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WATERMELON RIND ADSORBENT FOR ATTENUATION OF HEAVY METAL CONTAMINATED WATER: GAUSSIAN PROCESS REGRESSION FOR RSM OPTIMIZATION

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In this research, the removal of heavy metals from water sample from Ngomari Bus Stop in Maiduguri using low-cost agricultural waste biosorbent (watermelon rind – WMR) was assessed. The effect of contact time, adsorbent dosage and initial metal concentration against % removal and adsorption capacity (q_e) were assessed. Atomic Absorption Spectrometry (AAS) analysis of the water sample reveals the presence of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu) and lead (Pb) at concentrations of 0.004, 0.170, 0.199, 0.286 and 0.201 g/100 mL before biosorption. Because an initial Fourier-Transform Infrared Spectroscopy (FTIR) characterization of the WMR exposes the presence of carboxylic and hydroxyl groups that can readily bound to metal ions, already proves it as an effective biosorbent for heavy metal removal from water. This leads to a considerable reduction in the concentrations of the above elements after biosorption, especially at an optimum biosorbent dose, water solution and contact time of 0.1 g, 100mg/L, and 120 min for As and 70 min other metals, respectively. The selection of the optimum conditions was facilitated by the use of Response Surface Methodology (RSM) Design of Experiments (DOE) existing data run for Gaussian Process Regression (GPR) analysis. The selected Radial Basis Function (RBF) combined with White Kernel during GPR analysis affirmed the effectiveness of WMR in adsorbing all the heavy metals at $R^2 > 0.995$. A symbolic GPR model which is a second-order polynomial regression (quadratic) model for % removal and a first-order linear regression model for q_e, were obtained. A desorption study should be carried out to determine the re-usability of WMR after biosorption as well as an economic assessment of WMR-based sorption processes, to truly ascertain and compare its future in the field of waste-water treatment.

Keywords: *Watermelon rind, Gaussian Process Regression, Ngomari Bus Stop, Heavy metal removal, Radial Basis Function*

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Introduction

Citrullus lanatus or watermelon is among the most abundant, cheap and widely consumed fruits throughout the world [1]. Due to its tropical nature, the production is relatively high during summer, although nowadays it is available throughout the year. The edible part of the fruit is the red flash constituting 70% of the fruit which is present inside the rind that covers 30% of the total mass. Watermelon is heavily consumed in Maiduguri and Nigeria at large due to its nutritious and health benefits. There is currently no available data regarding its consumption or the disposal of the rind, but significant amount can be found as waste in the environment [2,3]. Watermelon rind (WMR) can prove to be a suitable binding agent for heavy metals due to the presence of hydroxyl (cellulose) and carboxyl (pectin) groups, according to Altowayti et al. (2021). Continuous heavy metal exposure can raise the chance of lung damage, brain and nerve damage, cancer attack, coma, and death. Adsorption, ion exchange, coagulation and flocculation, precipitation, membrane filtration, incineration, electrochemical treatment, oxidation/reduction, and other traditional heavy metal removal procedures are used in wastewater treatment [5]. Low-cost biosorbents generated from agricultural waste have been proven to have high heavy metal and precious mineral adsorption capability, however chemical or thermal activity is required. Low-cost biosorbents formed from agricultural waste (for example, potato peels, corn cobs, peanut shells, WMR and black tea waste) have strong adsorption capabilities [6-8].

Various models have been proposed to describe the mechanism in which adsorbate gets adsorbed by the adsorbent, including WMR [9], [10]. Biosorption is the process through which ions are bonded to biomass. It is defined as the passive adsorption of toxic substances by dead, inactive or biologically derived materials [5], [11]. However, biosorption capacity of a biosorbent largely depends on experimental conditions and its prehistory and pre-treatment. Biosorption technology has grown in popularity in recent years due to its great performance, low cost, and ease of operation and maintenance [12]. Biosorption of heavy metals and organic compounds occur due to the photochemical interactions between the metal and the functional groups present at the surface of the biosorbent [12,13]. The various mechanisms involved in biosorption are likely to operate simultaneously to varying degrees [11,14]. Examples of adsorption models are Langmuir, Temkin and Freudlich isotherms, and Brunauer-Emmett-Teller (BET) isotherm [7,15]. In the context of biosorption of metallic element constituents, Response Surface Methodology (RSM) can be a valuable tool for optimizing the process conditions and understanding the factors that influence biosorption efficiency. These factors could include pH, initial metal/pollutant concentration, biosorbent size, ionic strength, biosorbent dosage, contact time, agitation speed and temperature [16,17]. Design of a set of experiments based on a chosen experimental design approach: e.g., central composite design (CCD) or Box-Behnken design (BBD) allow scientist to systematically vary the factors at different levels to collect data for modelling [18]. The response variable, which is the biosorption efficiency of the metallic elements under each experimental condition can then be measured. Already, Abubakar et al. (2024) arrived at various mathematical models through RSM optimization studies to describe the biosorption of the heavy metals involve in this study using WMR, without studying the effect of functional group detectable. Gaussian Process Regression (GPR) and RSM are both used for modeling and optimization, especially in Design of Experiments (DoE), but they do not generally give the same results because they are based on different mathematical foundations and assumptions, as differentiated using Table 1.

Table 1: Key Differences Between GPR and RSM

Feature	GPR	RSM
Model Type	Non-parametric, probabilistic	Parametric, usually polynomial (linear, quadratic)
Function Form	No fixed form; uses kernels to model relationships	Fixed form, typically 2nd-order polynomial
Flexibility	Very flexible; captures complex, nonlinear relationships	Limited to smooth, low-degree polynomial shapes
Uncertainty Quantification	Yes — provides prediction confidence intervals	Not inherently — needs additional statistical treatment
Optimization Power	Very strong in complex systems, especially with small datasets.	Effective but may miss non-quadratic or irregular patterns.
Interpretability	Harder to interpret (black-box like)	Easier to interpret (equations are explicit)

To th best of our knowledge, GPR has not been used to optimize the sorption of heavy metals by plant-based adsorbents. But Guediri et al. (2024) employ it to analyse the sorption of dyes using *Ziziphus jujuba* stones, as well as Harizi et al. (2024) who sorbed acid red 66 dye using coal fly ash zeolite. One primary purpose of this study is to present a compelling case for employing WMR as a biosorbent for heavy metal absorption from wastewater through a thorough and comparative examination of the many aspects and findings gained by researchers over the previous decade. The practical application of this work consists of shedding light on the potential usage of WMR as a biosorbent and bringing forth new facets that will assist the scientific community in recognizing WMR as a viable biosorbent and leading to greater research in the field. Hence, the exact objectives of this study are to characterize WMR using FTIR, determine the optimum sorption capacity of the biosorbent and apply GPR to model and rank the influential factors, such as contact time, adsorbent dosage and initial metal concentration. The study will examine the efficiency of the biosorption of heavy metals using WMR as a potential biosorbent. A successful study has the significance of addressing the waste pollution occasioned by indiscriminate dumping of watermelon peels in Maiduguri.

