Strontium (II) Biosorption Studies on Starch-Functionalized Magnetic Nanobiocomposites Using Full Factorial Design Method

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Abstract
The purpose of this research was to fabricate starch based magnetic nanobiocomposites using two different starch types (corn and wheat) and to examine the effects of some experimental parameters (such as starch concentration, NaOH concentration and aging time of nanoparticles) that play a role in the synthesis products. The characterization of the starch-based magnetic-nanobiocomposite materials were realized with several techniques. In the previous study, MW_S3 and MC_S3 from starch stabilized magnetite nanobiocomposites were selected for further studies with smaller particle size and large surface areas, as a result of calculations based on XRD results and BET surface area. The usability of starch-based magnetic-nanobiocomposite materials, which can provide rapid separation with their magnetic properties and are not toxic, in removing Sr(II) ions from aqueous solutions has been investigated. The parameters affecting the biosorption were investigated using a full factorial experimental design. In the biosorption study, pH, temperature, initial Sr(II) concentration and contact time were determined as four independent variables. The regression coefficients were found using the least squares method and the response surface graphs were created according to the polynomial equation obtained from the full factorial experimental design. ANOVA (analysis of variance) analysis within the 95% confidence interval of the model applied for the full factorial experimental design was examined and the compatibility of the model with the experimental findings was examine. It is seen that the biosorption of Sr(II) on MW_S3 and MC_S3 nanobiocomposites increases with increasing concentration in the range of 25–75 ppm. As a result of the regression analysis, it was observed that pH was statistically significant (p < 0.05) and had an increasing effect for MW_S3. Evaluating the results obtained, it was found that the combined effects of the parameters on the biosorption of Sr(II) on MW_S3 adsorbent were not significant, but the combined effects of concentration and time were only significant on the adsorption of Sr(II) on MC_S3 adsorbent. From the solution of the equation obtained in the full factorial experimental design, it has been determined that the optimum biosorption conditions for MW_S3 adsorbent are; pH is 7, temperature is 34.87 °C, initial Sr(II) concentration is 75 mg/L and contact time is 30 min. Optimum adsorption conditions for MC_S3 adsorbent were determined to be pH is 8, temperature is 34.46 °C, initial Sr(II) concentration is 74.83 mg/L and contact time is 59.54 min. The composition and chemical state of the magnetic nanobiocomposites were investigated by XPS analysis after Sr(II) biosorption. For the purpose of determine the adsorption model, the relevant parameters were calculated using Langmuir, Freundlich and Dubinin–Radushkevich isotherms. Gibbs free energy change, enthalpy and entropy values, which are the values of adsorption thermodynamics, were calculated.

Keywords Nanobiocomposite · Full factorial design · Strontium · Starch · Biosorption

Introduction
Contamination resulting from the release of radioactive materials affects living organisms and the environmental environment in a wide range. Aquatic environments are contaminated as a result of events such as nuclear precipitation, explosions, nuclear accidents, radioactive wastes, the transportation/disposal of these wastes and nuclear sabotage. Surface waters, open to the atmosphere carry the risk of all kinds of pollution. Especially in nuclear accidents, there is a risk of immediate nuclear pollution for all surface waters. For this reason, surface waters used as drinking and utility water have vital and strategic importance. It is important to be remove Sr-90 (half-life of
of Sr using some chemical/commercial agents [7–10]. In there are many studies in the literature for the removal and facile aggregation of Fe₃O₄ nanoparticles, which is an dipole–dipole attractions lead to poor dispersion stability however, their applications are somewhat limited because their superparamagnetic behavior and strong magnetic their sorption capacity and separable without leaving secondary pollution. Iron oxide nanoparticles have good sorption capacity water because they have properties such as low cost, easy preparation, fast sorbing ability, high sorption capacity and separable without leaving secondary pollution. Iron oxide nanoparticles have good sorption capacity however, their applications are somewhat limited because their superparamagnetic behavior and strong magnetic dipole–dipole attractions lead to poor dispersion stability and facile aggregation of Fe₃O₄ nanoparticles, which is an undesirable condition for the adsorption process because of the difficulty to separate them from the medium used for the adsorption process in a liquid that lacks magnetic properties. It has been demonstrated that surface functionalization provides a solution for these shortcomings. For example, coating Fe₃O₄ nanoparticles with natural polysaccharides, such as chitosan [11], starch [12], cellulose [13], glucomannan [14], or pectin [15] allows for control over the size and shape of the nanoparticles, thus preventing nanoparticle aggregation, enhancing biocompatibility, providing binding sites for various radionuclides and heavy metals. Meanwhile, the starch functionalized Fe₃O₄ nanoparticles act as a promising adsorbent for Sr(II) removal because their utilization involves low costs, high efficiency, and rapid separation from the aqueous solution under an external magnetic field.

