Synthesis of a new magnetic adsorbent using green tea leaf extract and its application in phenol removal by RSM method

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Abstract

In this research, iron oxide nanoparticles were prepared by green synthesis and identified by scanning electron microscopy, X-ray diffraction, infrared spectroscopy, and vibrational magnetometer. The tea leaves extract was used as a reducing agent to synthesize iron oxide nanoparticles. The systematic study of the process was performed using Design Expert 10 software to determine the relationship between the four process variables, namely iron concentration, extract volume, time, and temperature effect. The square model was significant for the response variables. The iron oxide nanoparticles had super-magnetic properties. Then, iron oxide nanoparticles were used for magnetization of activated carbon (MAC). Finally, the MAC were used for phenol removing by response surface methodology (RSM) method. The results manifested that the generated MAC is quite effective in removing phenol. Various parameters such as pH, extraction time and adsorbent amount were optimized by the RSM method. The absorption of phenol was measured by using a spectrophotometer at a maximum wavelength of 510 nm. It was also indicated that phenol in an aqueous solution was removed up to 98%.

1. Introduction

Removal of organic compounds from industrial wastewaters with biological treatment processes is difficult or impossible. Phenols, as a class of organic matter, are structurally similar to conventional materials such as herbicides and insecticides. Phenols are widely used for the commercial production of a wide range of resins, including phenolic resins, which are used as structural materials for epoxy resins, adhesives and polyamides for various applications [1]. Phenols also consist of the breakdown of "bisphenol A", which is used as a monomer to produce polycarbonate and epoxy resins. Phenol is the 11th of 126 chemicals designated as priority pollutants by the US Environmental Protection Agency (EPA) and calls for reducing phenol levels in wastewater to less than 1 mg/l [2]. There are many methods for removing phenol from wastewater and water such as ozone / hydrogen peroxide oxidation [3], ion exchange [4], electrochemical oxidation [5], reverse osmosis [6], catalytic degradation [7] and adsorption [8-12].

The treatment with activated carbon is an effective method for removing phenol from wastewater because of its large surface area, micro porosity, high adsorption capacity, high purity and availability [13]. However, it is very difficult to separate activated carbon from solutions. Magnetization of activated carbon and then separating it from the solution by a magnet is one attractive way to solve this problem. One of the properties of these magnetic activated carbon (MAC) is that magnetic particles can be easily separated from sample solutions using an external magnetic field. The MAC have super-paramagnetic properties, meaning that they can be easily separated from the solution by an external magnetic field, and as a result may be reused or recycled. Therefore, suspended superparamagnetic particles were used as adsorbents for organic pollutants [14].

There are several reports on the synthesis of magnetic nanoparticles (MNPs) where different reducing agents such as hydrazine [13-16], dimethyl form amide (DMF) [9], sodium borohydride (NaBH₄) [17], carbon monoxide (CO) [18] etc. were used. However, such methods are toxic chemicals as reducing agents, organic solvents, not easily disposable due to environmental issues, have low production rate and are expensive [19]. For this reason, it is very desirable to devise alternative, 'green' methods of nanomaterial preparation that
reduce or eliminate toxic substances to restore the environment. Green synthesis of nanoparticles by inactivated plant tissue and plant extracts makes use of environmentally friendly, non-toxic and safe reagents [20].

In this research, green tea was used for magnetization of activated carbon. The aqueous extract of green tea contains gallocatechin gallate (GCG, > 45%), epigallocatechin gallate (EGCG, 36 to 40%), epigallocatechin (EGC 0.7-2.3%) and epicatechin (EC 0.5-2.2%) [18], which have antibacterial and antioxidant activity. These phenolic compounds have been reported to aid in the process of reducing the metal ions of Au, Ag and Fe [21]. Green tea extract is unquestionably a safe, green and environmentally friendly material, especially for herbals and medicines.

Response Surface Methodology (RSM) was used to independently minimize the absorption process. This method can also be employed to study the effect of various variables and interactions at different levels. Previously, researchers used the traditional 'one variable at a time' experiments 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 total research costs. The most important advantages of this technique are that the effects of individual parameters as well as their relative importance are obtained and that the interaction of two or more factors can be ascertained [22]. The surface response method has four main steps, including designing experiments, model fitting, model verification, and determining the optimal conditions. The design of experiments, like the central composite design (CCD), is useful for the response surface method because it requires a small number of experiments. In the present work, micro-porous activated carbon was magnetized using green tea extract employing green method and then used for adsorption of phenol from aqueous solution by RSM methodology.