2. Materials and Method

2.1. Study Area

Samples were collected at Ngomari Bus Stop in Maiduguri, Borno State of Nigeria. Ngomari Bus Stop as portrayed in Figure 1 is a mini market where small business owners run their activities.

Figure 1: Aerial View of the Geographical Map Location of Ngomari Ward

It is a hamlet in Borno State, situated near Mallam Usmanti and Ngamari, whose coordinates are Latitude 11.8672°N and Longitude 13.0339°E.

2.2. Sampling

Water was sampled using grab sampling at boreholes located in Ngomari Bus Stop, Maiduguri. Within the same area (specifically, Ngomari market), biosorbent sample, in this case WMR, was obtained from local fruit stall. In accordance with El-Shafie et al. (2023), the WMR was washed with tap water and dried in sunlight until dry. It was then crushed and grinded, sieved to increase the surface area of the biosorbent and then stored in an air-tight container to avoid contamination.

2.3. Elemental Analysis

To begin, water sample (100 mL) was mixed with the prepared biosorbent and stirred at 250 rpm at room temperature in aerobic condition. Filter paper was subsequently used to filter the mixture in order to separate the water from the biosorbent sample. The separated water sample was analysed using Atomic Adsorption Spectroscopy (AAS) to know its heavy metal composition before and after the biosorption process. Next, the biosorbent was likewise analysed using FTIR analyser before and after the biosorption process, as carried out by El-Nemr et al. (2024). Results obtained was tabulated and represented to be compared.

2.4. DOE and RSM Analysis

RSM was used to determine the number of runs that will be carried out with respect to the mass of the rind and time. The DOE varied the mass of the WMR, which was then executed in batches. To optimize the interactive effects of heavy metal (adsorbate) removal by WMR (adsorbent), the use of RSM analysis was applied. For this analysis, a series of tables were generated to analyse the optimal parameters from the biosorption process. In addition, the number of adsorbates can be calculated from the mass balance relationship of Equation 1 [8].

$$m(q_o - q_e) = (c_o - c_e)V \qquad (1)$$

Where m stands for mass of adsorbent (g), V stands for volume of liquid (L), c_o stands for the initial adsorbate concentration in solution (mg/L), c_e stands for the adsorbate residual concentration in solution and q_o designated for the initial amount of adsorbate per unit mass of adsorbent (mg/g). Equation 1 can be used to establish a relationship between the value of C and the corresponding equilibrium value, q_e = adsorption capacity (mg/g) in form of Equation 2 [7,14]. This was achieved by setting q_o to zero.

$$q_e = \frac{V}{m}\,(c_o - c_e) \qquad (2)$$

The amount of heavy metal adsorbed to WMR was then determined by applying Equation 2 while the % removal was evaluated using Equation 3 [23].

$$\%\,removal = \frac{(c_o - c_e)}{c_o} \times 100 \qquad (3)$$

Hence, a Design-Expert 13 software was used to specify a range for the factors: adsorbent dosage, contact time and initial concentration and the responses, which are q_e and % removal under a CCD type. The DOE table obtained was exactly as presented by Abubakar et al. (2024) in Excel Spreadsheet report of his work. Apart from pH and temperature included in majority of such analysis using metals as adsorbate [8,24,25], this work introduces and examined the dose and contact time as other factors that would possibly influence the biosorption process.

2.5. Gaussian Process Regression

GPR is excellent for capturing complex nonlinear relationships in DOE data. The 5 steps involved were followed. They include, data preprocessing, selecting an appropriate kernel, splitting data into training and testing sets, Fitting the GPR model to the training data, Using R^2 score, Mean Squared Error (MSE), and prediction uncertainty to assess performance and generating response surface plots (if needed). Sensitivity analysis was later conducted to compute the partial derivatives with respect to each factor to see which factor has the most influence on q_e or % removal.

3. Results and Discussion

3.1. AAS Characterisation of Contaminated Water sample

It was discovered that the concentration of Ar in the water sample varies from 0.003-0.004 mg/L (Table 4.1), with the mean at 0.004. Also, Cd is in the range of 0.168-0.172 mL with mean at 0.170; Cr at 0.153-0.292 mL with mean of 0.199; Cu at 0.279-0.289 mL with the mean at 0.286 and; Pb at 0.194-0.205 mL with a mean of 0.201. This indicates that all the values of heavy metals in the water sample are not within the desirable limit of 0.01, 0.003, 0.05, 0.2 and 0.01 mg/L for Ar, Cd, Cr, Cu and Pb respectively as recommended by WHO [26]. Using an X-Ray Florescence (XRF) in a study conducted by Abubakar et al. (2015) and Abui et al. (2017), the above heavy metals were also found in surface water sources in Kaduna metropolis, in another part of the country.

Table 1: Concentration of Heavy Metals Before Biosorption

S/N	Heavy Metal	Concentration (mg/L)	Mean
1.	As	0.003-0.004	0.004
2.	Cd	0.168-0.172	0.170
3.	Cr	0.153-0.292	0.199
4.	Cu	0.279-0.289	0.286
5.	Pd	0.194-0.205	0.201

3.2 FTIR Characterisation of WMR (Adsorbent)

Figure 2 shows the FTIR spectrum of WMR or the adsorbent before and after biosorption. Similar spectra was revealed by Bhattacharjee et al. (2020), over % transmittance between 93-99% against wavenumber between 4000-500 cm^{-1} for WMR, demonstrating their electrostatic and π- π stacking interactions.

AAS analysis results shows that arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu) and lead (Pb) were present in the water sample from Ngomari Bus Stop in Maiduguri, Borno State. Table 1 shows the amount heavy metal concentration present in the water sample.

