



Parametric optimization and structural feature analysis of humic acid extraction from lignite

Tazien Rashid^{a,b}, Farooq Sher^{c,*}, Mazura Jusoh^{b,d,e}, Tayab Ali Joya^f, Shengfu Zhang^{g,h}, Tahir Rasheedⁱ, Eder C. Lima^j

^a Department of Chemical Engineering Technology, Government College University, Faisalabad 38000, Pakistan

^b Institute of Bioproduct Development, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia

^c Department of Engineering, Nottingham Trent University, Nottingham NG11 8NS, United Kingdom

^d Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia

^e Advanced Material and Separation Processes Research Group (AMSET), Universiti Teknologi Malaysia, Johor Bahru, Johor, Malaysia

^f Department of Chemical Engineering, NFC Institute of Engineering and Fertilizer Research, Faisalabad, Pakistan

^g College of Materials Science & Engineering, Chongqing University, Chongqing 400044, PR China

^h Chongqing Key Laboratory of Vanadium-Titanium Metallurgy & Advanced Materials, Chongqing University, Chongqing 400044, PR China

ⁱ Interdisciplinary Research Center for Advanced Materials, King Fahd University of Petroleum and Minerals (KFUPM), Dhahran 31261, Saudi Arabia

^j Institute of Chemistry, Federal University of Rio Grande do Sul (UFRGS), Av. Bento Goncalves 9500, PO Box 15003, ZIP 91501-970, Porto Alegre, RS, Brazil

ARTICLE INFO

Keywords:

Energy engineering
Environmental management
Lignite coal
Humic acid
pH fractionation
Response surface methodology and bioenergy

ABSTRACT

Humic acid (HA) is a complex organic compound made up of small molecules. A variety of raw materials are used to manufacture HA, due to which the structure and composition of HA vary widely. In this study, nitric acid oxidation of two coal samples from Lakhra (Pakistan) was followed by HA extraction using 2.5, 3.0 and 3.5% KOH solutions. The impact of different operating parameters such as; the effect of KOH concentrations, KOH-coal proportion, extraction time and pH range influencing the HA extraction efficiency was optimally investigated. Commercial HA applications possess numerous challenges, including valuable applications and sub-optimal extraction techniques. A significant limitation of conventional experimental methods is that they can only investigate one component at a time. It is necessary to improve the current processing conditions, this can only be achieved by modelling and optimization of the process conditions to meet market demands. A comprehensive evaluation and prediction of HA extraction using Response Surface Methodology (RSM) are also being reported for the first time in this study. The maximum HA extraction efficiency of 89.32% and 87.04% for coal samples 1 and 2 respectively was achieved with the lowest possible pH of 1.09 (coal sample 1) and 1 (coal sample 2), which is remarkably lower as compared to those reported in the literature for conventional alkaline extraction process. The model was evaluated for two coal samples through the coefficient of determination (R^2), Root Means Square Error (RMSE), and Mean Average Error (MEE). The results of RSM for coal sample 1 ($R^2 = 0.9795$, RMSE = 4.784) and coal sample 2 ($R^2 = 0.9758$, RMSE = 4.907) showed that the model is well suited for HA extraction efficiency predictions. The derived humic acid from lignite coal was analyzed using elemental analysis, UV-Visible spectrophotometry and Fourier-transformed infrared (FTIR) spectroscopy techniques. Scanning Electron Microscopy (SEM) was applied to analyze the morphological modifications of the extracted HA after treatment with 3.5% KOH solution. For agricultural objectives, such as soil enrichment, enhancing plant growth conditions, and creating green energy solutions, this acquired HA can be made bioactive. This study not only establishes a basis for research into the optimized extraction of HA from lignite coal, but it also creates a new avenue for the efficient and clean use of lignite.