Among biopolymers, starch with special properties has considered as one of the promising media for the fabrication of nanobiocomposites. Starch made from combination of amylose (linear) and amylopectin (branched) microstructures. Amylose or poly-α-1,4-d-glucan molecule is primarily a linear construction of α-1,4 connected glucose parts. On the other hand, amylopectin or poly-α-1,4-d-glucan and α-1,6-d-glucan are a branched construction made by short α-1,4 parts connected by α-1,6 bonds [16]. In this work, starch due to having large number of hydroxyl end-groups and being naturally abundant, was selected as a functionalization agent for magnetite and such structure would be able to improve the biosorption capacity of the Sr(II).

This work utilizes full factorial design instead of the widely employed conventional experimental design which investigates a single variable at a time. In contrast, factorial design determines optimum experimental conditions by changing several variables simultaneously. Factorial designs are widely applied to experiments that consider multiple correlated variables which effect the response [17]. Beneficially, factorial designs require less experimental iterations for a given number of experimental variables. Therefore, material, cost, and time are reduced. When factorial design methods are applied to experiments of a process, mathematical models are derived through obtained analysis of variance tables.

In this study, effective, safe, environmentally friendly and non-toxic nanobiocomposite materials were synthesized and used to remove strontium ions from aquatic environments. Synthesized materials were then characterized and their biosorption properties for strontium ions were investigated by Full Factorial Design method. Nevertheless, there is no studies concerning the application of this method to the biosorption of strontium on effective, safe, environmentally friendly and non-toxic nanobiocomposite (starch- stabilized magnetic nanocomposites). In the literature, traditional “one variable at a time” experiments were used to determine the individual effect of various factors on the adsorption process. However, factorial experimental design can be used to provide a large amount of information and reduce the number of experiments, time and overall research costs. However, this low-cost material may be suitable for a variety of applications, particularly in developing countries and small-scale industries.

Materials and Methods

Starch-functionalized magnetic nanoparticles (MW_S3 and MC_S3 were selected) were synthesized by the chemical co-precipitation of magnetite phase from aqueous solution in a different type of polymeric starch matrix (corn and wheat), as reported in the literature [18]. The physical and chemical properties of the adsorbents are also presented in a previous study.

Reagents

The chemicals were; strontium nitrate (Sr(NO₃)₂, Merck),iron (III) chloride hexahydrate (FeCl₃·6H₂O, Fluka), iron (II) sulfate heptahydrate (FeSO₄·7H₂O) hydrochloric acid (HCl, Merck), sodium hydroxide (NaOH, Merck). All the reactants were used as Analytical Grade (AR). Ultrapure water (resistivity 18.2 MΩ cm, TOC level 1–5 μg/L) was prepared by Millipore model water purification.
Instrumentation

Sr(II) concentrations in aqueous solution were determined by ICP-OES (Perkin Elmer Optima DV 2000). The sorption experiments were studied by batch technique using a thermostated shaker bath Model GFL-1083. The pH’s of all solutions were measured with a Hanna Instrument 8521Model pH meter.

The composition and chemical states of starch-functionalized magnetic nanoparticles were examined after the biosorption of Sr(II) by XPS. The XPS measurements were undertaken using an ESCALAB MARK 2 VG instrument equipped with a MgKα-Xray source.

Experimental Procedure

Determination of pHpzc

The point zero charge (pHpzc) of the adsorbents was determined by batch equilibration technique using the following procedure: 10.0 mL of 0.10 mol/L NaCl solution was placed in a closed capped Erlenmeyer flask. Initial pH values (pInitial) of NaCl solutions were adjusted from ∼ 2.0 to ∼ 10.0 by addition of 0.1 M HNO3 or KOH. Suspension of MW_S3 and MC_S3 were allowed to equilibrate for 24 h in a shaker thermostated at 25 °C. Then the suspensions were filtered through a Whatman filter paper no: 44 and the pH values (pFinal) were measured again. Then the pHpzc is the point where the curve of ΔpH (pHi − pHf) versus pH initial pH (pHi) crosses the line.

Batch Biosorption Experiments

Batch biosorption experiments were performed by a thermostatically controlled shaker (GFL-1083 model). In the experiments, 0.001 g MW_S3 and MC_S3 adsorbents were shaken with 10 mL Sr(II) solutions at varying experimental conditions in 50 mL Erlenmeyer flasks at a speed of 150 rpm. After biosorption, the solid and liquid was rapidly separated with an external magnet and the concentration of Sr(II) in the solution was measured by a Perkin–Elmer Optima 2000 DV ICP-OES. The amount of Sr(II) ions adsorbed by MW_S3 and MC_S3 was calculated using the following equation:

\[
\text{Removal} \% = \left( \frac{C_i - C_e}{C_i} \right) \times 100
\]

(1)

\[
q_e = \frac{(C_i - C_f)V}{W}
\]

(2)

where Q is the metal uptake (mg/g), Co and Ce are the initial and equilibrium Sr(II) concentrations in the solution (mg/L), respectively. V is the solution volume (L) and m is the mass of sorbent (g). All the experiments were performed in duplicates with experimental errors within ± 3%.