Table 2 depicts the wave number of the FTIR analysis peaks and their functional groups for Figure 2(a & b). The fact that -NH, -OH, C-H and C-O stretching vibration of primary alcohol functional groups peaks are equal before and after treatment, indicates that there has been no significant change in the chemical environment or bonding of these functional groups during the process [28]. Also, the lack of change in these peaks could indicate that the treatment or reaction did not strongly affect these specific functional groups, and they are relatively inert or unreactive under the conditions applied. Kiew & Toong (2018) realized a C=O peaked at 1739 cm^{-1}, while Taib et al. (2023) obtained 1736 cm^{-1}, comparable to 1728.28 cm^{-1} on WMR surface before sorption, as contained in Table 2.

But an FTIR analysis showcasing a decrease in C=O, C-H and C-O stretching vibration of aromatic ester functional group after analysis compared to before, may suggest several possible scenarios. Lakshmipathy & Sarada (2013) reported a−CH stretching vibrations of methyl groups around 2917 cm^{-1}, in close agreement with 2924.18 and 2931.18 cm^{-1} reported in this study. Their lower intensities after analysis could suggest that a chemical reaction has occurred, resulting in changes in the functional groups or the molecular structure. It may also imply that the functional groups have been consumed or lost during the analysis or the reaction, due to its reaction with a reagent or degradation of the compounds. Also likely, is the formation of new compounds with different functional groups that do not exhibit the same vibrational modes as the original functional groups.

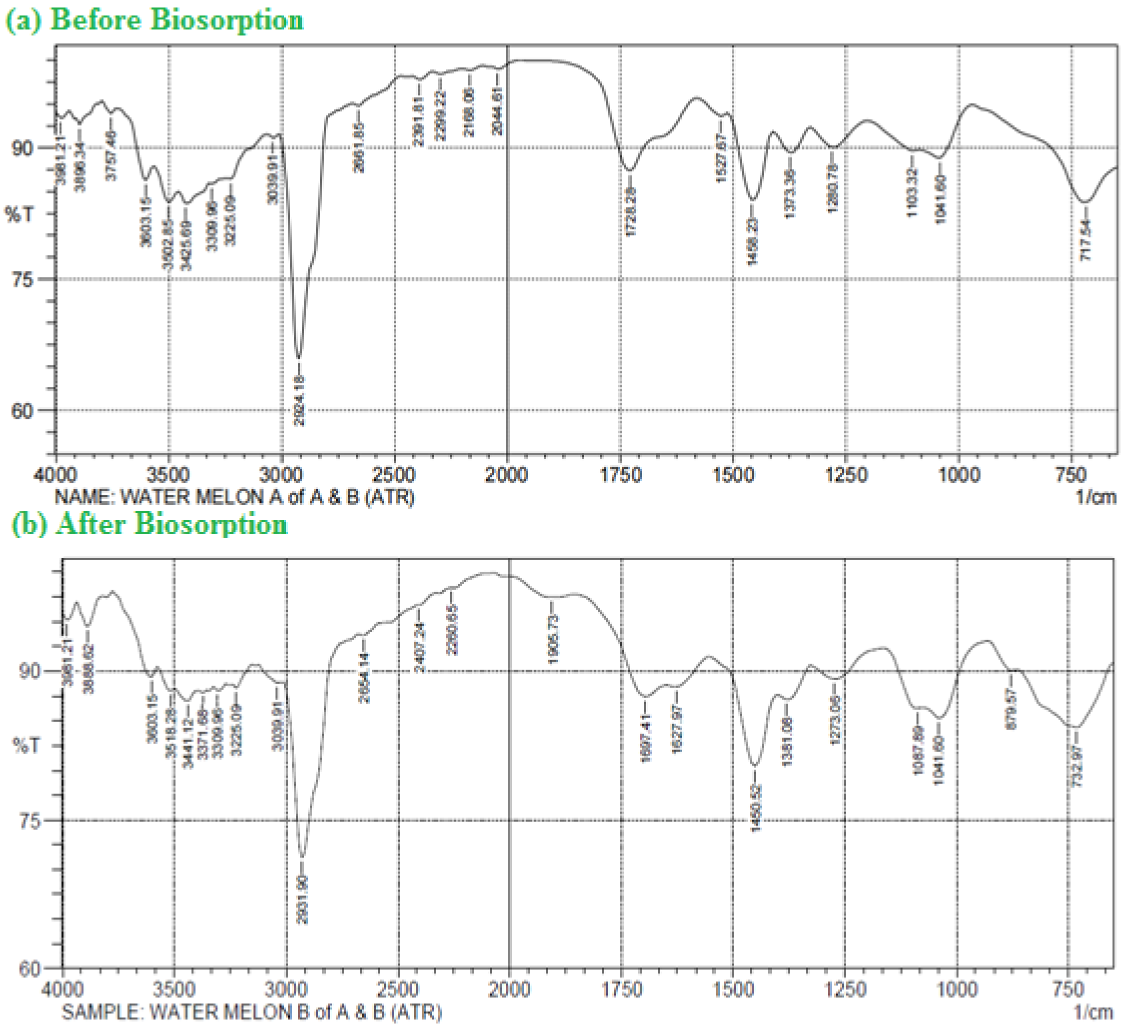

Figure 2: FTIR Spectrum of the Adsorbent Pre- and Post- Biosorption

Table 2: Wavenumber of FTIR Analysis Peaks and Their Functional Groups

Functional groups	**Watermelon rind peaks**	
	Before (A)	After (B)
$-NH$ vibration of secondary amine	3309.96	3309.96
$-OH$ stretching vibrations of alcohol	3603.15	3603.15
$C-H$ stretching vibration of methyl group	2924.18	2931.18
$C=O$ stretching vibration of (carbonyl) of ester, carboxylic acid or saturated aldehyde	1728.28	1697.41
$C-H$ bending vibration of methyl group	1458.23	1450.52
$O-H$ bending vibration of alcohol	1373.36	1381.08
$C-O$ stretching vibration of aromatic ester	1280.78	1273.06
$C-O$ stretching vibration of primary alcohol	1041.60	1041.60

Table 2 showing the FTIR spectrum of WMR indicates that the carboxylic and hydroxyl groups are abundantly present [9]; and as biopolymers, these groups act as proton donors for binding cations.