1. Introduction

Lignite, consisting 40% of the naturally occurring coal reserves

possesses a tremendously complex structure and composition (Sarlaki et al., 2019). Lignite is considered a low-grade fuel as it has low calorific value and higher moisture, ash, and organic oxygen contents (Fatima

* Corresponding author. Department of Engineering, School of Science and Technology, Nottingham Trent University, Nottingham NG11 8NS, United Kingdom.
E-mail address: Farooq.Sher@ntu.ac.uk (F. Sher).

et al., 2021; Zhang et al., 2019). In addition, coal burning leads to carbon emissions and acid rain which leads to the reconsideration of coal in clean and highly effective ways (Sarlaki et al., 2019; Fatima et al., 2021). It is not suitable to burn lignite directly, therefore it is recommended to develop feedstocks for value-added chemicals as it contains higher organic oxygen contents. Amongst all other techniques utilizing lignite as a non-fuel humic acid extraction is of utmost importance (Sarlaki et al., 2019). Humic acid is a macromolecular substance consisting of various aromatic components with a complex structure. The heavy presence of carboxyl- and phenol-functional groups in a single macro-molecule creates a complex set of contrasting properties (Sarlaki et al., 2019; Cheng et al., 2019). This allows application in a variety of fields that includes pharmaceuticals, agronomy, environmental protection and bio-based industry (Sarlaki et al., 2019; Fatima et al., 2021; Chen et al., 2022).

The compounds within the humic acid are subdivided into two groups i.e. majority compounds and minority compounds. The majority of compounds are anionic oxygen groups phenol, carboxyl and hydroxyl groups. Minor compound groups contain carbonyl, meth-oxy and sulfonic groups (Wang et al., 2017; Ciarkowska et al., 2017). The main techniques to extract humic acid from lignite are biological methods and acid/alkaline extraction methods (Das et al., 2015). The acid extraction method has many impurities due to which this method is not much practiced and hence humic acid production is restricted. A possible reason for that could be HA is insoluble in an acidic environment (Fatima et al., 2021). The biological method offers many advantages over the acid extraction method for example mild reaction conditions, environmental friendly and highly active product is achieved (Fatima et al., 2021; Li and Yuan, 2021). Unfortunately, the reaction rates are very low with a long reaction time. Presently, alkaline extraction is the widely used technique for humic acid production due to its low-cost operation and easy recyclable solvents (Cheng et al., 2019; Kurniati et al., 2018a).

The major limitation of alkaline extraction method is that the free humic acid contents achieved are not much high which makes this process limited for commercial humic acid production. There is a need to optimize pH conditions of the alkali extraction process in order to increase the yield of HA. This could be achieved by adopting peroxidation of the lignite coal samples with nitric acid as well as optimizing the alkali extraction process (Cheng et al., 2019; Doskočil et al., 2018). Pakistan has large coal reserves of various coal types. By far, 185 billion tons of coal reserves have been confirmed of which, 63% of coal is of low quality and primarily is lignite under coal classification having a high content of humic acid (Zara et al., 2017; Sabar et al., 2020). Large reserves are found in the central and southwest of Sindh province (Thar, Lakhra). Baluchistan also has lignite coal mines, like Chamalang, Loralai, etc. Khushab, Mianwali and Makarwal are other known areas of lignite coal within Punjab. Recently, considerable quantities of lignite have been identified in Kotli (Azad Kashmir) and Naran-Chilas region in the Khyber-Pakhtunkhwa (Zara et al., 2017; Sabar et al., 2020). The use of Pakistani coal for the extraction of humic acid has been rarely investigated.

Lignite coal is widely used for the effective separation of humic acid. NaOH has been commonly employed as a HA extractant because of its reduced cost. It does, however, have a number of limitations such as sodium humate possesses undesirable high Na contents $\approx 7.5\%$ (Das et al., 2015). Due to its negative effects on soil permeability and nutrient balance, adding Na to soil has a negative impact on soil fertility (Nazarbek et al., 2022). Utilizing KOH as an extracting agent is a preferred choice as it not only produces HA with the highest purity yields but also has a high amount of K contents (Cheng et al., 2019). As increased K contents in soil result in increased crop yield and protected abiotic and biotic stresses. In addition, potassium is essential for the movement of sugars and other photosynthetic byproducts from leaves to storage organs (Ye et al., 2022). Additionally, it has been proven that KOH eliminates bioactive components from Leonardite coal including

bio-stimulants and natural growth hormones (Wang et al., 2017).

