Hungarian University of Agriculture and Life Sciences

Doctoral School of Biological Sciences

Ph.D. Thesis

Removal of micro-pollutants from wastewater by bioremediation

By

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Gödöllő, Hungary

2022

Title: Removal of micro-pollutants from wastewater by bioremediation

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BACHGROUND AND OBJECTIVES

Water is a vital natural resource, as it is a prerequisite for life, and its properties make it a key basic component of production in various industrial sectors. Water in sufficient quality and quantity is an important raw material and as such its production is an important task.

In global scale it is estimated that 80% of wastewater is released to the environment without adequate treatment (UNESCO, 2017). Moreover, The United Nations' (UN) World Water Report 2017 highlights new and rapidly expanding pollutants that represent a clear knowledge and research gap. Such pollutants include the family of organic (pharmaceutical residues, pesticides, paints) and inorganic (heavy metals, cyanides) micropollutants.

Micropollutants are pollutants that are found in the environment at very low concentrations (μg/l, ng/l). The long-term effects of micropollutants on humans and the environment are not yet known and proven. It is therefore essential to carry out research that will help us understand the dynamics of these pollutants, their impact on the environment and on the organism, and to develop methods to remove them from wastewater. As there is a lack of regulation of new pollutants, appropriate studies need to be carried out (Afsane Chavoshani et al., 2020).

Humanity has used materials since ancient times that are capable of staining other materials, initially working with natural colors of animal and vegetable origin. However, nowadays the modern textile industry uses synthetic dyes to color their products producing wastewater containing organic matter with strong color (Salleh et al., 2011).

Inorganic micropollutants include heavy metals. In recent years, there have been growing ecological and global public health concerns about metal pollution in the environment. Cadmium, perhaps one of the most toxic heavy metals, is a major concern due to its high mobility, bioaccumulation and high solubility, which makes it crucial to remove from the industrial wastewaters (Bashir et al., 2018).

The main problem is that wastewater treatment plants cannot fully remove these substances with the technology currently used, so they can leach into surface water and end up in drinking water, which is then returned to the body.

1.1. Objectives

This dissertation is based on five research, one review paper (internationally accepted scientific articles with impact factor), as well as a university note. The main idea and topic of all these papers is the removal of organic, synthetically produced dyes and cadmium micropollutants from water by environmentally friendly bioremediation techniques. In our research, adsorption techniques were used to remove emerging contaminants. Household and industrial waste and, in the case of cadmium, cosmetic clay were used as adsorbents.

The first **aim** of this thesis was to develop an alternative remediation method for the removal of inorganic and organic micropollutants and to determinate the optimal dye removal conditions. Another focal aim of the thesis is the characterization of adsorbents (eggshell, brewery's yeast, Aslavital cosmetic clay) and contaminants using known and practical analytical methods. Analytical instrumental studies help in the knowledge of the adsorption mechanism, as the measurements provide insight into the chemical, physical and surface properties of the adsorbent and the contaminant. To further understand the adsorption mechanisms, beside the large-scale instrumental results, mathematical models were carried out.

MATERIALS AND METHODS

Adsorbent preparation for dye removal

This thesis investigates the adsorbent characteristics, adsorption capacity, dye removal properties and optimization of two wastes, eggshell and brewer's yeast.

Eggshells were collected from kitchen waste. To prevent decomposition and to remove dirt particles, the samples were washed several times with tap water, subsequently with deionized water (MilliQ), and finally dried in a drying cabinet (Memmert UN75 PLUS) at 80 °C until mass equilibrium was reached. The samples were kept in an airtight box until later use. The dried eggshells were used in four forms for different reasons: (1) approximately 0.5 cm diameter eggshell units for the structure study; (2) powdered; (3) calcined and (4) alginate embedded for adsorption study. (1) To study the chicken eggshell structure before and after dye adsorption, thin sections were made. (2) The dried eggshells were crushed in a mortar, shredded using Bosch TSM6A013B electric grinder, and then adjusted to different particle sizes (treatment <=160 µm, 160 – 315 µm) using a geological sieve. The eggshell powder was used as an adsorbent without any physical or chemical pre-treatment. (3) The 160 µm particle sized powdered eggshell was calcined at 1,000 ^{o}C for 4 hours with a Nabertherm 30 – 3,000 ^{o}C oven. (4) In our study, the adsorption capacity of eggshell in immobilized form was also studied by dropping 1.5 g of eggshell in a mixture of 30 mL of deionized water, 1 g of sodium alginate, 2 mL of ET-OH into 200 mL of 0.2 M $CaCl_2$ solution using a hypodermic needle to form small beads

Saccharomyces cerevisiae yeast (BY) was supplied from a brewery factory in Romania and was used as a biosorbent after preparation. In the brewing process, after a few fermentation cycles, the brewer's yeast by-product was lyophilized. For lyophilization of yeast in aqueous solution, we used the Telstar Cryodos 50 lyophilization system, it operates at -30 °C and $4x10^{-2}$ mbar pressure. The yeast solution was placed in 50 mL centrifuge tubes and frozen at -80 °C, and then mounted on the distribution tubes of the lyophilization system. The lyophilization was carried out until the samples were completely dry (24 hours).

Details about the Aslavital cosmetic clay adsorbent and experimental design

The sorbent (ACC) used in this research is a particular Aslavital Diatomaceous earth (100% natural diatomaceous clay) manufactured and marketed by the Farmec S.A. It comes from the Pădurea Craiului Mountains, therefore, has a well-defined chemical and mineral composition.