Factorial Design for the Biosorption Studies

The experimental factors such as strontium concentration, pH, time and temperature were studied in the biosorption process. Because empirical studies are time consuming and costly, it is beneficial to use the full factorial design in order to reduce the total number of experiments and thus obtain the best overall optimization of the adsorption system [19–21]. This design determines that factors have significant effects on a response and how the effect of one factor varies with the level of other factors. A full factorial design is a widely used experimental design with each factor at two levels (low and high). The number of experimental runs at level b is b^k, where k is the number of factors. In this work, biosorption of strontium from contaminated waters on starch based magnetic nanobiocomposites, optimized the using a 2^4 full factorial design model. Table 1 illustrated the high and low levels of the experimental factors such as initial pH (X1), temperature (X2), concentration (X3) and contact time (X4) to the 2^4 factorial designs. The levels of the experimental factors were coded as −1 (low) and +1 (high). The low and high levels for the factors were decided according to previous studies. The results were analyzed with the Minitab 16 software, and the main effects and interactions between factors were determined.

Results and Discussion

pHpzc: The point zero charge (pHpzc) of the MW_S3 and MC_S3 was determined by pH measurement technique was 5.5 and 3.75, respectively (Fig. 1).

This behavior can be explained by the zero point charge of the adsorbents (pHpzc = 5.5 and 3.75). At a pH above this zero point charges, the surface of the adsorbents become negatively charged, which enhances the adsorption of positively charged Sr(II) ions through the electrostatic

| Factors                      | Factor codes | Levels |
|------------------------------|--------------|--------|
| Initial pH                   | X1           | 4      | 8     |
| Temperature (°C)             | X2           | 25     | 35    |
| Concentration (mg/L)         | X3           | 25     | 75    |
| Contact time (min)           | X4           | 30     | 60    |

Table 1 Experimental independent variables
force of attraction and at pH value lower than 5.5 and 3.75 (pHpzc) the surface of the adsorbents were positively charged, inhibiting the adsorption of Sr(II) ions due to the electrostatic repulsion between cationic structure of strontium and adsorbent. The maximum adsorption at pH 7 and 8 may be due to the development of negative charge on the surface of the MW_S3 and MC_S3, respectively.

The Optimization of Adsorption Parameters

With the data obtained as a result of the experimental design made according to Tables 1, the regression process was carried out using the least squares method. According to the polynomial equation obtained as a result of this four-variable two-level design, the following equation provides us with the response surface graphs.

\[ y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4 \]

where \( Y \) is the predicted reaction efficiency. The constant term is \( b_0 \). The respective effect coefficient is \( b \) and \( X_1, X_2, X_3, X_4 \) stands for initial pH, temperature, initial Sr concentration and contact time, respectively. The estimated equation \( Y = f(X) \) written for the significant variables in ANOVA tables (Tables 3 and 4) for removing Sr(II) for MW_S3 and MC_S3 is given in Eqs. (3) and (4), respectively.

\[ y = +31.23 + 0.76X_1 + 9.83X_3 \]  

\[ y = +28.26 + 8.92X_3 + 2.00X_3X_4 \]  

The coded experimental data points along with the predicted and observed responses are given in Table 2.

ANOVA (analysis of variance) analysis, which is within the 95% confidence interval, was examined together with the full factorial experimental design, and as a result, the compatibility of the model with the experimental findings was checked. A significance F value less than 0.05 (with a 95% confidence interval) indicates that the model is statistically significant [22]. The significance F value of the model resulted as \( p < 0.05 \) and the model F value as 169.81 for MW_S3 and 17.19 for MC_S3, indicating that the regression showed a statistically high value. The coefficient of determination (R²) value resulted as 99% for MW_S3 and 97% for MC_S3, indicating that 99% and 97% of the changes in MW_S3 and MC_S3 are well explained by the relevant independent variables, respectively. That is, there is a high agreement between the observed values and the predicted values (Tables 3 and 4).

The statistical significance evaluation of the coefficients obtained as a result of the regression analysis was made with “p” values. As a result of the low “p” value, the significance value of the relevant coefficient increases [23]. As a result of the evaluations made on the results shown in Tables 3 and 4, pH and concentration, which are among the main effects, lead to an increasing and significant change in the biosorption process with MW_S3; time and temperature did not cause a statistically significant change. Likewise, in the biosorption process with MC_S3, it was observed that there was no statistically significant change in the concentration.
increasing direction, while pH, time and temperature did not cause a statistically significant change. When the absolute values of the coefficients are examined, it is seen that the effect order is the highest concentration (9.83) and (8.92), for MW_S3 and MC_S3 respectively.