Optimizing any operation means determining the optimum value of different parameter involved that provide maximum desirable output. Totally, optimization in analytical chemistry has been carried out by monitoring the influence of one factor at a time on an experimental response [22]. Its major disadvantage is that it does not include the interactive effects among the variables studied. The RSM consists of several experimental techniques dedicated to the evaluation of relationship between a group of controlled experimental factors and measured responses based on one or more criteria [23]. RSM can be used to evaluate the effects of individual parameters, the interaction of variables, and the optimum conditions for responses [24]. The absorption of phenol from the stock solutions prepared onto the MAC was statistically analyzed using version 10 of the Design Expert software. What makes this study significant is its design which is derived from the Design Expert. The four-factor central composite design (CCD) was used to investigate the effect of the selected parameters on the phenol removal capacity by the adsorbent particles. The pH (X1), temperature (X2), initial phenol concentration (X3), and the adsorbent dosage (X4), were selected as the independent variables, and the phenol removal capacity was considered as the response (dependent variable). The variables were coded according to the equation 1:

\[
x_i = \frac{x_i - X_0}{\Delta x}
\]

Eq. (1)
Where $X_i$ and $X_0$ are the coded value, and the real value at the center point of an independent variable, respectively, and $\Delta X$ is the step change value.

RSM is a combined mathematical and statistical technique based on the fit of a polynomial equation (empirical models) to the experimental data. This method generates a polynomial function for response relating it to the variables involved [25]. In doing so it deals with the variables only at specific levels (mostly -1, 0, 1). RSM generates an experimental design for model preparation. An experimental design is a specific set of experiments defined by a matrix composed of the different level combinations of the variables studied [26]. Different methods of determining the response surface require a different experimental design. The simplest model which can be used in RSM is based on a linear function (Eq. (2)):

$$Y = \beta_0 + \sum_{j=1}^{k} \beta_j x_i$$  \hspace{1cm} \text{Eq. (2)}$$

Where $k$ is the number of variables, $\beta_0$ is the constant term, $\beta_j$ represents the coefficients of the linear parameters, $x_i$ represents the variables, and $\epsilon$ is the residual associated to the experiments.

The next level of the polynomial model should contain additional terms, which describe the interaction between the different experimental variables [27]. In order to determine a critical point (maximum, minimum, or saddle), it is necessary for the polynomial function to contain quadratic terms according to the equation (3) [27].

$$Y = \beta_0 + \sum_{j=1}^{k} \beta_j x_j + \sum_{j=1}^{k} \beta_{jj} x_j^2 + \sum_{i<j}^{k} \beta_{ij} x_i x_j + \epsilon$$  \hspace{1cm} \text{Eq. (3)}$$

Where, $\beta_{ij}$ represents the coefficients of the quadratic parameter. A second-order model can significantly improve the optimization process when a first order model suffers lack of fit due to interaction between variables. The mathematical model found after fitting the function to the data sometimes doesn't describe the studied experimental domain satisfactorily. So, the quality of the model fitted is evaluated by the application of analysis of variance (ANOVA).

2. Material And Methods

2.1. Materials

All chemicals used were analytical grade and were used without further purification. Iron (II) chloride (FeCl$_2$), sodium hydroxide and HCl were purchased from Merck (Darmstadt, Germany). A stock solution of phenol (1000.0 mg L$^{-1}$) was prepared by dissolving 1.000 g of analytical reagent grade phenol in 1.0 L distilled water. The test solution with desired concentration was then prepared by diluting the stock solution. The pH of the solution was adjusted to the required value by using 0.1 M HCl and 0.1 M NaOH solutions.

2.2. Instrumentation

The absorbance was measured using a DR-5000 UV-visible spectrophotometer. The JEOL 2010F UHR was used for SEM analysis and the samples were gold-sputtered with a thin layer of gold. A Tensor II
Spectrometer was used for FT-IR analysis in the range of $400-4000 \text{ cm}^{-1}$ using the KBr disk. The X-Ray diffractometer Model Bruker AXS D8 advance with radiation $\lambda_{\text{Cu}K\alpha} = 1.5406 \text{ Å}$ was employed to assesses the crystalline structure. The XMF-104 was used to determine the chemistry of a sample by measuring the fluorescent X-ray emitted from the sample. The Lake Shore 4700 was used to assesses of magnetic properties.