Adsorption of Cd^{2+} on Aslavital cosmetic clay (ACC) was carried out by the batch equilibrium method. The Cd^{2+} concentration was investigated with the help of flame atomic absorption spectrophotometer.

Influencing parameters

The efficiency of liquid phase adsorption, and therefore the optimal operation of the water treatment process, depends on several parameters. The most studied influencing factors (initial dye concentration, aqueous solution pH, adsorbent volume and particle size, and temperature) will be presented through our results from dye (indicators and textile dyes) and Cd^{2+} adsorption with different adsorbents (eggshell, yeast and ACC) in the results and discussion part. Moreover, our result will be compared with the results of research over the last five years (2017-2021). General trends will be formulated based on the results obtained, considering the effects of the factors.

Analytical measurements

A wide range of analytical techniques are used to study the biosorption process, to characterize the contaminants and adsorbents, and to study the adsorption mechanism between the adsorbent and the micropollutant. In the adsorption process, the concentration of the contaminants in the aqueous solution was determined using a UV-Vis spectrophotometer and an atomic adsorption spectrometer. SEM and EDX studies were performed to visualize the morphology and study the elemental composition of the biosorbents. Furthermore, FTIR, Raman analysis was performed to determine the functional groups of the adsorbent, the active sites of the biosorbent. TGA was used to study the thermal stability information of the eggshell. The crystal structure of the cosmetic adsorbent was determined by X-ray diffraction (XRD).

Mathematical models

The four, most widely used (Langmuir, Freundlich, Temkin, Dubinin-Radushkevich) two-parameter isotherm models in linear form were used in all of the six articles that this thesis is built on.

In case of RR and yeast adsorption, beside the four linear, two-parameter isotherm models, the non-linear versions of the Langmuir, Freundlich, Temkin, Dubinin-Radushkevich two-parameter and Liu, Toth, Kahn, Sips, Redlich-Peterson and Radke-Prausnitz three-parameter isotherm models were investigated.

In case of Cd^{2+} and clay adsorption the non-linear versions of the Langmuir, Freundlich, Temkin two-parameter and Liu, Toth and Kahn three-parameter isotherm models were studied.

In addition to the kinetic models (pseudo-first-Lagergren and second-order-Ho and McKay), the mechanism of adsorption can be also described by diffusion, which is determined by the adsorption phenomena.

RESULTS AND DISCUSSION

The influence of initial parameter changes in dye adsorption

The effect of initial micropollutant concentration

The effect of initial dye concentration relies on the immediate relation between the dye concentration and the available binding sites on the adsorbent surface (Ta Wee Seow and Chi Kim Lim, 2016). During our research the effect of CR, BPB anionic and MB, MG cationic indicators uptake by powdered eggshell was examined using different initial dye concentrations between 10-50 mg/L. With the increase of initial dye concentration in case of CR, MB and MG, the adsorption capacity also increased, whereas in case of BPB there was no such trend.

The effect of the initial dye concentration on the uptake of RBV-5R dye by and calcined eggshell was studied (C_i = 20-100 mg/L). Compared to powdered eggshell adsorption, in case of calcined eggshell no clear trend was observed regarding the increase in concentration.

In the present study, the effect of RR concentration on the adsorption of brewer's yeast was investigated using 16 different concentration values ranging from 5 to 1,000 mg/L (Figure 1). We observed an initial increase in dye removal efficiency, reaching a maximum of 80.6 % at a concentration of 40 mg/L. At concentrations of 40, 50 and 60 mg/L, the E was almost constant, as the active sites were saturated. After saturation, the number of binding sites were limited. The values of quantity in equilibrium (q_e) were also studied. The q_e increased with increasing concentration ($q_{e;5\ mg/L}$= 0.2 mg/g; $q_{e;1000\ mg/L}$= 21.7 mg/g).

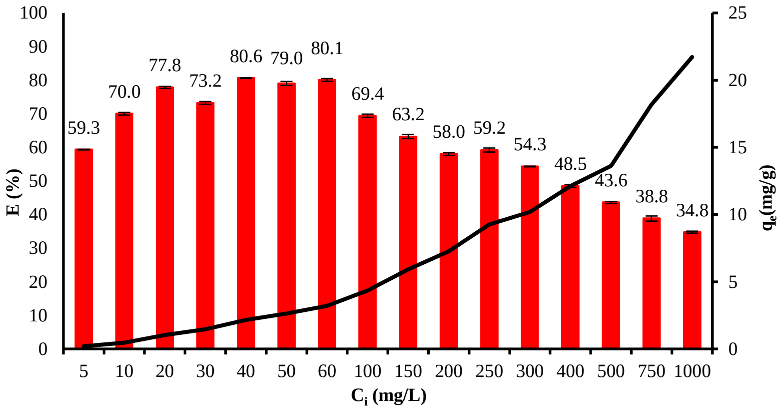

Figure 1. The effect of initial RR concentration on yeast adsorption, C_i = 5–1,000 mg/L, 1.5 g

The effect of solution pH

In our study, we investigated the adsorption processes by varying the pH of aqueous solutions of indicator dyes (pH=2-10). The highest adsorption efficiency of CR dye was obtained at pH=2, but E% was above 93% in all cases. The highest efficiency of BPB dyes was also at pH=2 (E=67%). In the case of MB, adsorption was most efficient at pH=10, with an efficiency of 75%, while the lowest was at pH=2, where E=14%. It can be said that the BPB anionic dye favored the acidic medium, while the MB cationic dye favored the basic medium, while there was no significant change for CR and MG, as the efficiency was high at all pH.