Literature has reported that process optimization is an effective tool for the implementation and assessment of each process variable on the overall efficiency of any process (Rashid et al., 2018). The “one-factor-at-a-time” approach is the most commonly used but unfortunately, it is complicated as well as inefficient and time taking. Additionally, the projected optimized parameters are rarely assured (Rashid et al., 2021a). Empirical approaches can be used to address the drawbacks of the one-factor-at-a-time optimization strategy. The statistical-based technique (Response Surface Methodology) is the basic approach to these empirical methods. Box and Wilson established the Response Surface Methodology (RSM) (empirical method), which is generally employed for statistical analysis, experimental designing, factor evaluation and selection of ideal conditions (Rashid et al., 2021b). It can use a limited amount of experimental data to optimize processes in the chemical industry. Response surface methodology (RSM) is widely used for response surface mapping to the section of a specific study, yield optimization as well as operating parameters selection (Maran et al., 2017). RSM was recently used to manage and optimize the operating conditions for the osmotic dehydration of papaya, banana, pepper, and potato (El-Aouar et al., 2006; Ozdemir et al., 2008; Mercali et al., 2011; Tazien et al., 2021). Recently, RSM was used to improve the efficiency of lignin extraction utilizing protic ionic liquids while maintaining the lignin's natural structure (Rashid et al., 2018, 2021b).

The extraction of humic acid from Pakistani lignite coal has rarely been investigated. Therefore, in present study the process of acquiring HA from various samples of Pakistani lignite was investigated with a focus on exploring the optimal process conditions and optimization by using Response Surface Methodology (RSM) to achieve the highest yield. To the best of our knowledge, no significant research has yet been focused on the ideal process parameters and optimization of HA produced from Pakistani lignite coal. The research reports that HA extraction efficiency is significantly influenced by metallic impurities and pH. The optimized conditions for pH can lead to an increased yield of HA for commercial applications. The product, humic acid and raw lignite were characterized using UV spectroscopic analysis, Fourier transform infrared (FTIR) spectroscopy and Scanning Electron Microscopy (SEM).

2. Materials and methods

2.1. Materials

Coal samples were acquired from different local coal mines in Baluchistan. Analytical grade potassium hydroxide in controlled concentrations (65% and 98%), concentrated HCl (36.9%) and nitric acid (99%) was purchased from Merck, Karachi, Pakistan. All the chemicals were used without further purification. Solutions of required concentrations (2.5, 3, 3.5 and 4 wt% of KOH) were prepared with triple distilled water. The raw coal samples were pulverized and sieved to create three ranges of particle sizes i.e. (0.1–0.3 mm), (0.3–0.5 mm) and (0.5–1 mm). Proximate analysis of all coal samples was performed (Sher et al., 2020) and their parent humic acid content was determined by FTIR spectroscopy (Rehman et al., 2022).

2.2. Proximate and ultimate analysis

Bulk coal samples of approximately 25 kg were collected from Lakhra. About 5 kg of two coal samples were selected for the experimental study. Various particle size ranges (0.1–0.3 mm), (0.3–0.5 mm) and (0.5–1 mm) were prepared by rolling and crushing using a disc mill. For test work minimum particle size (0.1–0.3 mm) was selected and sealed in plastic bags (Rashid et al., 2018). Proximate and ultimate analysis for the two coal samples acquired from different coal mines of Lakhra was performed (Doskočil et al., 2018; Rashid et al., 2018). The chemical compositions of the coal samples were analyzed from NIBGE. The ash and moisture contents were calculated using the corresponding

standard techniques i.e. (LAP-005) and (LAP-001) respectively. The results of proximate and ultimate analysis are given in Table 1.