2.3. Preparation of the green tea extract

The green tea extract was prepared by heating $60.0 \text{ g L}^{-1}$ green tea until boiling. After 1.0 h, the mixture was filtered two times with Whatman no-1 filter paper to obtain a clear extract. The green tea extract was then stored at $4^\circ \text{C}$ for further use.

2.4. Optimization of MNPs

Central composite design has been studied by many statisticians in response to surface analysis and is perhaps the most popular class of second order designs. The CCD, the most popular RSM, and Design Expert 10 statistical software were used to determine the optimum conditions in the co-precipitation method and produce the best nanoparticles. Four experimental effective factors, iron concentration (denoted as A), extract volume (denoted as B), time (denoted as C), and temperature (denoted as D) effect was considered as the response. Three levels of the factors were used in optimization by RSM (Table 1). Experimental factors were selected based on having the most significant effect on the efficiency of the controlled precipitation method. Previous experimental trials were used to select Factor levels.

2.5. Synthesis of magnetic activated carbon (MAC)

Co-precipitation method was used for the preparation of MAC. For this purpose, based on the information provided, experimental design software was used under optimal conditions for the synthesis of iron nanoparticles and 1 g of activated carbon was added to 100 ml of solution in optimal molarity of iron (II) chloride and then stirred for 30 minutes. After this time and also reaching the optimum temperature, green tea leaf extract was added drop by drop to this solution. The pH of the solution was adjusted with the $0.1 \text{ M}$ of hydrochloric acid at 6 and the resulting suspension was stirred for one hour. Finally, the sample was separated using a centrifuge at 6000 rpm for 10 min and washed several times with distilled water. It was dried in an oven at $100^\circ \text{C}$ and finally calcinated in an oven at $450^\circ \text{C}$ for 2 hours.

2.6. Adsorption procedure

In order to optimize the selected effective parameters, the response surface methodology was used and 22 design absorption experiments and the effect of the following parameters were studied: pH, initial concentration of phenol, time and the adsorbent dosage on the phenol removal was studied. Each experiment was carried out in a 100 mL Erlenmeyer flask installed in a shaker (160 rpm) with a constant reaction temperature of $25^\circ \text{C}$. An experiment with the same initial concentration of phenol and without adding MAC was always added in order to detect any phenol loss during the experiments. The final concentration of phenol in this experiment is almost the same as the initial concentration, which confirms that nothing happened. The reaction was started by adding MAC to 30 ml solution containing phenol. The reaction was
performed by adding different doses of MAC to 30 ml of solution containing 30 to 1000 mg L\(^{-1}\) of phenol. The pH values of phenol solutions were adjusted with 0.1 M HCl and/or 0.1 M NaOH after adding MAC and the experiments were performed in the initial pH range of 3.0−12.0. The effect of MAC dose on the adsorption of phenol was investigated by adding different adsorbent doses from 10 to 150 mg into different concentrations of phenol solution (based on the design of experiments) and removal efficiency was measured at contact times from 0 to 120 minutes. After equilibrium in that times, the mixing was stopped, and the mixed solution was separated from the absorbent by a magnet. By using Eq. 4, the residual phenol could be calculated.

\[
E_r = \frac{C_o - C}{C} \times 100
\]  
\[
\text{Eq. (4)}
\]

\(C_o\) is the initial concentration of the phenol in solution (mg L\(^{-1}\)) and \(C\) is the time concentration of the phenol (mg L\(^{-1}\)).

3. Results And Discussion

3.1. Preparation and properties of MNPs

In the first step, a combination of different factors was used to investigate the effect of important factors and their interaction with each other on the production of nanoparticles. Reaction time, iron concentration, amount of green tea extract and reaction temperature were used as effective parameters.

The experiments were designed based on these four parameters and also the obtained amounts of nanoparticles in each experiment were used to evaluate the RSM [27]. Table 2 shows the variables used in the design of the experiments and the initial results (based on weight) to determine the factors influencing in the synthesis.

Table 3 provides statistical analysis of the data to investigate the main effects of the parameters individually and interfering on the weight of nanoparticles produced [28]. These results show that only two factors, namely the concentration of iron and the amount of green tea extract have a significant effect on the amounts of nanoparticles produced (\(P <0.05\)). The correlation coefficient of these two variables shows their positive effects on the response. The presence of factors (reaction time and reaction temperature) separately did not affect the production of iron nanoparticles. P-value of iron solution concentration and amount of green tea extract indicate that they are the most important factors in the efficiency of iron nanoparticle synthesis among all the studied factors.