Reactive dyes such as RBV-5R, RR and RB are also anionic in nature. This property means that the dyes can adsorb with higher efficiency in acidic medium. In the case of adsorption on the surface of powdered eggshell, the dye adsorbed with highest efficiency in acidic medium (at pH = 2, E>94%), on the other hand, it was lowest at pH = 11 (E=54.69%). Unlike powdered eggshell, there was no significant change in E and q_e values for calcined eggshell. The calcined eggshell used in our study contains CaO, which is alkaline in chemistry and has a strong effect on the pH of the aqueous medium. At the end of the adsorption experiments, the solutions were filtered, and the pH of the filtrate was checked. The pH of all solutions was around 11. The highest adsorption efficiency was obtained for RR and RB dyes at pH=3 (ERR=98.33%; ERB=99%). Our assumptions were also confirmed for the adsorption of RR dye by yeast, as the highest efficiency (88.5%) was obtained at pH=3, the lowest at pH=11, where E=46.5%.

The effect of adsorbent dosage

The amount of biomass is an important factor in the adsorption process. Theoretically, the higher the amount of adsorbent present in the aqueous medium, the more binding sites are available for the dye molecules. In our study, we investigated the adsorption parameters of different starting amounts of powdered (0.5; 1; 1.5; 1.5; 2; 2.5 g) and calcined eggshell (0.5; 1; 1.5; 1.5; 2 g) and yeast (0.5; 1; 1.5; 1.5; 2; 2.5 g). As the amount of adsorbent (powdered eggshell) was increased, the removal efficiency of RBV-5R increased up to 1.5 g/100 mL but reached saturation thereafter. Based on the results, the highest removal efficiency (E% = 96.83) of RBV-5R was obtained for 1.5 g calcined eggshell (E% = 96.83). The adsorption efficiency of RR dye was highest for 1 g adsorbent, where E = 97.83%, while for 1.5 g adsorbent, E = 97.33% was obtained. A largely constant but slightly decreasing trend can be seen. On the other hand, the adsorption of RB dye was highest when adsorbed with 1.5 g of calcined eggshell (E=98.83%) and lowest (E=92%) when 0.5 g of calcined eggshell was added to the dye solution. In our study, the highest efficiency was obtained with the addition of 2.5 g yeast in a 5 mg/l RR dye solution suspension. On the other hand, the q_e decreased from 0.59 mg/g to 0.13 mg/g with increasing the mass.

The effect of adsorbent particle size

We tested the effect of particle size on the biosorption process. The rate of paint removal shows a decreasing trend as the particle size increases. Both the biosorption capacity (1.26; 1.23; 1.21) and the efficiency (94.39; 92.09; 90.87) decrease with increasing eggshell powder particle size (160 µm; 315 µm; Unsorted). The highest efficiency (94%) was obtained in case of 160 µm.

The effect of adsorption shaking speed

In our experiments with the adsorption of RBV-5R and powdered eggshell the efficiency (82; 96.6%) of dye removal increased as the shaking speed (350; 700 rpm) increased.

The effect of solution temperature

The temperature can affect the efficiency of the sorption differently depending on the adsorbent and the pollutant. The maximum efficiency was 94.4% at 20 °C, while 92.4% at 30 °C and 89.7% at 40 °C in case of powdered eggshell. It can be observed that the efficiency and the quantity in equilibrium decreases with the increase in the temperature of the aqueous medium. Similar results were obtained for calcined eggshells, but with lower efficiency (20 ºC: 96.83, 30 ºC: 93.17, 40 ºC: 89.33). This was anticipated because the molecules' thermal movement increases with the increase of temperature, and thus adsorption decreases. In our study, with RR dye removal by brewery's waste, both the efficiency and q decreased with increasing temperature, at 20 °C, the efficiency/ quantity in equilibrium was 94.4%/1.04 mg/g, while at 30 °C it was 92.4%/0.82 mg/g and at 40 °C it was 89.7%/0.79 mg/g. Results indicate that the sorption can be attributed to weak Van der Waals and dipole forces and bonds.

Based on thermodynamic data, it can be said that RBV-5R dye biosorption on eggshell (powdered and calcined) surface is a spontaneous and endothermic process. Physical adsorption occurs between the dye molecules and the surface of the eggshell. Based on the enthalpy value obtained, the adsorption is an endothermic process and physical adsorption takes place between the yeast and the dye.

The effect adsorbent properties

The nature of the biosorbent is of major importance for the performance of adsorption: availability of binding sites, growth (in the case of living biomass) and treatment history, physical or chemical modification. Calcined eggshell binds the dye with the highest efficiency (96.83%), in contrast with powdered 95.07% and alginate embedded 89.78% eggshell. Under the same experimental conditions, the adsorption equilibrium with the plain eggshell was around 300 min, while with the calcined eggshell it was 30 min, and for the eggshell embedded in alginate beads this time was 390 min. Taking all this into account, it is preferable to use eggshells in calcined form.

Analytical measurements for dye adsorption

Morphology and elemental composition

Eggshell thin section

Each layer has a different composition. After adsorption, the membrane, mammillary and cuticle layers show the characteristic elements of the dye molecule, namely, N, S and Cu, proving the eggshell's adsorptive capability. The palisade, composed of columnar calcite crystals, contains Ca, O and C. After the adsorption experiment on the eggshells, the amount of magnesium increased, but the characteristic elements (Cu, S, N, O) of the dye could not be detected, which suggests that the dye did not reach the inner layers of the eggshell, even when a 2 g/L dye solution was used, presumably due to the structure and/or composition of the eggshell layer.