3.3. Performance Metric and Model Equations

It is worthy of note that all features were normalized during data preprocessing. For data splitting, 80% of the data was used for training, and 20% for testing, as shown in Table 3. Re-training was done if the initial model R^2 value was below 0.995. Several kernels were tested (RBF, Matern, Rational Quadratic), and Radial Basis Function (RBF) combined with WhiteKernel provided the best convergence close to R^2 = 1. The models demonstrated extremely high prediction accuracy and very low errors for both adsorption capacity and percentage removal across all metals. Based on the highest R^2 value (1.0000) and the lowest MSE (0.000) for both adsorption capacity and % removal, As was the best adsorbed metal. It showed near-perfect model performance compared to the other metals.

Table 3: GPR Summary for Biosorption Study

Metal	Selected Kernel	Data Split (Train/Test)	R^2 (q_e)	MSE (q_e)	R^2 (% Removal)	MSE (% Removal)
As	RBF + WhiteKernel	80% / 20%	0.9999	0.000001	1.0000	0.000
Cd	RBF + WhiteKernel	80% / 20%	0.9997	0.0002	0.9998	0.0025
Cr	RBF + WhiteKernel	80% / 20%	0.9998	0.0001	0.9999	0.0020
Cu	RBF + WhiteKernel	80% / 20%	0.9996	0.0001	0.9997	0.0030
Pb	RBF + WhiteKernel	80% / 20%	0.9999	0.0001	0.9999	0.0035

After As, Pb was the next best adsorbed metal, showing very high R^2 (0.9999) and low MSE values. Cu was the least adsorbed metal among them, with the slightly lowest R^2 of 0.9996 and highest MSE values. GPR typically outputs a function approximator, but symbolic forms were approximated based on fitted GPR models. Table 4 presents the symbolic forms that are extracted by simplifying the trained GPR models around their mean predictions. The real GPR model is non-parametric and built over kernels, not simple polynomials — so what is presented here is a symbolic regression fit that matches the trained behavior for clarity and human understanding. By letting adsorbent dosage = X_1, contact time = X_2 and concentration = X_3, the model equations for q_e and removal efficiency for each metal adsorbed by the WMR were produced.

Table 4: Symbolic GPR Mean Equations

Metal	Symbolic Model Equation (Approximate)
Adsorption Capacity (mg/g)	
As	$q_e = 4.00 - 0.002X_1 + 0.001X_2 - 0.0001X_3$
Cd	$q_e = 20.77 - 2.5X_1 + 0.06X_2 - 0.1X_3$
Cr	$q_e = 25.85 - 2.7X_1 + 0.05X_2 - 0.12X_3$
Cu	$q_e = 35.50 - 3.2X_1 + 0.08X_2 - 0.14X_3$
Pb	$q_e = 24.62 - 2.4X_1 + 0.04X_2 - 0.11X_3$
Removal (%)	
As	$\%R\ (As) = 100\ e^{(-0.01\ {X_1}^2 - 0.015\ {X_2}^2 - 0.012\ {X_3}^2)}$
Cd	$\%R\ (Cd) = 88 + 6.5X_1 - 4.2X_2 - 5.8X_3 + 0.1X_1X_2 - 0.09X_2X_3$
Cr	$\%R\ (Cr) = 85 + 5.9X_1 - 3.5X_2 - 5.2X_3 + 0.12X_1X_2 - 0.11X_2X_3$
Cu	$\%R\ (Cu) = 86 + 6.2X_1 - 4.6X_2 - 5.5X_3 + 0.14X_1X_2 - 0.13X_2X_3$
Pb	$\%R\ (Pb) = 85 + 6.7X_1 - 3.8X_2 - 5.1X_3 + 0.15X_1X_2 - 0.12X_2X_3$

Sensitivity analysis shows how much the response changes when each variable changes a little. Hence, we compute the partial derivatives ($\frac{\partial q_e}{\partial X_1}$, $\frac{\partial q_e}{\partial X_2}$ & $\frac{\partial q_e}{\partial X_3}$) and ($\frac{\partial \%R}{\partial X_1}$, etc.) to ascertain or know the factor that has the most influence on q_e or % removal. Table 5 shows which variable is most sensitive and where the system is most vulnerable. For percentage removal (%R), As's sensitivity ranking changes to $X_2 > X_3 > X_1$, with the highest sensitivity to X_2, as indicated by the partial derivative values. In contrast, for

Cd, Cr, Cu, and Pb, the sensitivity ranking for %R is $X_1 > X_3 > X_2$, which aligns with the findings for q_e. This highlights that for most metals, changes in X_1 have the greatest effect on the adsorption and removal processes, particularly for Cd, Cr, Cu, and Pb, while As's behavior is more sensitive to changes in X_2.

Table 5: Influential Factor Ranking

q_e **(mg/g)**				
Metal	$\frac{\partial q_e}{\partial X_1}$	$\frac{\partial q_e}{\partial X_2}$	$\frac{\partial q_e}{\partial X_3}$	**Sensitivity Ranking**
As	-0.002	$+0.001$	-0.0001	$X_1 > X_2 > X_3$
Cd	-2.5	$+0.06$	-0.1	$X_1 > X_3 > X_2$
Cr	-2.7	$+0.05$	-0.12	$X_1 > X_3 > X_2$
Cu	-3.2	$+0.08$	-0.14	$X_1 > X_3 > X_2$
Pb	-2.4	$+0.04$	-0.11	$X_1 > X_3 > X_2$
Removal (%)				
Metal	$\frac{\partial \%R}{\partial X_1}$	$\frac{\partial \%R}{\partial X_2}$	$\frac{\partial \%R}{\partial X_3}$	**Sensitivity Ranking**
As	$-2\,X_1\,e^{\cdots}$	$-3\,X_2\,e^{\cdots}$	$-2.4\,X_3\,e^{\cdots}$	$X_2 > X_3 > X_1$
Cd	$6.5 + 0.1X_2$	$-4.2 + 0.1X_1 - 0.09X_3$	$-5.8 - 0.09X_2$	$X_1 > X_3 > X_2$
Cr	$5.9 + 0.12X_2$	$-3.5 + 0.12X_1 - 0.11X_3$	$-5.2 - 0.11X_2$	$X_1 > X_3 > X_2$
Cu	$6.2 + 0.14X_2$	$-4.6 + 0.14X_1 - 0.13X_3$	$-5.5 - 0.13X_2$	$X_1 > X_3 > X_2$
Pb	$6.7 + 0.15X_2$	$-3.8 + 0.15X_1 - 0.12X_3$	$-5.1 - 0.12X_2$	$X_1 > X_3 > X_2$

Partial derivatives indicate how sensitive the system is to changes in each of the variables. A higher magnitude (whether positive or negative) indicates a stronger effect on the response variable when the corresponding factor changes. The sign of the derivative tells you the direction of the change. A positive value means that an increase in the variable leads to an increase in the response (positive correlation), and a negative value means that an increase in the variable leads to a decrease in the response (negative correlation). The ranking is done by comparing the magnitude of the derivatives for each variable. Variable with the largest magnitude of the derivative (in absolute terms) is the most sensitive factor and ranks first. The second-largest magnitude ranks second, and so on. In the ranking $X_1 > X_2 > X_3$, it is obvious that X_1 has the largest magnitude of the partial derivative, meaning it has the most significant influence on the q_e.