The results of ANOVA test (Table 3) show the good fit of this newly designed model due to the high value of F and the low value of P-value. Also, the detection coefficient R-Square = 0.9982 and the adjusted coefficient Adj R-Square = 0.9941 show the accuracy of the model. The remaining normal probability diagram is shown in Figure 1. As shown in the figure, the residues are normally distributed in a straight line.

Regression equation in terms of encoded factors according to factorial design experiment is presented in Eq. (5):

\[
E_r = \frac{C_o - C}{C} \times 100
\]  
\[
\text{Eq. (5)}
\]
Y=0.17+0.043*A+0.042*B-8.830E-006*C-1.616E-006*D+1.998E-003*AB+0.039*AC-8.022E-004*AD+0.039*BC-4.272E-004*BD+1.145E-003*BD-3.437E-003*CD-0.020*A^2-0.021B^2-1.417E-003C^2-0.12D^2 Eq......(5)

Figure 2 shows the response surface diagram of iron nanoparticle production with the effects of key factors. According to this diagram, the maximum range of iron nanoparticle production is achieved when the concentrations of iron solution and tea extract are 67-100 mM and 12.4 to 20 ml, respectively. The highest production efficiency of nanoparticles by the improved model is 0.2 g per reaction with optimal amounts of iron chloride and green tea extract. As a result, experiments were performed under optimal conditions.

Based on the SEM image of iron nanoparticles (Fig. 1S), the particle size of Fe_3O_4 is approximately 23 nm.

The FTIR diagram of the extract prepared from green tea leaves was shown in Fig. 2S. The strong and high-intensity band at 3380 indicate the presence of the O-H and the band at 1698 cm^{-1} indicate the presence of the C = C. The band at 1138 cm^{-1} is attributed to the C-O-C and C-OH tensile states. The bands at 1611, 1447 and 1046 cm^{-1} attributed to the C = C, C-H and C-O which indicates the presence of polyphenolic compounds.

Fig. 3S shows the spectrum of the prepared Fe_3O_4 nanoparticles, and as can be seen, the two Sharp peaks in the region of 485 nm and 543 cm^{-1} belong to the Fe-O functional group, which confirms the formation of Fe_3O_4.

XRD is a common technique for determining the morphology and crystal structure of nanoparticles. This technique is used to determine the metallic nature of particles. The XRD pattern of Fe_3O_4 nanoparticles synthesized using green tea is presented in Fig. 4S. As can be seen, the peak X-ray diffraction in the range of 2θ with 30, 35.5, 43, 57 and 62 degrees is due to the presence of Fe_3O_4 [28].

Fig. 5S shows the results of saturation magnetic analysis at room temperature. The sample did not show any hysteresis and the magnetic curve was completely reversible so that it shows the supra-magnetic behavior of the prepared nanoparticles. The amount of saturated magnet particle synthesis was about 40 emu.

3.2. Results of magnetic activated carbon analysis by iron nanoparticles

Fig. 6S demonstrated the phase identification and crystalline structures of the MAC. From the X-ray diffraction patterns obtained for the AC@Fe3O4 synthesized using green tea found that there exist strong diffraction peaks with 2θ values of 30°, 35.5°, 43°, 57° and 63° that corresponds Fe_3O_4 NPs [29,30].

Fig. 7S shows ED-XRF spectra of the MAC, and as can be seen existence of C, O, N, Fe and S elements in the MAC with weight ratios of C (82.27%), O (7.45%), N (4.41%), Fe (3.76%) and S (2.11%) was confirmed.

FT-IR analysis was carried out to determine the present functional groups onto the activated carbon and their possible involvement in the synthesis of Fe_3O_4-MNPs. The FT-IR analysis of MAC (Fig. 8S) shows vibration bands at 3500 cm^{-1} that attributed to stretch of O-H in polyphenols; 1623 cm^{-1} that assigned to C=C aromatic bonds. The presence of Fe-O bond at about 696 and 641 cm^{-1} confirms the formation of iron oxide onto the surface of activated carbon by using green method. The absorption peaks observed around 1138 cm^{-1} is attributed to the C−O−C and aromatic C−OH stretching modes, respectively [31,32]. The stretching vibrations
at 1623 cm$^{-1}$ and 3500 cm$^{-1}$ corresponding to polyphenols in the MAC. The occurrence of stretching vibrations of polyphenols in MAC confirms the capping activity of magnetite surface by tea polyphenols.