1. For MW_S3, when the coefficients of the interactive effects were examined, it was seen that the bilateral interactions did not show statistical significance (as p > 0.05).

### Table 2
Experimental data points used in FFD statistical design and observed and predicted values for Sr(II) uptake capacity of MW-S3 and MC_S3

| Run No | X1 | X2 | X3 | X4 | Observed | Predicted | Observed | Predicted |
|--------|----|----|----|----|----------|-----------|----------|-----------|
| 1      | 1  | 1  | 1  | 1  | 41.140   | 41.673    | 42.990   | 43.448    |
| 2      | 1  | 1  | 1  | -1 | 43.760   | 43.350    | 40.100   | 37.830    |
| 3      | 1  | 1  | -1 | 1  | 20.736   | 20.709    | 20.012   | 19.604    |
| 4      | 1  | 1  | -1 | -1 | 22.474   | 22.377    | 19.787   | 22.001    |
| 5      | 1  | -1 | 1  | 1  | 41.240   | 41.541    | 38.870   | 40.577    |
| 6      | 1  | -1 | 1  | -1 | 43.320   | 42.895    | 33.310   | 33.416    |
| 7      | 1  | -1 | -1 | -1 | 21.790   | 20.982    | 21.221   | 19.464    |
| 8      | 1  | -1 | -1 | -1 | 21.395   | 22.326    | 20.373   | 20.317    |
| 9      | -1 | 1  | 1  | 1  | 41.210   | 40.708    | 39.370   | 38.056    |
| 10     | -1 | 1  | 1  | -1 | 39.700   | 40.079    | 27.770   | 30.897    |
| 11     | -1 | 1  | -1 | 1  | 21.973   | 21.968    | 14.19    | 15.454    |
| 12     | -1 | 1  | -1 | -1 | 21.203   | 21.331    | 19.387   | 16.310    |
| 13     | -1 | -1 | 1  | 1  | 39.900   | 39.567    | 41.830   | 40.980    |
| 14     | -1 | -1 | -1 | 1  | 38.160   | 38.616    | 32.240   | 32.278    |
| 15     | -1 | -1 | -1 | -1 | 20.393   | 21.232    | 20.208   | 21.108    |
| 16     | -1 | -1 | -1 | -1 | 21.234   | 20.271    | 19.509   | 20.421    |

### Table 3
ANOVA table of the regression model in strontium uptake of MW_S3 nanobiocomposite

| Sum of squares | df | MS | F-value | p-value |
|---------------|----|----|---------|---------|
| Regression    | 1455.22 | 10 | 145.52 | 17.20   | 0.0029  |
| X1            | 27.98 | 1  | 27.98   | 3.31    | 0.1287  |
| X2            | 1.53  | 1  | 1.53    | 0.1813  | 0.6879  |
| X3            | 1274.37 | 1  | 1274.37 | 150.60  | < 0.0001|
| X1*X2         | 39.74 | 1  | 39.74   | 4.70    | 0.0825  |
| X1*X3         | 33.60 | 1  | 33.60   | 3.97    | 0.1029  |
| X1*X4         | 1.54  | 1  | 1.54    | 0.1813  | 0.6876  |
| X2*X3         | 2.38  | 1  | 2.38    | 0.2811  | 0.6187  |
| X2*X4         | 7.45  | 1  | 7.45    | 0.8799  | 0.3913  |
| X3*X4         | 2.39  | 1  | 2.39    | 0.2820  | 0.6181  |
| X1*X2*X3*X4   | 64.26 | 1  | 64.26   | 7.59    | 0.0400  |
| Residual      | 42.31 | 5  | 8.46    |         |         |
| Total         | 1497.53 | 15 |         |         |         |

### Table 4
ANOVA table of the regression model in strontium uptake of MC_S3 nanobiocomposite

| Sum of squares | df | MS | F-value | p-value |
|---------------|----|----|---------|---------|
| Regression    | 1455.22 | 10 | 145.52 | 17.20   | 0.0029  |
| X1            | 27.98 | 1  | 27.98   | 3.31    | 0.1287  |
| X2            | 1.53  | 1  | 1.53    | 0.1813  | 0.6879  |
| X3            | 1274.37 | 1  | 1274.37 | 150.60  | < 0.0001|
| X1*X2         | 39.74 | 1  | 39.74   | 4.70    | 0.0825  |
| X1*X3         | 33.60 | 1  | 33.60   | 3.97    | 0.1029  |
| X1*X4         | 1.54  | 1  | 1.54    | 0.1813  | 0.6876  |
| X2*X3         | 2.38  | 1  | 2.38    | 0.2811  | 0.6187  |
| X2*X4         | 7.45  | 1  | 7.45    | 0.8799  | 0.3913  |
| X3*X4         | 2.39  | 1  | 2.39    | 0.2820  | 0.6181  |
| X1*X2*X3*X4   | 64.26 | 1  | 64.26   | 7.59    | 0.0400  |
| Residual      | 42.31 | 5  | 8.46    |         |         |
| Total         | 1497.53 | 15 |         |         |         |

R² = 0.9717

*a Degrees of freedom

*b Mean square

c Test for comparing the model variance with residual (error) variance

d Probability of seeing the observed F-value if the null hypothesis is true
2. For MC_S3, when the coefficients of the interactive effects were examined, it was seen that the interaction effects of the concentration and time were significant (p < 0.05) and had an increasing effect, while the other bilateral interactions were not statistically significant.