Eggshell powder

The surface characterization (morphology and texture) of the homogenous eggshell powder before and after adsorption was determined by scanning electron microscopy (SEM).

We saw that the porous, cross-linked structure of eggshell disappears in comparison to the control sample. After contacting the dye, the surface became smoother as if it had been polished, with apparently fewer and smaller pores.

The EDS results obtained are the means and standard deviations of 17 analyses (C_{RBV-5R}=100 mg/L, 160 μm). The control sample contains a high proportion of carbon (23±9 wt%), oxygen

(44±1 wt%) and calcium (29±10 wt%). The RBV-5R dye consists of carbon (33.5±2 wt%), oxygen (38±11 wt%), nitrogen (2.4± 5 wt%), sulphur (0.6±0.8 wt%) and in traces copper (0.08±0.15 wt%), which appear in the eggshell composition after biosorption. The appearance of S and Cu and the increased amount of N clearly demonstrate the ability of the eggshell to adsorb RBV-5R.

Calcined eggshell

SEM figures (Figures 2A. a-b.) show the porous structure of the calcined eggshell between the irregular shaped structures. Moreover, on the surface some small crystals of about 300 nm can be found. Following the adsorption, this porous and irregular structure disappears, with the molecules of the dye filling the "gaps". The EDX results show a decrease in Ca after adsorption and an increase in C and O in all cases due to the dissolution of the dye after adsorption. After RBV-5R adsorption, C and N increased by more than 500%, which is typically due to the dye being an azo dye. The presence of small amounts of S (present in the dye content as in RR, RB dyes) indicates binding of dye molecules on the surface of calcined eggshells.

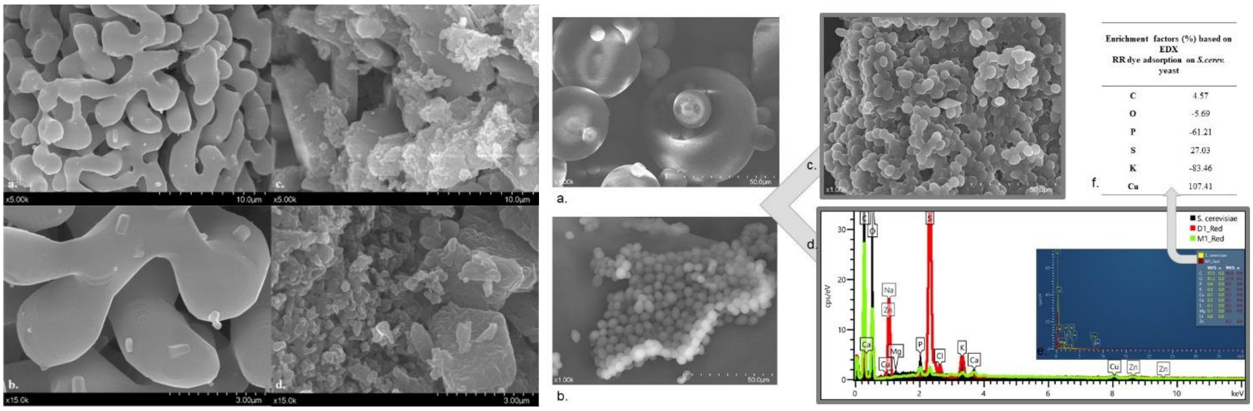

Figure 2. ***A.*** SEM (a, b) control and (c, d) RBV-5R dye adsorbed calcined eggshell. ***B.***Adsorbent characterization, where SEM micrographs (a) RR dye, (b) control *S.cerev.* (c) RR adsorbed yeast; EDS spectra (d) comparison of *S.cerev.* (black), RR dye (red), yeast sample after RR adsorption (green), (e) comparison of *S.cerev*. (yellow), yeast sample after RR adsorption (red) with numerical values; (f) enrichment factor calculations based on EDS measurements

Brewery's yeast

The SEM images show the spherical, cellular, peculiar structure of the dye. After adsorption, the porous structure disappears, which can be seen in the composition of the peaks, the cells appear to fuse together, and the cell morphological difference is also visible. Presumably, the process has caused the structure to change and the 'gaps' to become saturated with dye molecules. The EDX results show that the dye contains trace amounts of S (0.16 ± 0.06) and Cu (0.56 ± 0.34 wt%), and that the yeast sample contained Cu after adsorption due to dye uptake. The enrichment factor results showed an increase of C and S in the sample.

Determination of functional groups, surface chemistry

Eggshell surface chemistry before and after RBV-5R adsorption

Following adsorption, new bands appeared in FTIR spectra, including at 1398 cm^{-1}, representing sulfonic groups characteristic of the dye; at 1648 cm^{-1}, indicating naphthalene; and between 1980 and 2281 cm^{-1}, representing the dye fingerprint zone. Stretching vibrations appear above 2967 cm^{-1}, specific to phenolic O–H, secondary amine N–H, and aromatic C–H bonds (Ribeiro et al., 2017; Shah et al., 2016; Török, 2015).

The Raman spectrum of dye-adsorbed eggshell contains some characteristic bands of the dye as well (with a smaller or greater intensity, namely, 520, 581-582, 992-998, 1261, 1307, 1334, 1402 and 1437 cm^{-1}). The newly emerging bands typically correspond to aliphatic C–S bonds and N=N bonds (HORIBA, 2018).