In order to study the morphology of MAC and how iron oxide nanoparticles spread onto surface of activated carbon, transmission electron microscopy (TEM) imaging was used at different magnifications. These images are shown in Figure 9S(a-c) at the specified scales of 20, 40 and 90 nm, respectively. The black and gray dots on these images are related to magnetic oxide particles alone or together [33,34]. As can be seen in Figure 9Sa, the magnetic nanoparticles of iron oxide are well placed on the activated carbon and are mostly bonded together, but the particles that are single and non-bonded are approximately less than 20 nm in size. Also, their cohesive particles are made up of smaller nanoparticles. Figure 9Sb also shows that the magnetic nanoparticles of iron oxide, in addition to mostly sticking together, are well dispersed on the activated carbon, and also Figure 9Sc shows this dispersion more clearly. Observing these images, it can be stated that the magnetic nanoparticles of iron oxide are well deposited on the activated carbon sample.

Figure 3 shows, the SEM of the prepared MAC and activated carbon. Figure 3B clearly shows the formation of iron oxide nanoparticles on the surface of activated carbon. The size of Fe$_3$O$_4$ particles is between 12 and 20 nm.

The magnetic properties of the MAC particles were investigated with a VSM that shown in Figure 10S. The nanocomposite revealed good magnetic properties in the magnetic field. After the preparation, a test with a magnet showed that the particles were superparamagnetic and were completely attracted to the magnet. The saturation magnetization (Ms) of the nanocomposite is 21 emu/g.

3.3. Adsorption experiments

The design of experiment for the phenol adsorption using the Design Expert is shown in Table 4 together with its effective removal percentage of phenol from the prepared stock solutions. The results obtained were utilized to further analyze the removal percentage of phenol from the prepared stock solutions with the usage of Design Expert that induces the optimum conditions for removal of phenol from the prepared stock solutions. “Analysis of Variance” (ANOVA) from the Design Expert Software was used to study the attained optimized parameters and the successful removal percentage from Tables 1 and 2. Results from the ANOVA for the removal percentage of phenol from the prepared stock solutions are listed in Table 5. Based on the results obtained from the ANOVA, the Fischer F-test value can be correlated to the mean square of the regressed model that leads to the comparison of the mean square of the residuals (errors). Efficiency of the model is validated as the F value increases. In contrast, the p value or lower probability indicates higher significance for the regression model.

Meanwhile, the R-square and Adj R-square also hold an important function in determining the significance of the model. According to Table 1, the values of R-square and Adj R-square for the adsorption phenol onto the MACs are 0.9991 and 0.9989, respectively. This clearly shows that both values are quite close to each other, hence, indicating high significance and efficiency of the model. Evolved model equation for the removal of phenol from the prepared stock solutions is presented in Eq. (6):
\[ y = -89.4687 + 41.332A + 0.0136B + 57.976C + 0.45199D + 1.5478 \times 10^{-4}AB + 0.19643AC - 6.085 \times 10^{-4}AD - 0.018133BC + 1.1785 \times 10^{-5}BD + 0.1086CD - 2.7258A^2 - 2.047B^2 - 87.39371C^2 - 1.76570E^{-003}D^2 \]  
Eq. (6)

where, “A” represents the coded value of pH the prepared stock solution, “B” represents the coded value of the concentration, “C” amount of adsorbent dosage and “D” represents the coded value of the agitation time or the contact time. In addition, the coefficient of single factor in the equation represents the effect of that respective particular factor while the coefficients of double factors in the equation represent the effect and interaction between those two respective factors.

Figure 4 illustrate the values obtained from the developed model compared with the experimentally obtained values and indicates an acceptable prediction of the model developed for optimizing effective in removing phenol.

Three-dimensional diagrams were plotted to observe the relationship between optimizing conditions and the phenol removal percentage (Fig. 5).

3.3.1. Effect of pH

Adsorption of phenol on the adsorbent depends upon the nature of the adsorbent surface and the species distribution of phenol. Surface distribution mainly depends upon the pH of the system. This is attributed to the change of the charge of the adsorbent surface with the change in pH value. It can be seen in Fig. 5 that the removal efficiency almost increased when the pH increased from 3.0 to 8.0, and dropped sharply with the increase of pH higher than 8.0. The pKa value of phenol is 9.9 and the pH of the zero-point charge of the MCA is about 6.2 [35]. At low pH values, the surface of the MAC would be protonated and resulted in a stronger attraction for negatively charge phenolate ions. Phenol, partially ionizes in solution. These ions are negatively charged and are directly attracted to the protonated surface of MAC via to electro-static force. Un-ionized phenol molecules would also be attracted, possibly, by physical force. At high pH, OH⁻ ions would compete with the phenol molecules for sorption sites. Sorption of excess of OH⁻ ions could convert an initial positively charged surface of MAC into a negatively charged surface resulting repulsion of negatively charged phenoxide ions and adsorption decreased [36].