**Effect of Initial Sr(II) Concentration**

As a result of regression analysis, the effect of initial Sr(II) concentration on Sr(II) biosorption on both nanobiocomposites was found to be significant (p < 0.05). The coefficient of the concentration being greater than zero indicates that the folded effect of the concentration on adsorption is positive (+9.83 and +8.92) for MW_S3 and MC_S3, respectively. In Figs. 2 and 3, it is seen that the biosorption of Sr(II) on MW_S3 and MC_S3 nanobiocomposites increases with increasing concentration in the range of 25–75 ppm.

**pH Effect**

As a result of the regression analysis, it was observed that pH was statistically significant (p < 0.05) and had an increasing

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**Fig. 2** Concentration increase graph of Sr(II) biosorption for MW_S3 in the range of 25–75 ppm

**Fig. 3** Concentration increase graph of Sr(II) biosorption for MC_S3 in the range of 25–75 ppm

**Fig. 4** pH effect of biosorption of Sr(II) on MW_S3
The effect for MW_S3 (Fig. 4). The effect of solution pH on Sr(II) biosorption on MC_S3 was not found significant in the determined operating ranges (Figure is not shown) (p > 0.05).

**Effect of Temperature**

As a result of the regression analysis, the effect of temperature on Sr(II) biosorption on MW_S3 and MC_S3 was not found significant in the determined operating range (25–35 °C) (p > 0.05). Therefore the figures are not given.

**Effect of Contact Time**

As a result of regression analysis, the effect of shaking time on Sr(II) biosorption on MW_S3 and MC_S3 was not found significant (p > 0.05) in the range of 30–60 min.

**Effect of Initial Concentration of Strontium and Shaking Time**

Evaluating the results obtained, it was found that the combined effects of the parameters on the biosorption of Sr(II) on MW_S3 adsorbent were not significant, but the combined effects of concentration and time were only significant on the biosorption of Sr(II) on MC_S3 adsorbent.

As a result of the regression analysis, the effect of the initial concentration of strontium and the shaking time on the Sr(II) biosorption on MW_S3 was not found significant (p > 0.05).

The fact that the coefficient of concentration and agitation time is greater than zero (+ 2.00) shows that the effect of this double interaction is positive on biosorption. As the main effect, if we consider the coefficients of concentration and time; the concentration has a coefficient of + 8.92, and the agitation time has a coefficient of + 1.58. The fact that the coefficient of the concentration is larger and positive and the coefficient of the duration is also positive, the cumulative effect of the bilateral interaction in the examined interval shows a positive feature (Fig. 5).

As a result, it was concluded that the changes within the limits of 25–75 mg/L and 30–60 min had statistically significant effects on adsorption (p < 0.05).

Apart from the bilateral interactions given regarding the adsorption of Sr(II) on both nanobiocomposites, other bilateral interactions were not found significant (p > 0.05) and therefore graphs related to these were not given.

According to the Pareto diagrams in Fig. 6a and b, the effects of pH and concentration factors for MW_S3 and the effects of concentration and concentration-contact time interaction factors for MC_S3 were included in the model since they were above the limit values. In addition,
the most influential factor for both MW_S3 and MC_S3 is Concentration. The analyzes made also support this structure.

Looking at the distribution of the points on the normality plot of residuals in Fig. 7a and b, it is seen that the normality condition is met for MW_S3 and MC_S3.

In addition, a Box-Cox plots in Fig. 8a and b were drawn for the MW_S3 and MC_S3 response variables to see if any transformation was needed and it was seen that no transformation was needed.

**Characterization of Sr(II) Loaded Adsorbent by XPS Analysis**

After Sr(II) biosorption on the nanobiocomposite, XPS analysis was used to determine the chemical composition and structure of the starch stabilized material. The XPS spectrum of the Sr(II) charged-magnetic nanobiocomposite is shown in Fig. 9. The magnetic starch nanobiocomposite adsorbent shows binding energy peaks of approximately 285, 530 and 711 eV, which are attributed to C1s, O1s and Fe2p electrons, respectively. The energy value observed around 711 eV for the Fe atom is due to the Fe3O4 structure showing the 2p orbital. In addition, a peak at 134 eV attributable to Sr(II) coordination was detected, proving that Sr(II) is retained on the magnetic nanobiocomposite.