Calcined eggshell surface chemistry before and after RBV-5R adsorption

Typical peaks of calcite and CaO are found at 874, 1442, 1795 cm^{-1} wavelengths, 713 and 1050 cm^{-1} typically exhibit peaks of $R\text{-}SO_2$, functional groups on 2923 and 2853 cm^{-1} represent CH.

Spectrums of the control and the dye adsorbed calcined eggshells contained peaks of calcite described in literature at 150-154, 712-711, 1087-1086 cm^{-1}. Peaks at 281-274 and 3618 cm^{-1} represent $Ca(OH)_2$. We also observe the characteristic peaks of the dye on the dye-adsorbed biomass sample: 582, 1261-1262, 1307-1306, 1437-1435 cm^{-1}. Newly emerging peaks may be suitable for aliphatic C-S, N = N bonds.

Thermal stability and textural property

Based on the TG curve (green curve), there are two main mass losses owing to temperature, below 800 ºC (disappearance of adsorbed water molecules and organic compounds) and in the range 800-900 ºC. In the second case, the main weight loss corresponds to 32.84% by weight when the $CaCO_3$ phase is transformed into a CaO phase. Since the mass of the sample remained constant after 900 °C, we can assume that the transformation is complete. According to the DTA curve, decomposition occurs at 728.6 ºC, which is an endothermic phenomenon.

Total surface area (St), pore volume (Vp) and pore radius (Rm) were calculated, and eggshell density was also determined with ethanol. The surface area of 160 µm pore size eggshell powder was 1.8 m^2/g, the pore volume was 0.01 cm^3/g and the density (ρ) was 1.3 g/cm^3.

Mathematical models

Adsorption isotherms, kinetic and diffusion models

The adsorption isotherms can be used to know the type of adsorption (physical or chemical nature), the surface properties of the adsorbent (homogeneous or heterogeneous surface). The adsorption capacity can be calculated and compared with the results obtained experimentally. Finally, an equilibrium relationship between the adsorbent (powdered-, calcined eggshell and yeast) and the adsorbate (CR, BPB, MB, MG, RBV-5R, RR, RB dyes) can be established and identified. MB and RR fits the Dubinin-Radushkevich isotherm model more closely, which indicates that chemical adsorption also occurs, ion exchange happens. In case of MG the liner regression coefficients are very near values, but it aligned closer to Freundlich isotherm model, while for BPB, CR, RBV-5R and RB the adsorption process can be described by Langmuir isotherm model.

In case of RR dye removal with brewery's yeast, the results were used to rank the best-fit models: Langmuir I. (R^2=0,923) > Freundlich (R^2 = 0.921) > Temkin (R^2 = 0.898) > Langmuir II. (R^2=0.892) > Dubinin-Radushkevich (R^2 = 0.712) > Langmuir III. (R^2=0.571) > Langmuir IV. (R^2=0.508). It is observed that under our experimental conditions, the Langmuir isotherm fits the equilibrium data with higher accuracy among the linear models. However, there was only a small difference compared to the Freundlich model.

Another similar characteristic of all the experiments conducted is that B – Temkin constant is less than 20 kJ/mol and E – energy is less than 8 kJ/mol. We can therefore assume that the adsorption occurs by physisorption, forming weak van der Waals interactions in a single-layer adsorption surface with equivalent binding sites.

Adsorption kinetic and diffusion models

For all dye adsorption data, the constant values of McKay pseudo-second-order kinetic models showed the best fit. The quantity in equilibrium from experiments q_e(exp) in some cases is very close or similar to the quantity in equilibrium calculated q_e(calc) value from the, this shows the adequacy of experimental measurement data to pseudo-second-order kinetic model. It can be concluded that during the binding of the dye on the surface of the eggshell, the intra-particle section is not rate-determining, nor does the liquid film diffusion affect the adsorption process. In summary, the speed of the process is only determined by biosorption.

Possible mechanisms

RBV-5R dye adsorption on eggshell surface

Based on our current knowledge, no binding process or mechanism between the eggshell and the dye has been described explicitly in any research article. Relying on our results and the little information found in the literature, we formulate our ideas about possible processes.

The initial pH of the solution is an important factor for adsorption processes. The pH can alter the chemical balance of the ions present both in the RBV-5R dye and eggshell adsorbent; thus, the pH influences the electrostatic interactions between the dye and sorbent. When the eggshell powder was mixed with the dye solution, calcium salts may partially dissolve and release Ca^{2+}, HCO_3^-, CO_3^{2-} and OH^- ions, which can form a negatively surfaced charge (Abdel-Khalek et al., 2017; Parvin et al., 2019). In acidic media (HCl), the eggshell surface exhibits a positive charge, so there is a high electrostatic attraction between the eggshell powder and the anionic, negatively charged dye (this dye contains aromatic rings such as phenolic OH and sulfonate SO_3^- groups that ionize in aqueous solution and form coloured anions (Ribeiro et al., 2017)). By adding NaOH, the number of negatively charged sites of eggshell increases, resulting in electrostatic repulsion.

The adsorption mechanism was studied by isotherm, kinetic and diffusion models. Since in our experimental conditions the Langmuir isotherm showed a better fit, adsorption takes place on a homogenous surface, and monolayer adsorption occurs. We found that $0.1<R_L<0.35$, which suggested favourable adsorption; however, R_L (separation parameter) values close to the lower acceptable range suggest high irreversibility. Constant calculations from the Temkin and Dubinin-Radushkevich models, as mentioned before, suggest the appearance of physisorption where weak van der Waals interactions are formed in a single-layer adsorption surface with equivalent binding sites. The physical nature and spontaneous and random characteristics of adsorption are suggested by the calculated thermodynamic parameters.