3.3.2. Effect of carbon dose

The removal of phenol increased with increasing adsorption capacity of MAC (Fig. 5). The increasing phenol removal may be due to the increased adsorbent surface area and availability of more vacant surfaced sites. The removal percentages of the phenol increase when the adsorbent dosage is increased. This is because the increment of the adsorbent increases the availability of the surface area for the adsorption process, in which more of the phenol uptake onto the surface of the MAC could occur [37,38].

3.3.3. Effect of time

Figure 5 shows the removal efficiency of the MCA increased with contact time. It was also observed that phenol uptake is rapid in the beginning and thereafter it proceeds at a slower rate and finally is constant. This is probably due to a larger surface area of the MAC being available at the beginning for the adsorption of
phenol. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which
the adsorbate is transported from the exterior to the interior sites of the adsorbent particles.

3.3.4. Effect of initial phenol concentration

Figure 5 shows that the removal efficiency decreases with the increase in the initial concentration of phenol.
The initial phenol concentration provides the necessary driving force to overcome the resistances to the mass
transfer of phenol between the aqueous phase and the solid phase. The increase in initial phenol
concentration also enhances the interaction between phenol and the MCA. Therefore, an increase in initial
concentration of phenol enhances the adsorption uptake of phenol. This is due to the increase in the driving
force of the concentration gradient produced by the increase in the initial phenol concentration [11,39].

4. Conclusions

The Fe$_3$O$_4$ nanoparticles has been successfully synthesized by a green method using green tea extract. RSM
was used to find out the best conditions in the production of Fe$_3$O$_4$ nanoparticles. The optimum parameters
for green synthesis of Fe$_3$O$_4$ nanoparticles are the concentration of iron chloride salt (67 mmol), extract
volume (12.5 ml), time (92 min), and temperature (53 °C). This green procedure has many advantages such
as, high yields and easy to use on an industrial scale as well as economically viable. No toxic reagents or
surfactant template was required in this protocol, which consequently enables the bioprocess with the
advantage of being environmentally friendly. The optimum parameters for green synthesis of Fe$_3$O$_4$
nanoparticles were used for green synthesis of MAC. The characteristic of MAC was assessed by using SEM,
XRD, FTIR, and VSM. The XRD, FE-SEM and VSM results revealed that the synthesized MAC was
paramagnetic with a saturation magnetization of 25 emu/g at room temperature and consequently could be
separated from a solution by using a magnet. All the obtained results indicate that MAC can be used as an
economical and effective adsorbent for phenol removal from industrial effluents and wastewater. The RSM
method was successfully used to develop a mathematical model for reducing phenol. The value of $R^2 > 0.99$
for the obtained quadratic model indicates the high correlation between the experimental value of response
and response value predicted by the mathematical model. Numerical optimization using RSM led to the
optimum operating condition as agitation time of 65 min, phenol concentration of 500 mg/L and MAC dose
of 0.08gr (per 30 ml phenol solution) yielding phenol removal of 98%.

Declarations

Conflict of interest

"The authors declare that they have no competing interests" in this section.

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Tables

Table 1: Experimental factors and levels of the independent test variables.
| Factor | Name | Units | Type       | Subtype     | Minimum | Maximum | Coded | Values |
|--------|------|-------|------------|-------------|---------|---------|-------|--------|
| A      | A    | mmol  | Numeric    | Continuous  | 1       | 149.5   | -1.000=1 | 1.000=100 |
| B      | B    | ml    | Numeric    | Continuous  | 1       | 29.5    | -1.000=1 | 1.000=20  |
| C      | C    | min   | Numeric    | Continuous  | 5       | 267.5   | -1.000=5 | 1.000=180 |
| D      | D    | C     | Numeric    | Continuous  | 25      | 80      | -1.000=25 | 1.000=80  |

