuir model, less often by the Freundlich model, and the process kinetics is most often described by the pseudo-second-order model. Given the large volume of fish-scale formation on a global scale, we can recommend it as a promising, environmentally friendly sorption material for the removal of pollutants from natural and wastewaters.

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Conflicts of Interest

The authors declare no conflict of interest.

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