FTIR and Raman analyses (both for powdered eggshell and for different layers of eggshell) proved the presence of specific functional groups from organic and inorganic compounds such as ^-OH, C=O, $=CH_2$, aromatic, –SH and –COOH groups. All these surface functional groups indicate that eggshell exhibits a moisture adsorption capability, which makes this material a potential adsorbent by participating in adsorption. FTIR spectra of RBV-5R showed bands that correspond to phenolic O–H, aromatic C–H, amide N–H, aliphatic $C–H_n$, amide C=O, C=C, N=N, $R–SO_3^-$ and C–S functional groups (Ribeiro et al., 2017).

The results obtained from the pH studies and FTIR/Raman analyses indicate that adsorption occurred mostly via electrostatic attraction, where the protonated eggshell surface attracted the anionic dye sulfonate group. Considering two previous articles (Chatterjee et al., 2007; Ribeiro et al., 2017), three possible interactions can be between the dye and adsorbent: hydrogen bonding between hydroxyl groups of eggshell and electronegative residues of RBV-5R; ionic interactions at pH values where surface charge is neutral and physisorption occurs; and π-electron resonance.

RR dye adsorption on yeast

Live yeast cells can perform the stain removal in two different ways. The dye is adsorbed on the cell wall of the yeast, penetrates the cell wall, accumulates inside the cell or biodegradation can occur by various enzymes (oxidases and reductases). Irrespective of the nature of the yeast cell (living or dead), biosorption occurs between the contaminant and the yeast cell wall, which can be by electrostatic interaction, complexation, chelation and microprecipitation, ion exchange or physical and chemical adsorption, depending on a number of factors (Danouche et al., 2021).

The mechanism of dye biosorption on yeast is complex and not fully understood, is a sophisticated and multi-faceted process, and may involve more than one mechanism (Castro et al., 2017).

Some studies have described the structure and components of the *S. cerevisiae* yeast cell and the functional groups that occur on its surface. Its composition includes proteins, amino acids, polysaccharides and lipids. Accordingly, carboxyl, hydroxyl, amide, amino, phosphate and other charged groups have been identified, which show strong binding forces with the dye molecules. It has been shown that the biosorption process can also be achieved by chelation and the formation of ionic bridges between the dye molecules and the functional groups.

Depending on the type of interaction between the adsorbent surface and the contaminant, the biosorption process can be divided into two types: (i) chemical adsorption, an irreversible process resulting in the formation of strong chemical bonds; and (ii) physical adsorption, which is reversible, in most cases characterized by weak van der Waals forces, H-bonds, polarity and dipole-dipole H-bonding interactions. Furthermore, FTIR studies have demonstrated that Yoshida H-bonding, dipole-dipole H-bonding, π-π and n-π interactions can occur upon adsorption of dye molecules on yeast cells (Danouche et al., 2021).

Effectiveness and Characterization of Novel Mineral Clay in Cd^{2+} Adsorption

Characterization of Cosmetic Clay

SEM images showed the porous structure of ACC, moreover, the surface of the adsorbent is filled with 10–300 µm holes. The porous structure of ACC disappeared after adsorption, the surface is smoother, and some aggregates appear on the surface.

From EDS results, we can conclude that ACC contains a relatively high percentage of Al (W_t(%) = 11.4 ± 0.9) and Si (W_t(%) = 13.7 ± 1.4), moreover Mg (W_t(%) = 0.2 ± 0.01), K (W_t(%) = 1.5 ± 0.2), Ti (W_t(%) = 0.4 ± 0.03), and Fe (W_t(%) = 0.6 ± 0.1), in small quantities. Therefore, it can be affirmed that ACC is an alumina-silicate mineral. After the adsorption process Cd^{2+} appears in the sample (W_t(%) = 0.2 ± 0.01).

After the adsorption with Cd^{2+} solution made from $Cd(NO_3)_2 * 4H_2O$ salt, a particularly strong vibration was observed in FTIR spectra at 1384 cm^{-1} that can be attributed to NO_3 asymmetric stretching (Chen et al., 2014; Nekhlaoui et al., 2021; Niño et al., 2013).

As expected, the sample, in XRD study, being clay contains silicon oxide-SiO_2 (in the form of quartz). The other two identified components are phyllosilicate minerals, based on silicate groups. One phase is Potassium Aluminium Silicate Hydroxide-$(KH_3O)Al_2Si_3AlO_{10}(OH)_2$, known as a form of illite and Aluminium silicate hydroxide-$Al_2Si_2O_5(OH)_4$ known as kaolinite. The following database reference codes were used in the actual identification: 99-201-2847 for quartz, 99-200-3858 for kaolinite and 00-026-0911 for illite.

The most intense Raman bands (~146, 200, 398, 511 and 638 cm^{-1}) are characteristic of anatase (TiO_2), which is a typical phase detected in kaolinite-bearing clays (Murad, 1997). The weak Raman signals of kaolinite can be attributed to the observed bands at around 130, 259, 333, 426, 464, 704 m 791 and 910 cm^{-1} (Michaelian, 2011). Rare crystals of quartz with intense bands at 126, 200 and 464 cm^{-1} could also be detected. Illite could not be directly detected with Raman spectrometry since it has overlapping peaks (Liu, 2001) with both quartz (~464 cm^{-1}) and kaolinite (~464 and ~705 cm^{-1}). Raman band, which can be associated with the absorption band of NO_3 (Cd solution was made from $Cd(NO_3)_2 * 4H_2O$ salt) on the FTIR could not be detected.