**Table 2:** The central composite design matrix and the value of response function (gr)
| Std | Run | A: Fe Concen. | B: Extract Volume | C: Time | D: Temperature | R1(gr) |
|-----|-----|---------------|-------------------|--------|----------------|--------|
| 12  | 1   | 100           | 1                 | 180    | 80             | 0.001  |
| 6   | 2   | 1             | 20                | 180    | 25             | 0.0006 |
| 16  | 3   | 149.5         | 10.5              | 92.5   | 52.5           | 0.1787 |
| 11  | 4   | 100           | 20                | 5      | 80             | 0.0092 |
| 19  | 5   | 50.5          | 10.5              | 267.5  | 52.5           | 0.1624 |
| 22  | 6   | 50.5          | 10.5              | 92.5   | 52.5           | 0.1687 |
| 13  | 7   | 1             | 20                | 180    | 80             | 0.0014 |
| 5   | 8   | 100           | 1                 | 180    | 25             | 0.0025 |
| 4   | 9   | 100           | 20                | 5      | 25             | 0.01875|
| 3   | 10  | 1             | 20                | 5      | 25             | 0.0007 |
| 7   | 11  | 100           | 20                | 180    | 25             | 0.1626 |
| 8   | 12  | 1             | 1                 | 5      | 80             | 0.0003 |
| 20  | 13  | 50.5          | 10.5              | 92.5   | 52.5           | 0.1787 |
| 14  | 14  | 100           | 20                | 180    | 80             | 0.2162 |
| 18  | 15  | 50.5          | 29.5              | 92.5   | 52.5           | 0.1721 |
| 15  | 16  | -48.5         | 10.5              | 92.5   | 52.5           | 0      |
| 2   | 17  | 100           | 1                 | 5      | 25             | 0.0014 |
| 1   | 18  | 1             | 1                 | 5      | 25             | 0.0003 |
| 21  | 19  | 50.5          | 10.5              | 92.5   | 52.5           | 0.1621 |
| 9   | 20  | 100           | 1                 | 5      | 80             | 0.0006 |
| 10  | 21  | 1             | 20                | 5      | 80             | 0.0006 |
| 17  | 22  | 50.5          | -8.5              | 92.5   | 52.5           | 0      |

**Table3**: The ANOVA for response surface quadratic model for magnetic nanoparticles
| Source               | Sum of squares | df | Mean square | F value | Prob > F |
|---------------------|----------------|----|-------------|---------|----------|
| **Model**           | 0.15           | 14 | 0.011       | 70.48   | 0.0001   |
| **A-Fe Concen.**    | 0.036          | 1  | 0.036       | 229.13  | 0.0001   |
| **B-Extract volume**| 0.034          | 1  | 0.034       | 221.81  | 0.0001   |
| **C-Time**          | 2.528E-005     | 1  | 2.528E-005  | 0.16    | 0.6985   |
| **D-Temperature**   | 1.099E-004     | 1  | 1.099E-004  | 0.71    | 0.4278   |
| **AB**              | 1.999E-003     | 1  | 1.999E-004  | 1.29    | 0.2936   |
| **AC**              | 0.018          | 1  | 0.018       | 116.20  | 0.0001   |
| **AD**              | 6.707E-005     | 1  | 6.707E-005  | 0.43    | 0.5316   |
| **BC**              | 0.018          | 1  | 0.018       | 115.65  | 0.0001   |
| **BD**              | 9.084E-005     | 1  | 9.084E-005  | 0.59    | 0.4691   |
| **CD**              | 2.297E-004     | 1  | 2.297E-004  | 1.48    | 0.2631   |
| **A^2**             | 7.773E-003     | 1  | 7.773E-003  | 50.11   | 0.0002   |
| **B^2**             | 8.424E-003     | 1  | 8.424E-003  | 54.31   | 0.0002   |
| **C^2**             | 6.499E-005     | 1  | 6.499E-005  | 0.42    | 0.5381   |
| **D^2**             | 0.047          | 1  | 0.047       | 303.83  | 0.0001   |
| **Residual**        | 1.086E-003     | 7  | 1.551E-004  |         |          |
| **Lack of Fit**     | 9.460E-004     | 5  | 1.892E-004  | 2.71    | 0.2913   |
| **Pure Error**      | 1.397E-004     | 2  | 6.985E-005  |         |          |
| **Cor Total**       | 0.15           | 21 |             |         |          |