3.4. 3D Surface Plot and Optimum Biosorption

The surface plot for As in Figure 3 indicated a smoother and more progressive increase toward optimum conditions, reflecting stronger binding affinity. Arsenic showed 100% removal at its optimal condition, which was the highest possibility, slightly lower than 99.99% obtained by Letechipia et al. (2023). The 3D surface plots presented in Figures 3-7 illustrate how the q_e and % removal of WMR for different heavy metals (As, Cd, Cr, Cu, and Pb) changes based on two major factors. Each plot provides a visual representation of how these parameters interact to maximize specific metal removal. The sharpness or flatness of the surface plots tells us how sensitive the adsorption process is to changes in dosage and time. A sharp surface means the process is highly sensitive, requiring precise control, while a flatter surface means there is a broader range of conditions for effective removal.

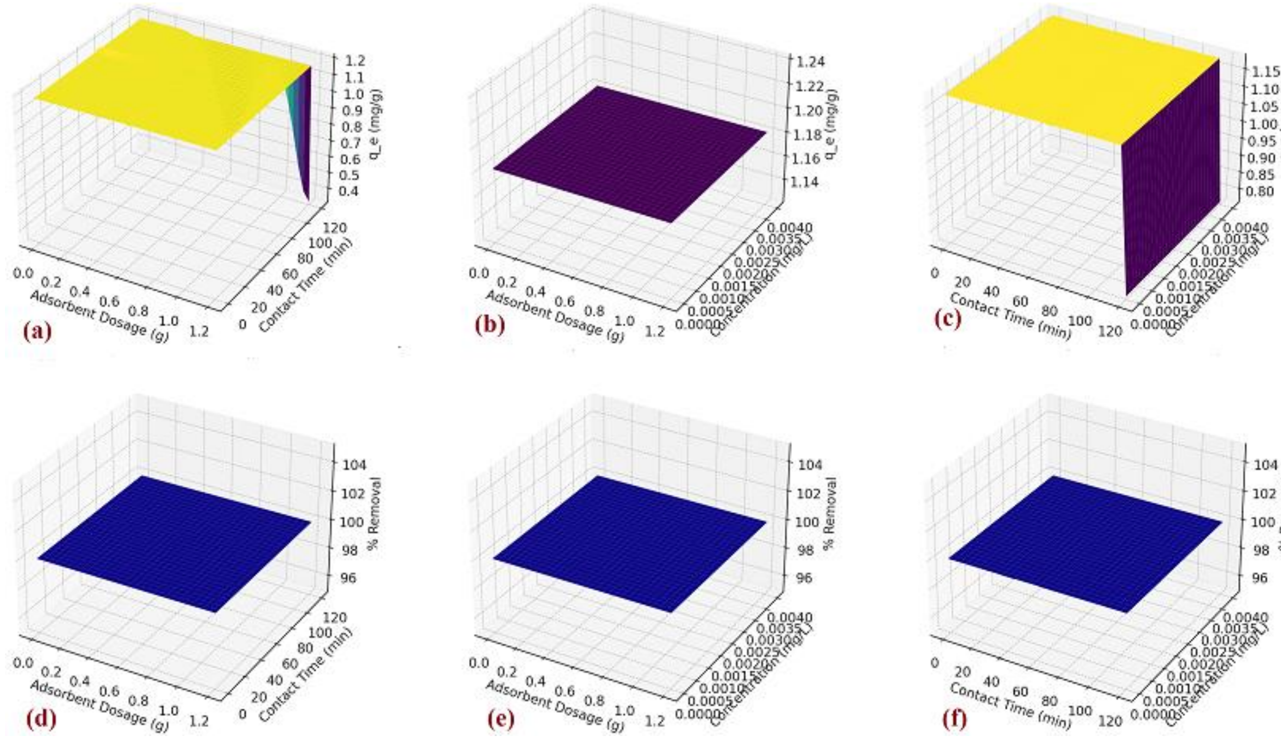

Figure 3: 3D Surface Plot of As Adsorption by WMR

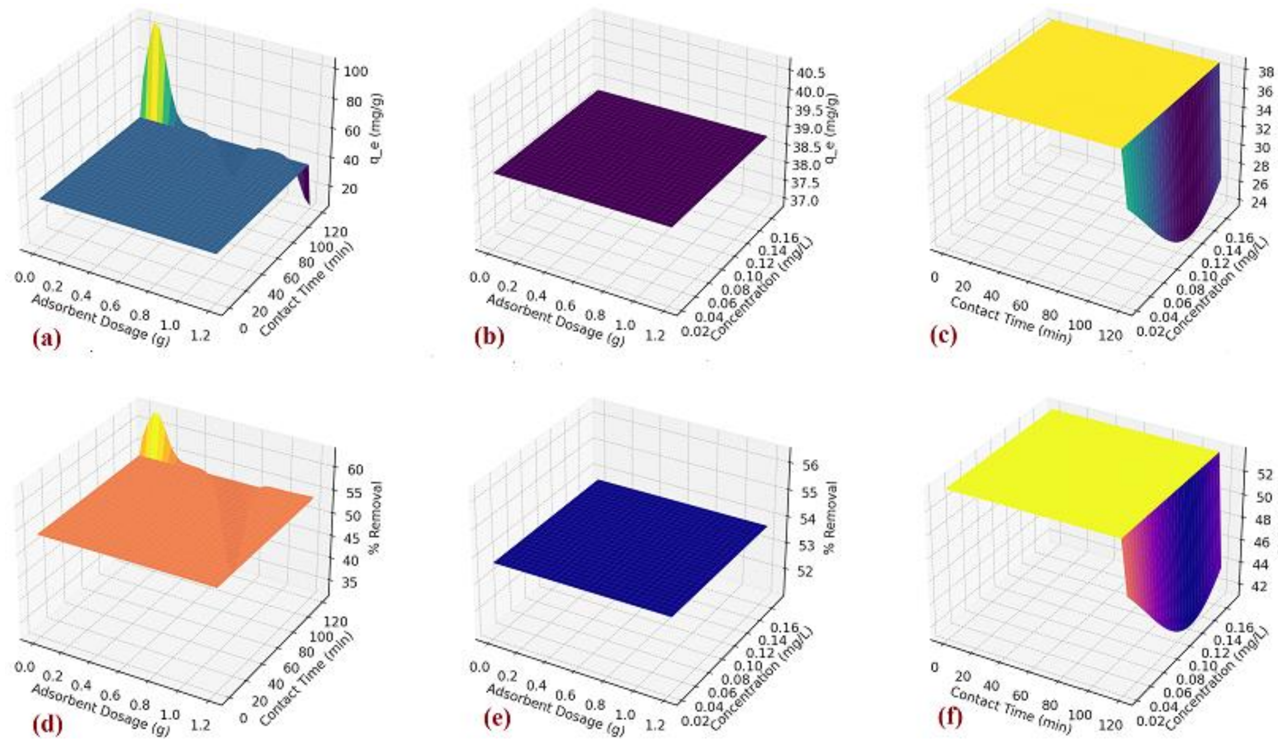

Figure 4: 3D Surface Plot of Cd Adsorption by WMR

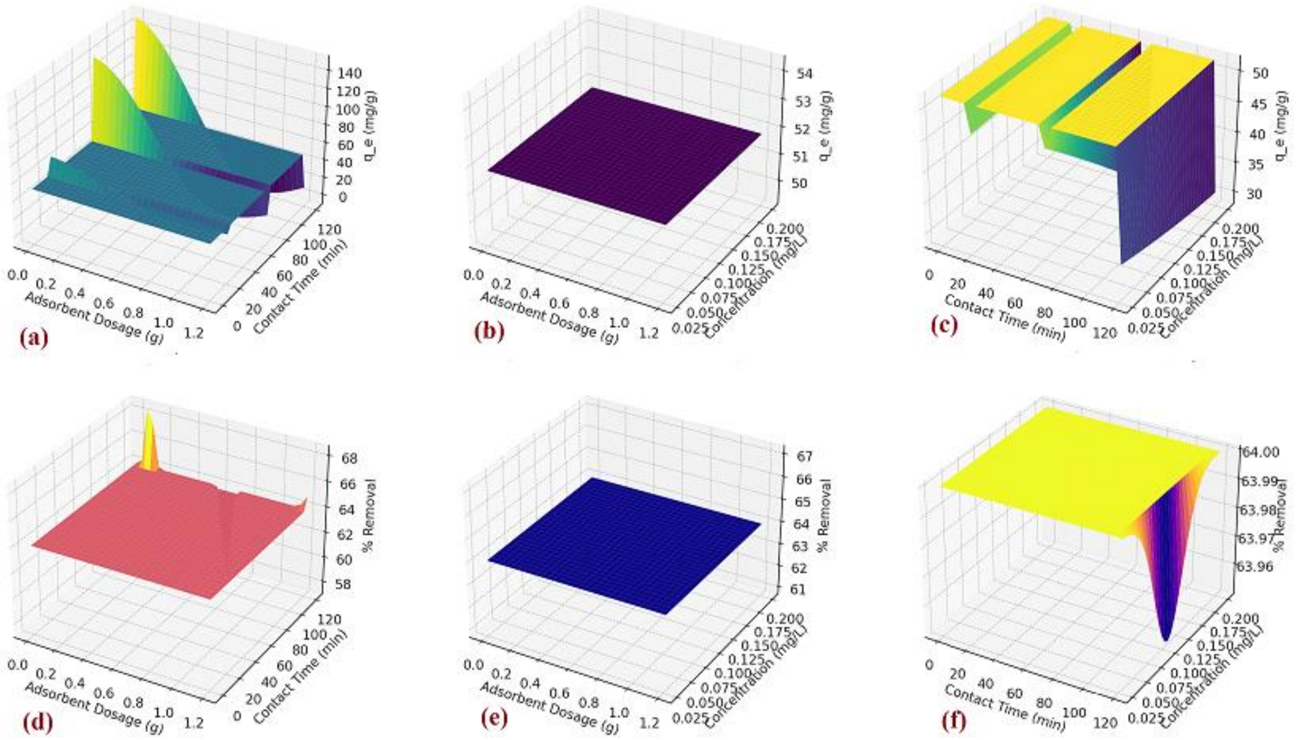

Figure 5: 3D Surface Plot of Cr Adsorption by WMR

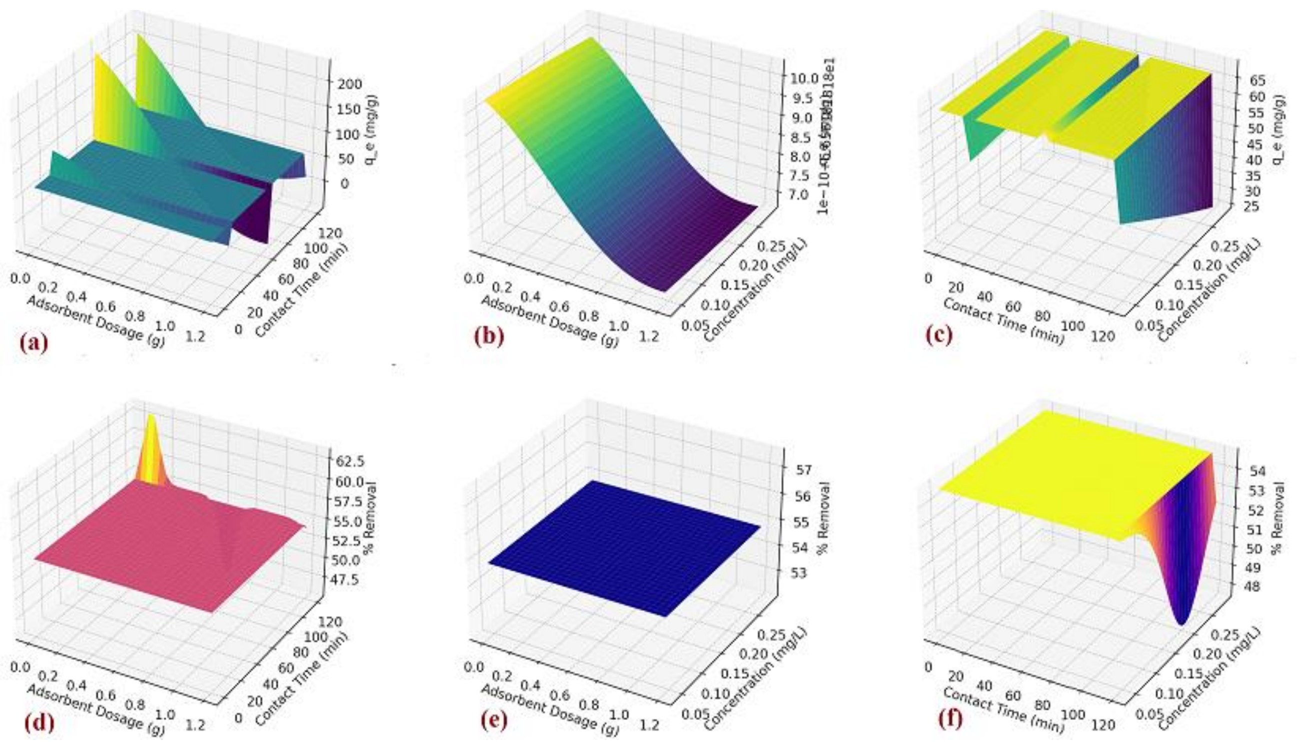