Adsorption Experiments of Cd^{2+} and clay

The adsorption efficiency of Cd^{2+} ions on ACC were investigated at various initial concentrations between 10–160 mg/L via the batch adsorption method. In equilibrium, results showed that the adsorption capacity (q) increased from 1.07 to 8 mg/g as the initial concentration increased from 10 to 160 mg/L. On the other hand, with the increase in concentration, the efficiency (E) decreased from 99 to 51%. This can happen because more cadmium ions were adsorbed at higher Cd^{2+} concentrations.

Adsorption Isotherms, Kinetic and Diffusion Models

Langmuir, Freundlich, Temkin and Dubinin–Radushkevich linearized isotherm models were employed to investigate the interaction between the Cd^{2+} ions and clay using different initial concentrations of Cd^{2+} (10–160 mg/L). Based on the results, we established the order of correspondence of the applied isotherm models: Langmuir II. (R^2 = 0.954) > Dubinin–Radushkevich (R^2 = 0.933) > Freundlich (R^2 = 0.885) > Temkin (R^2 = 0.859) > Langmuir I. (R^2 = 0.798) > Langmuir IV. (R^2 = 0.744) > Langmuir III. (R^2 = 0.605).

R_L values calculated for Langmuir II. isotherm were in the range of 0.037–0.027; this result suggests that in our experimental conditions, the adsorption of Cd^{2+} ions was favorable but with a high tendency of irreversibility. According to the theoretical properties of Langmuir isotherm, the adsorption occurs on a homogenous surface, and only one layer is formed (monolayer adsorption) (Mustapha et al., 2019; Nagy et al., 2013). The precisely calculated isotherm parameters tell us about the nature and type of the adsorption. In our experimental conditions, these constants (B-Temkin: 1×10^{-4} J/mol < 20 kJ/mol; E-Energy: 3.16 kJ/mol < 8 kJ/mol) indicated that the adsorption is a physical one, where weak van der Waals bonds are formed on the ACCs monolayer surface. Moreover, the binding sites on ACC surface are equivalent.

Comparing the obtained linear regression coefficients (R^2 ; the larger the better) and Chi-squared (χ^2; the smaller the better), in case of non-linear fitting, the degree of fit follows the following order: Liu (the best fit: $R^2 = 0.965$, $\chi^2 = 1.101$) > Toth > Khan > Langmuir > Freundlich > Temkin.

In this study, pseudo-I-order (Lagergen) and pseudo-II-order (Ho and McKay) kinetic models were calculated when the initial concentration of Cd^{2+} was changed (between 10–160 mg/L). Based on the obtained linear regression coefficient values, it can be observed that the adsorption system did not follow a pseudo-I-order model, as the value of R^2 was higher in the case of the pseudo-II-order model. The values of q_e(cal) also depicted a better fitness of the model since they were almost identical with the pseudo-II-order q_e(exp) values, this model was better obeyed.

The pore diffusion coefficients vary between 2.64×10^{-9} and 2.94×10^{-8} cm^2/s with changing concentration. The linear plots of intra-particle and liquid film diffusion do not cross the origin, indicating that boundary layer diffusion was involved in the adsorption process. Intra-particle diffusion and liquid film diffusion are thus not separate rate-determining steps. Thus, liquid film diffusion and intra-particle diffusion together control the adsorption process by which Cd^{2+} is removed from the aqueous solution by ACC (Oyelude et al., 2017; Tonk et al., 2017).

New scientific results

1. We have improved the adsorption process, an alternative bioremediation method. Novel, recycled, environmentally friendly industrial and household wastes were used as adsorbents for the treatment of wastewater from indicator-, textile dyes and Cd micropollutants.

2. During dye (Indicators: Congo Red (CR), Bromphenol Blue (BPB), Methylene Blue (MB) and Malachite Green (MG); Textile dyes: Remazol Brilliant Violet 5R (RBV-5R), Remazol Brilliant Red F3B (RR) and Remazol Brilliant Blue R (RB)) adsorption with powdered-, calcined eggshell and brewery's yeast, we observed that with the increase of initial dye concentration the adsorption capacity also increased.

3. The composition of the powder eggshell $CaCO_3$ and the calcined eggshell CaO provided a basic feature to the dye solutions, thus the adsorption of CR, MG powder with eggshell, RBV-5R, RR and RB textile dyes with calcined eggshell was not affected by the solution chemistry, and for all dye removals 90% efficiency was achieved.

In the case of MB and BPB dyes, the removal mode typical of anionic and cationic dyes was clearly distinguished, i.e. anionic dyes bind more efficiently in acidic media, whereas cationic dyes bind more efficiently in basic media.

The anionic RR textile dye on the surface of the brewer's yeast achieved maximum efficiency (E=88.5%) in acidic medium (pH=3), while the lowest efficiency was obtained at pH 11, E=46.5%.

4. The increase of adsorbent (powdered and calcined eggshell, brewer's yeast) dosage negatively affected the RBV-5R, RB and RR dye adsorption capacity. For example, qe decreased from 0.59 mg/g to 0.13 mg/g as the yeast mass increased in case of RR removal.

5. Studying powdered, calcined eggshells and eggshells embedded in alginate beads we concluded that calcined eggshell is the most effective, both in removal efficiency, highest quantity in equilibrium and time effectiveness.