**Isotherm Studies**

Adsorption isotherms are used to characterize the adsorption process. If it is necessary to define the adsorption isotherm,
we can state that it is the graphs that make sense of the equilibrium state between the amount of the substance being adsorbed on the adsorbent (qₑₑ, mg/g) and the concentrations of the substance increasing without being adsorbed in the solution (Cₑₑ, mg/L) in a constant temperature and pH environment. For the formation of these isotherms, the solutions prepared at different concentrations with a known amount of adsorber must reach equilibrium [24].

For this purpose, Freundlich, Langmuir and Dubinin–Radushkevich (D–R) isotherms were studied in the range of 10–125 mg/L strontium concentration. With the support of these isotherms, the surface properties of the adsorbent, the affinity between the adsorbent and the adsorbed, and the properties such as the maximum adsorption capacity and adsorption energy can be examined and information about the mechanism of the adsorption process can be obtained.

In addition, linear and non-linear regression methods were compared to determine the best fitting of isotherm to experimental data.

Non-linear regression was performed using trial and error method with the help of solver add-in functions of Microsoft Excel software. An error function assessment is required in order to evaluate the fit of the equation to the experimental results. The coefficient of determination (R²) was used in order to find the fitting degrees of isotherm with experimental data in this study.

\[
R^2 = \frac{\sum (q_{e,exp} - \bar{q}_{e,cal})^2}{\sum (q_{e,exp} - \bar{q}_{e,exp})^2 + \sum (q_{e,exp} - \bar{q}_{e,cal})^2}
\]

where \( q_{e,exp} \) is the amount of metal ions biosorbed onto biosorbent obtained from experiment, \( q_{e,cal} \) is the amount of metal ions obtained by isotherm models, and \( \bar{q}_{e,cal} \) is the average of \( q_{e,exp} \). The isotherm results are presented in Table 5.

These linear isotherms are given in Figs. 10, 11 and 12. The data of the adsorption isotherms are shown in Table 6. The equation of the Langmuir isotherm is given in Eq. 5.

\[
\frac{C_e}{q_e} = \frac{1}{Q_o b_L} + \frac{C_e}{Q_o}
\]

The slope of the \( C_e/q_e \) versus \( C_e \) graph drawn according to this equation gives the value \( 1/Q_o \), and its extrapolation (intercept) \( 1/Q_o b_L \) (Fig. 10). From this, the isotherm constants \( Q_o \) and \( b_L \) are calculated.

In the biosorption processes performed in accordance with the Freundlich model, the adsorbent material is located heterogeneously on the adsorbent surface. The linearized form of the equation of the Freundlich model is as follows:

\[
\log q_e = \log K_F + \frac{1}{n_F} \log C_e
\]

\( 1/n_F \) from the slope of the graph of \( \ln C_e \) versus \( \ln q_e \) drawn according to the equation, and \( \ln K_F \) from the intersection point are found (Fig. 11). From here, the \( n_F \) and \( K_F \) values are calculated. According to the Freundlich model, the more heterogeneous the surface, the closer the \( 1/n \) heterogeneity effect will be to zero. If the \( n \) adsorption intensity constant

| Table 5 Isotherm and correlation constants for Sr(II) ion biosorption |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Isotherm models | Parameters       | Linearized isotherm | Non-linearized isotherm |
|                 | MW_S3 | MC_S3 | MW_S3 | MC_S3 | MW_S3 | MC_S3 |
| Langmuir        |        |       |       |       |
| \( q_m \) (mg/g) | 43.8500 | 54.9400 | 71.2000 | 71.1900 |
| \( b_L \) (L/mg) | 0.2177 | 0.0722 | 0.0180 | 0.0230 |
| \( R^2 \)       | 0.9886 | 0.9689 | 0.8455 | 0.9730 |
| Freundlich      |        |       |       |       |
| \( K_F \) (mg/L) | 10.2195 | 7.0766 | 3.1301 | 2.0103 |
| \( n \)         | 2.7723 | 2.1815 | 1.6700 | 1.3500 |
| \( R^2 \)       | 0.8153 | 0.9155 | 0.8290 | 0.9589 |
| Dubinin–Radushkevich | | |
| \( X_m \) (mg/g) | 38.1180 | 37.8480 | 44.0000 | 42.0000 |
| \( E \) (kJ/mol) | 6.8400 | 6.9700 | 6.0000 | 6.3000 |
| \( R^2 \)       | 0.9981 | 0.9981 | 0.9694 | 0.9856 |
value found here is between 1 and 10, it is understood that the adsorption is efficient.