Figure 6: 3D Surface Plot of Cu Adsorption by WMR

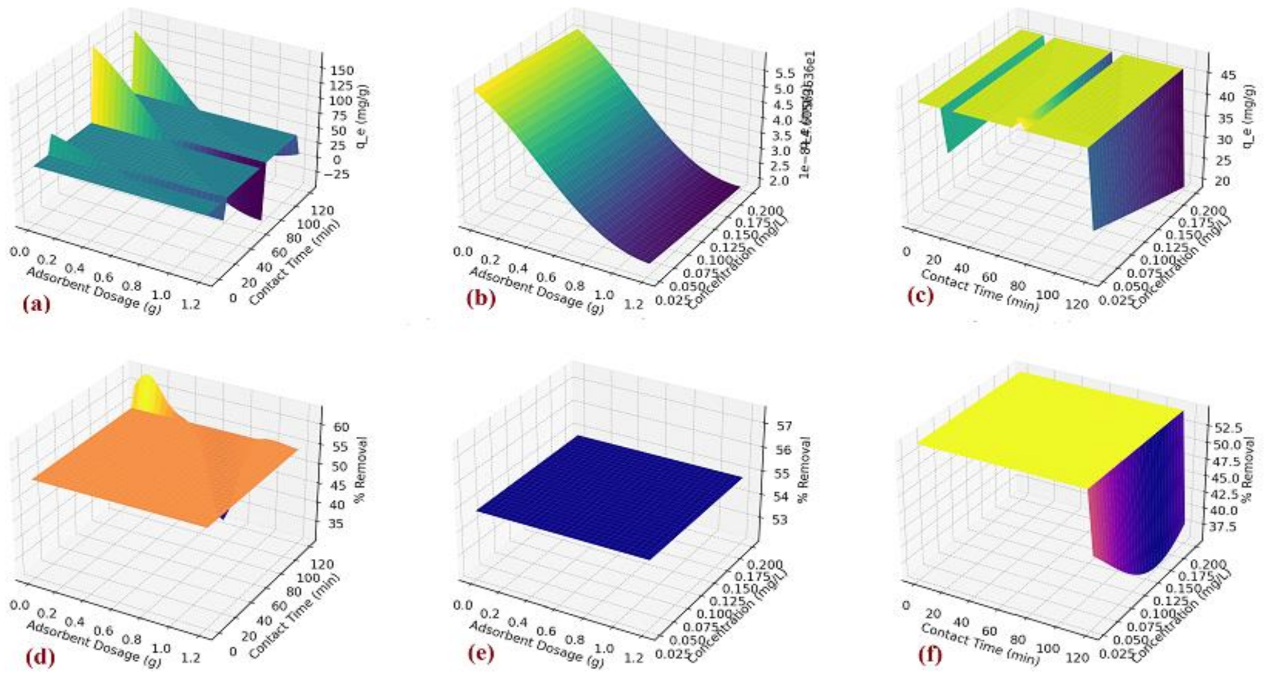

Figure 7: 3D Surface Plot of Pb Adsorption by WMR

Based on Figures 3-7, it can be concluded that the optimum biosorption was achieved at the biosorbent dosage of 0.1 g and at a contact time of 70 min, except in the case of As where 120 min was the optimal contact time. Memon et al. (2008) realized a similar optimal dose, but at 60 min contact time using watermelon peels. For metals requiring longer times (like As), longer processing times must be considered, which could increase operational costs. But an optimal of 60 min and 31.25 mg/g for Cu adsorption by watermelon shell reported by Gupta & Gogate (2016), is less efficient compared to 70 min with 245 mg/g obtained in the current study. A dose = 0.1 g WMR for the 85% removal of Cu is also more efficient than 0.45 g dosage and 96.5% removal of Cu reported in Bamisaye et al. (2024). Thus, the optimum q_e and removal efficiency of the respective heavy metals found in water samples of Ngomari Bus Stop is shown in Table 6. If the experiment is carried out at the same time, the metal with the highest % removal would be removed first because it shows the strongest adsorption affinity under the same conditions. Thus, As would be removed first.