**Table 4**: The central composite design matrix and the value of response function (Removal%)
| Std | Run | A: pH | B: Concent. | C: Time | E: Dosage | Response 1 |
|-----|-----|-------|-------------|---------|-----------|------------|
| 5   | 1   | 3     | 30          | 10      | 0.15      | 21.68      |
| 20  | 2   | 7.5   | 515         | 65      | 0.08      | 95.21      |
| 14  | 3   | 12    | 30          | 120     | 0.15      | 51.16      |
| 16  | 4   | 12    | 1000        | 120     | 0.15      | 44.17      |
| 10  | 5   | 12    | 30          | 120     | 0.01      | 42.49      |
| 8   | 6   | 12    | 1000        | 10      | 0.15      | 17.84      |
| 13  | 7   | 3     | 30          | 120     | 0.15      | 47.12      |
| 19  | 8   | 7.5   | 515         | 175     | 0.08      | 98.71      |
| 22  | 9   | 7.5   | 515         | 65      | 0.08      | 95.41      |
| 6   | 10  | 12    | 30          | 10      | 0.15      | 25.78      |
| 21  | 11  | 7.5   | 515         | 65      | 0.08      | 95.21      |
| 18  | 12  | 7.5   | 515         | 65      | 0.22      | 99.61      |
| 4   | 13  | 12    | 1000        | 10      | 0.01      | 13.86      |
| 3   | 14  | 3     | 1000        | 10      | 0.01      | 8.35       |
| 11  | 15  | 3     | 1000        | 120     | 0.01      | 33.69      |
| 2   | 16  | 12    | 30          | 10      | 0.01      | 19.41      |
| 12  | 17  | 12    | 1000        | 120     | 0.01      | 38.51      |
| 7   | 18  | 3     | 1000        | 10      | 0.15      | 12.41      |
| 1   | 19  | 3     | 30          | 10      | 0.01      | 15.25      |
| 9   | 20  | 3     | 30          | 120     | 0.01      | 39.48      |
| 15  | 21  | 3     | 1000        | 120     | 0.15      | 39.25      |
| 17  | 22  | 7.5   | 1485        | 65      | 0.08      | 69.23      |

**Table 5:** The ANOVA for response surface quadratic model
| Source  | Sum of squares | df | Mean square | F value | P-value  |
|---------|---------------|----|-------------|---------|----------|
| Model   | 20833.94      | 14 | 1488.14     | 42965.80| <0.0001  |
| A-pH    | 80.96         | 1  | 80.96       | 2337.35 | <0.0001  |
| B-Concen.| 184.21        | 1  | 184.21      | 5318.62 | <0.0001  |
| C-Dozage| 146.23        | 1  | 146.23      | 4221.94 | <0.0001  |
| D-Time  | 2532.35       | 1  | 2532.35     | 73114.58| <0.0001  |
| AB      | 1.80          | 1  | 1.80        | 52.04   | 0.0002   |
| AC      | 0.061         | 1  | 0.061       | 1.77    | 0.2253   |
| AD      | 0.36          | 1  | 0.36        | 10.48   | 0.0143   |
| BC      | 6.06          | 1  | 6.06        | 175.08  | <0.0001  |
| BD      | 1.58          | 1  | 1.58        | 45.66   | 0.0003   |
| CD      | 2.80          | 1  | 2.80        | 80.76   | <0.0001  |
| $A^2$   | 9590.07       | 1  | 9590.07     | 2.769E+005| <0.0001  |
| $B^2$   | 234.29        | 1  | 234.29      | 6764.54 | <0.0001  |
| $C^2$   | 1.85          | 1  | 1.85        | 53.50   | 0.0002   |
| $D^2$   | 298.17        | 1  | 298.17      | 8608.82 | <0.0001  |
| Residual| 0.24          | 7  | 0.035       |         |          |
| Lack of Fit | 0.22   | 5  | 0.043       | 3.24    | 0.2527   |
| Pure Error  | 0.027     | 2  | 0.013       |         |          |
| Cor Total | 20834.18   | 21 |             |         |          |

**Figures**
Figure 1

a) Normal plot and b) predicted values of residuals of Fe3O4 MNPs

Figure 2

Response surface graph showing variable interactions to different parameters
Figure 3

SEM image of A) activated carbon and B) MAC
Figure 4

a) Normal plot of residuals and b) predicted values of MAC
Figure 5

Response surface graph showing variable interactions to different parameters, (a) concentration and pH, (b) dosage and concentration, (c) time and pH, (d) dosage and concentration, (e) time and concentration and (f) time and dosage.

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