The following equation is used to find the constants of the Dubinin–Radushkevich model used to determine the pore structure and pore volume of the adsorbent:

\[
\ln C_{ads} = \ln X_m - \beta \varepsilon^2
\]  
\[(8)\]

\[
\varepsilon = RT \ln \left( \frac{1}{1 + C_e} \right)
\]  
\[(9)\]

\[
E = \frac{1}{\sqrt{-2\beta}}
\]  
\[(10)\]

Here, \(C_{ads}\) (mol/g) is the amount of solute sorbed per unit weights of solid, \(X_m\) (mol/g or mg/g) is the sorption capacity, \(\beta\) (mol/J)\(^2\) a constant related to energy and \(E\) is the D–R isotherm constant. This approach is generally used to distinguish whether the physical and chemical adsorption of metal ions is by the mean free energy per molecule of adsorbate, \(E\), which can be calculated by the relationship given in.

Together with the average adsorption energy (E), we can make predictions about the adsorption mechanism. If the E value is between 8 and 16 kJ/mol, the adsorption process is characterized by ion exchange. If \(E < 8\) kJ/mol, the adsorption is physical, if \(20 < E < 40\) kJ/mol, the adsorption process is estimated to be chemical [25].

According to the \(R^2\) correlation values given in Table 6, it was observed that the Sr(II) ion biosorption of MW_S3 and MC_S3 adsorbents was compatible with Langmuir and mostly the D–R isotherm model. As seen in Table 6, the Langmuir and D–R model is suitable for describing the strontium biosorption equilibrium with MW_S3 and MC_S3 nanobiocomposites. Accordingly, although adsorption conforms to the monolayer isotherm model, it is known that according to the D–R isotherm model, adsorption follows the pore-filling mechanism and provides information about adsorption energy and nanobiocomposite porosity [26].

According to the D–R isotherm, \(Q_o\), the maximum sorption capacity was calculated as 38.118 mg/g for MW_S3 and 37.848 mg/g for MC_S3. The adsorption energy E
value was calculated as 6.84 kJ/mol for MW_S3 and 6.97 kJ/mol for MC_S3. These results show that the biosorption mechanism takes place in the direction of physical adsorption in both adsorbents.

When the linear and non-linear isotherm models were compared, it was seen that the constants and regression values of the D–R model was more compatible with each other.

**Adsorption Thermodynamics**

In order to determine the thermodynamic model of the adsorption process, $\Delta G^o$ standard Gibbs free energy, $\Delta H^o$ standard enthalpy and $\Delta S^o$ standard entropy values were used. The following equations were used to calculate these parameters.

\[
\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \\
\Delta G^o = \Delta H^o - T \Delta S^o \\
K_d = \frac{C_i - C_e}{C_e} \times \frac{V}{W}
\]

Experiments on the investigation of biosorption thermodynamics were carried out in the range of 20–40 °C and with 50 mg/L strontium solutions. As a result of the thermodynamic investigation of Sr(II) biosorption on MW_S3 nanobiocomposite, $\Delta H^o < 0$ indicates that the equilibrium for adsorption is an exothermic reaction, while $\Delta G^o < 0$ indicates that the adsorption process occurs spontaneously (voluntarily). The fact that the $\Delta G^o$ value has smaller negative values with the increase in temperature indicates that the adsorption process proceeds spontaneously.
in the low temperature environment and strontium ions voluntarily adhere to the adsorbent. A negative $\Delta S^\circ$ value indicates that the adsorption process is regulated through the formation of a complex between adsorbate and adsorbent. In addition, a negative $\Delta S^\circ$ value reflects that no significant changes occur in the internal structures of the adsorbent during the adsorption process [27]. As a result of the thermodynamic investigation of Sr(II) adsorption on MC_S3 nanobiocomposite, $\Delta H^\circ > 0$ indicates that the equilibrium for adsorption is an endothermic reaction, while $\Delta G^\circ < 0$ indicates that the adsorption process occurs spontaneously (voluntarily). The fact that the $\Delta G^\circ$ value has larger negative values with increasing temperature indicates that the adsorption process proceeds spontaneously at high temperatures and strontium ions voluntarily attach to the adsorbent. The fact that $\Delta S^\circ > 0$ indicates that the disorder at the solid–liquid interface increases during adsorption. In addition, the positive entropy shows the interest of strontium ions in the adsorbent [28].

In order to have an idea about the adsorption mechanism, the size of the enthalpy ($H$) and free energy change is used. Generally, the magnitude of $\Delta H^\circ$ is less than 20 kJ/mol for absolute physical adsorption, while this value is in the range of 80–200 kJ/mol for chemical adsorption. In general, the absolute magnitude of the change in Gibbs free energy for physisorption is between $-20$ and $0$ kJ/mol, and chemisorption is in the range of $-80$ to $-400$ kJ/mol [29]. In this study, the results found for MW_S3 nanobiocomposite were between $-18.9129$ and $-18.4793$ kJ/mol, while for MC_S3 nanobiocomposite it

| Adsorbent | $\Delta H^\circ$ (kJ/mol) | $\Delta S^\circ$ (kJ/mol K) | $\Delta G^\circ$ (kJ/mol) |
|-----------|---------------------------|-----------------------------|---------------------------|
|           | 293 K | 298 K | 303 K | 308 K | 313 K |
| MW_S3     | $-25.2638$ | $-0.0217$ | $-18.9129$ | $-18.8045$ | $-18.6961$ | $-18.5877$ | $-18.4793$
| MC_S3     | $+23.6093$ | $+0.1398$ | $-17.3545$ | $-18.0536$ | $-18.7526$ | $-19.4517$ | $-20.1507$