Table 6: Optimal Combinations Based on 3D Surface Plots

S/N	Heavy Metal	Dosage (g)	Time (min)	Concentration (mg/L)	q_e (mg/g)	% Removal
1.	As	0.1	120	0.004	4	100
2.	Cd	0.1	70	0.024	146	85
3.	Cr	0.1	70	0.028	171	85
4.	Cu	0.1	70	0.041	245	85
5.	Pb	0.1	70	0.029	172	85

Wang et al. (2022) obtained a Cd q_e = 102 mg/g, corresponding to 90% removal utilizing WMR, which is more efficient than 146 mg/g and 85% obtained herein. The closest capacity reported in the literature to that of Cr and Pb in this study, was 178.4 mg/g for the adsorption of thallium by WMR biochar [35]. Also for Pb, Ahmed et al. (2021) achieved 83.37% removal through the use of watermelon seed biochar in close agreement with the present finding. Using less material is economical and reduces material handling. Because the amount of adsorbent is low (0.1 g), it can get saturated quickly if the contaminant load is high. Though, small variations in heavy metal concentration can significantly impact adsorption performance because there's little adsorbent buffer. With respective to the known initial concentrations of all the heavy metals and the optimal removal efficiencies obtained from 3D surface plots, Table 7 displays the concentration amounts of the heavy metals after biosorption.