6. In our study, the optimal parameters for the most efficient dye removal were (160 µm, 700 rpm):

- CR + powdered eggshell: C_i=10 mg/L, 3 g, pH=8.05±0.2, T=20±2 °C, where E=99.04%
- BPB + powdered eggshell: C_i=30 mg/L, 1.5 g, pH=2±0.2, T=20±2 °C, where E=57.65%
- MB + powdered eggshell: C_i=30 mg/L, 1.5 g, pH=10±0.2, T=20±2 °C, where E=75.10%
- MG + powdered eggshell: C_i=40 mg/L, 1.5 g, pH=2.76±0.2, T=20±2 °C, where E=96.59%
- RBV-5R + powdered eggshell: C_i=20 mg/L, 1.5 g, pH=6.0±0.2, T=20±2 °C, where E=95%

- RBV-5R + calcined eggshell: C_i=20 mg/L, 1.5 g, pH=5±0.2, T=20±2 °C, where E=97%
- RR + calcined eggshell: C_i=60 mg/L, 1.5 g, pH=7±0.2, T=20±2 °C, where E=98.44%
- RB + calcined eggshell: C_i=80 mg/L, 1.5 g, pH=7±0.2, T=20±2 °C, where E=99%
- RR + yeast: C_i=20 mg/L, 1.5 g, pH=3±0.2, T=20±2 °C, where E=88.5%.

7. Results of various microscopic studies, EDS and Raman spectra only the cuticle and membrane layer of chicken eggshell adsorbed the RBV-5R dye.
8. In case yeast morphology study, we saw the spindle and pointed egg-shaped forms, that after the adsorption process disappeared, we observed a cellular morphology difference. EDS results proved that after adsorption with RR dye, the amount of C and S increased in the samples.
9. Our hypothesis proved that ACC, that is mainly consists of kaolinite and illite, is an excellent adsorbent as 99% Cd^{2+} removal efficiency was reached within 190 min.
10. The presence of clay bound Cd^{2+} adsorbate was confirmed by analyzing the elemental contents (EDS) on the surface alongside spectral analysis (FTIR, Raman) and XRD. After adsorption, Wt(%) = 0.2 ± 0.01 Cd^{2+} was detected in the sample.

CONCLUSIONS AND PERSPECTIVES

I. At the opening of my thesis, through a thorough review and presentation of the literature, we demonstrated that the development of an alternative bioremediation water purification method is an essential scientific task. Several methods can be used to remove dyes and cadmium micropollutants, but by studying the general drinking water production process, we have identified adsorption as an established method. To be economical and environmentally friendly, household and industrial waste, porous eggshells (in three forms), the *Saccharomyces cerevisiae* model organism most studied in biosorption research, and clay with proven high adsorption/absorption properties were used as adsorbents.

II. By selecting the adsorption technology - an alternative remediation method - and the possible adsorbents, we fulfilled one of the objectives of this dissertation.

Looking at the effect of the *initial dye concentration*, it is observed that a wide range of adsorbents can be used, with efficiencies of more than 90% even at high concentration values. Similar trend (C_i ↑ => q_{max} ↑) was observed in case of indicator and textile dye removals with powdered and calcined eggshell and yeast adsorbents, however, we could not clarify a specific trend between efficiency and variation of initial concentration.

It was shown that the *pH* of the dye solution significantly affects the adsorption process. In our studies we confirmed our hypothesis, however, for CR and MG dyes we found that pH was only slightly affected, this was attributed to the fact that the addition of eggshell ($CaCO_3$) to the solution imparted a basicity to the solution. To complement our research results, we compared the removal of 16 anionic and cationic dyes from literature data. When designing the adsorption process, it is important to keep in mind the ionic nature of the dye, thus reducing the time required for the optimization study.

The effect of the initial *adsorbent dosage* was investigated for 5 different adsorbent-pollutant pairs between 0.5 and 2.5 g. The conclusion of the literature review and our experiments is that with increasing amounts of adsorbent, the E of dye removal increases and q_e decreases.

The effect of *particle size* was only investigated for powdered eggshell. Considering that our results and the analyzed articles showed that the efficiency values ranged from 8 to 99% with decreasing grain size, particle size is a highly influential factor. Therefore, in future research, if feasible, it is important to increase surface area and porosity by reducing particle size.

The effect of aqueous solution *temperature* between 20 and 40 ^{o}C was investigated. In our experiments, we observed both endothermic and exothermic adsorption processes based on literature data. From a green chemistry point of view, the exothermic process is preferable, since no additional energy input is required for optimal adsorption by heating the system.

III. In the second major part of the thesis, another main objective was achieved. Adsorbents (eggshell, brewer's yeast, Aslavital cosmetic clay) and contaminants were characterised using known and commonly used analytical methods.

IV. A key question in adsorption studies is what happens, what process takes place between the adsorbent and the pollutant. Isotherm, kinetic and diffusion models provide the possibility to determine different adsorption characteristics. From the isothermal models investigated, it is shown that the primary bonds formed are physical in all cases. The second-order kinetic model is characteristic of all adsorption processes.

V. In the present work, the commercial cosmetic clay ACC-Aslavital has been studied morphologically and analytically and has been successfully applied for the removal of Cd^{2+} from water. Our hypothesis proved that ACC is an excellent adsorbent as we achieved 99% Cd^{2+} removal efficiency in 190 min. Isothermal results showed that physical bonds are formed during favorable adsorption. Structural studies showed that the clay is mainly composed of kaolinite and illite in the most significant amounts. The presence of Cd^{2+} on the surface of ACC was confirmed by spectral analysis (FTIR, Raman) and XRD as well as elemental analysis (EDX), with Wt(%) = 0.2 ± 0.01 Cd^{2+} detected in the sample.

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