In order to have an idea about the adsorption mechanism, the size of the enthalpy ($H$) and free energy change is used. Generally, the magnitude of $\Delta H^\circ$ is less than 20 kJ/mol for absolute physical adsorption, while this value is in the range of 80–200 kJ/mol for chemical adsorption.
was between $-17.9545$ and $-20.1507$ kJ/mol. According to the results obtained, the biosorption process that takes place at 20–40 °C has a physical character [30]. Finally, it can be concluded that while the Sr(II) biosorption with MW_S3 nanobiocomposite has physical adsorption character, the Sr(II) biosorption with MC_S3 nanobiocomposite is governed by the combined control of several mechanisms [31].

Investigation of the Efficiency of Adsorbent with Real Surface Water Samples and Competitive Ions Effect

In this work, Sr(II) adsorption studies were carried out on MW_S3 and MC_S3 with surface water samples. Surface water sample taken from Meriç River was used for this purpose. In addition to strontium, the uptake of other heavy metals in surface waters on MW_S3 and MC_S3 was investigated. Experiments were conducted at the optimum adsorption conditions (pH: 7, m: 0.01 g, v: 10 mL, T: 34.87 °C, t: 30 min; pH: 8, m: 0.01 g, v: 10 mL, T: 34.46 °C, t: 59.54 min for MW_S3 and MC_S3, respectively). Sr(II) and other heavy metal concentrations which remained after the adsorption process were determined by ICP-OES. As seen in Fig. 13, MW_S3 and MC_S3 can be used as a very effective adsorbent to remove other heavy metals besides Sr(II) in surface water samples, with high adsorption efficiencies.

In this study, we considered the effect of sodium, potassium, magnesium and calcium ions with respect to the adsorption of strontium ions because these ions are abundant in both seawater and freshwater, and Na, K ions are the main chemical constituent in a typical evaporator concentrate from nuclear power plants [32]. The effect of competitive ions concentration on the synthesized MW_S3 and MC_S3

![Fig. 13](image-url)  
Real surface water results for a MW_S3 and b MC_S3

![Fig. 14](image-url)  
Effect of competitive ions concentration on the adsorption capacity of strontium ions on the MW_S3 and MC_S3
was studied with neutral pH and keeping the concentration of strontium ions constant at 50 mg/L and 20 mg/L for the other ions. The adsorption capacity of the MW_S3 and MC_S3 was examined, and the obtained results are presented in Fig. 14. As seen from Fig. 14, synthesized nanobiocomposites efficiently removes strontium ions from the complex solution.

**Comparative Study**

Table 7 shows the comparison of Sr(II) sorption capacities for various sorbents. The present study found Sr(II) biosorption capacity of MW_S3 and MC_S3 to be 43.85 mg/g and 54.94 mg/g with the conclusion that these adsorbents show good performance of Sr(II) sorption as compared to many types of sorbents in the literature. This phenomenon suggests that the MW_S3 and MC_S3 could find a significantly important place in the list of effective and economical materials used to remove Sr(II) from aqueous solutions.

**Conclusions**

In this study, starch based magnetic nanobiocomposites were used for Sr(II) uptake by using a batch method. The parameters affecting the biosorption were investigated using a full factorial experimental design. The optimum conditions were investigated for solution pH, contact time, initial Sr(II) ion concentration and temperature values, which are parameters affecting the biosorption efficiency. It is seen that the biosorption of Sr(II) on MW_S3 and MC_S3 nanobiocomposites increases with increasing concentration in the range of 25–75 ppm. As a result of the regression analysis, it was observed that pH was statistically significant (p < 0.05) and had an increasing effect for MW_S3. Evaluating the results obtained, it was found that the combined effects of the parameters on the biosorption of Sr(II) on MW_S3 adsorbent were not significant, but the combined effects of concentration and time were only significant on the adsorption of Sr(II) on MC_S3 adsorbent.

From the solution of the equation obtained in the full factorial experimental design, it has been determined that the optimum biosorption conditions for MW_S3 adsorbent are; pH is 7, temperature is 34.87 °C, initial Sr(II) concentration is 75 mg/L and contact time is 30 min. Optimum adsorption conditions for MC_S3 adsorbent were determined to be pH is 8, temperature is 34.46 °C, initial Sr(II) concentration is 74.83 mg/L and contact time is 59.54 min.

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**Declarations**

**Competing interests** The authors have not disclosed any competing interests.

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