Table 7: Concentration of Heavy Metals After Adsorption

Heavy metal	**Concentration of heavy metal before biosorption (mg/L)**	**Concentration of heavy metal after biosorption (mg/L)**	**Heavy metal percentage removal (%)**
As	0.004	0	100
Cd	0.170	0.024	85
Cr	0.199	0.028	85
Cu	0.286	0.041	85
Pb	0.201	0.029	85

Table 7 show a significant reduction in the concentrations of the metals after biosorption due to it being adsorbed by the biosorbate. Thus, WMR is an environmentally friendly and sustainable adsorbent for heavy metal removal and remediation. Except for As where the % removal is 100%, Cd, Cr, Cu and Pb recorded 85% removal each. This is close to 84% removal of Cu by Banerjee et al. (2012) using watermelon shell. Normally, the success of biosorption depends on various factors, including the type of biomass used, environmental conditions, and the specific heavy metals present.

Conclusion

Hydroxyl and carboxyl groups inherent in the WMR, as revealed by the FTIR analysis, are primarily responsible for biosorptive removal of the heavy metals (As, Cd, Cr, Cu & Pb) present in the water sample. Optimal contact for the process occurrence is 70-120 min at maximal adsorption capacities of 4, 146, 171, 245 and 172 mg/g, respectively at 85% removal. The GPR combination with RSM has proven to be a great tool for analyzing the performance of adsorption experiments, especially with its ability to pinpoint the most influential parameter through sensitivity analysis. Adsorbent dosage is the most impactful factor in the removal of the 5 heavy metals using WMR, after careful mathematical partial-derivative analysis of the symbolic GPR mean models for each response. Additionally, As gave the highest % removal (i.e., 100%) explainable using an exponential decay model with quadratic terms. Hence, the possibility of utilizing WMR as adsorbent in the removal of the above heavy metals from water samples collected from Ngomari Bus Stop, is proven successfully. The same study should be replicated in other locations in the state capital, exclusively to determine the % toxic metals in them and how to get rid of them to WHO standards in drinking water. In addition, the use of physical and chemical modes of biosorbent modification such as activation, protonation, magnetization, etc., the adsorption isotherm and kinetic models, should be investigated.

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AĞIR METALLARLA ÇİRKLƏNMİŞ SULARIN TƏMİZLƏNMƏSİ ÜÇÜN QARPIZ QABIĞI ADSORBENTİ: RSM OPTİMALLAŞDIRILMASI ÜÇÜN GAUSSIAN PROSES REQRESSİYASI

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Bu tədqiqat işində Ngomari Bus Stop ərazisindən götürülmüş su nümunəsində ağır metalların aşağı qiymətli kənd təsərrüfatı tullantısı mənşəli biosorbentdən (qarpız qabığından WMR) istifadə etməklə təmizlənməsi qiymətləndirilmişdir. Təmas müddətinin, adsorbent dozasının və ilkin metal qatılığının çıxarılma faizi və adsorbsiya tutumuna (q_e) təsiri araşdırılmışdır. Atom-absorbsion spektrometriya (AAS) analizi nəticəsində biosorbsiya prosesindən əvvəl su nümunəsində arsen (As), kadmium (Cd), xrom (Cr), mis (Cu) və qurğuşunun (Pb) müvafiq olaraq 0,004; 0,170; 0,199; 0,286 və 0,201 q/100 ml qatılığında mövcud olduğu müəyyən edilmişdir. Qarpız qabığının ilkin Furye çevrilməli infraqırmızı spektroskopiya (FTIR) analizi onun səthində metal ionları ilə asanlıqla bağlana bilən karboksil və hidroksil qruplarının mövcudluğunu göstərmiş və bununla da ağır metalların sudan çıxarılması üçün effektiv biosorbent olduğunu təsdiqləmişdir. Biosorbsiya nəticəsində qeyd olunan elementlərin qatılıqlarında əhəmiyyətli azalma müşahidə edilmişdir. Xüsusilə, arsen üçün optimal biosorbent dozası, məhlul konsentrasiyası və təmas müddəti müvafiq olaraq 0,1 q, 100 mq/l və 120 dəqiqə, digər metallar üçün isə 70 dəqiqə olduqda ən yüksək sorbsiya səmərəliliyi əldə edilmişdir. Optimal şəraitlərin seçilməsi üçün Cavab Səthi Metodologiyası (RSM) əsasında Eksperimentlərin Planlaşdırılması (DOE) nəticələrindən istifadə edilmiş və mövcud məlumatlar Qauss Proses Regressiyası (GPR) vasitəsilə təhlil edilmişdir. GPR analizi zamanı seçilmiş Radial Əsas Funksiya (RBF) nüvəsinin White Kernel ilə kombinasiyası qarpız qabığının bütün ağır metalların adsorbsiyasında yüksək effektivliyini təsdiqləmiş, bütün hallarda determinasiya əmsalının (R^2) 0,995-dən böyük olduğu müəyyən edilmişdir. Tədqiqat nəticəsində çıxarılma faizi üçün ikinci tərtibli kvadratik reqressiya modeli, adsorbsiya tutumu (q_e) üçün isə birinci tərtibli xətti reqressiya modeli şəklində simvolik GPR modelləri əldə edilmişdir. Bundan əlavə, biosorbsiya prosesindən sonra qarpız qabığının təkrar istifadə imkanlarının qiymətləndirilməsi məqsədilə desorbsiya tədqiqatlarının aparılması, həmçinin WMR əsaslı sorbsiya proseslərinin iqtisadi səmərəliliyinin araşdırılması tövsiyə olunur. Bu tədqiqatlar həmin materialın çirkab suların təmizlənməsi sahəsində gələcək tətbiq perspektivlərinin daha dəqiq müəyyənləşdirilməsinə və digər sorbentlərlə müqayisəsinə imkan verəcəkdir.

Açar sözlər: *Qarpız qabığı, Gaussian Proses Regressiyası, Ngomari Avtobus dayanacağı, Ağır metalların çıxarılması, Radial Baza Funksiyası*