2.3. Humic acid extraction from lignite coal

In a typical run, a measured amount of lignite coal sample was contacted with 125 mL of potassium hydroxide (KOH) solution of variable concentration in a 200 mL Pyrex beaker. The beaker was stirred for a variable time, ranging from 120 to 360 min in a temperature-controlled oil bath at atmospheric pressure. The temperature of all measurements was maintained at 298.15 K. Upon the completion of this extraction step, the pH of the sample was modulated to less than 2 by the addition of HCl acid. The precipitates of humic acid are separated by centrifugation. In order to remove alkali metals, the precipitates were repeatedly washed using HNO₃ and HF solutions, followed by multiple washing with distilled cold water. This step leads to the removal of alkali metals from HA (Table 2). The precipitate was passed through a filtration medium using a vacuum filtration assembly. The residue of the filtration is the humic acid, which was then dried in a vacuum oven at 50 °C and analyzed for composition using Eq. (1) (Lamar et al., 2014; Lamar and Talbot, 2009). Fig. 1 shows the proposed methodology for the humic acid extraction in this study.

$$HA (\%) = \frac{\text{Dried weight of residual coal}}{\text{Dried weight of humates rich lignite coal}} \times 100 \quad (1)$$

2.4. Experimental design

The existing models are being used to optimize HA production and to create a process that is both energy efficient and sustainable. For the commercialization of HA production, such a study can be more helpful in achieving high HA production at lower energy inputs. The extraction parameters are KOH Concentration (2, 2.25, 2.5, 2.75, 3.0 and 3.5%), time (120, 180, 240 and 360 min) and pH (1, 1.25 and 1.50) respectively. For complete range of parameters, HA extraction efficiency (%) was calculated.

2.5. Characterisation

Various characterization techniques such as UV spectroscopic analysis, Fourier transform infrared (FTIR) spectroscopy and Scanning Electron Microscopy (SEM) (Kurniati et al., 2018b; Lu et al., 2020; Iftikhar et al., 2022) were used for the feed coal samples and the resulting humic acid product. Detailed testing on the coal samples and humic acid was performed to investigate the content of humate, K₂O, chloride and hazardous metals (lead, cobalt and arsenic) (Al-Atta et al., 2022).

2.6. Determination of humic acid through spectrophotometry

UV-Vis spectroscopy at a wavelength of 465 nm was performed to measure the concentrations of HA in the solution (Skulcova et al., 2017; Zhang et al., 2017), stock solutions of known concentrations (50–200 ppm) were prepared for calibration according to the procedure adopted by Rashid et al. (2016). The UV-Vis calibration curve obtained from concentration vs absorbance data were plotted (Asing et al., 2009). The standardized calibration curve method was used to calculate the concentration of each of the unknown coal samples (Rashid et al., 2016;

Table 1
Proximate and ultimate analysis of lignite coal samples.

| Lignite | Proximate analysis (wt%) | | | Ultimate analysis (wt%) | | | | | Atomic ratio | |
|---------------|--------------------------|----------------------|-------|-------------------------|-------|------|------|-------|--------------|------|
| | Moisture contents (MC) | Volatile matter (VC) | Ash | C | H | N | S | O | H/C | O/C |
| Coal sample 1 | 13.20 | 14 | 25.80 | 44.30 | 38.60 | 0.80 | 0.20 | 16.10 | 0.87 | 0.36 |
| Coal sample 2 | 14.70 | 13 | 26.10 | 43.10 | 38.10 | 0.90 | 0.20 | 17.70 | 0.88 | 0.39 |

Table 2

Alkali metal contents of raw lignite coal (sample 1 and sample 2) and HA after (HNO₃ and HF washing).

| Metal contents | Coal sample 1 | | Coal sample 2 | |
|----------------------|---------------|--------------------------------------|---------------|--------------------------------------|
| | Lignite coal | HA (HNO ₃ and HF washing) | Lignite coal | HA (HNO ₃ and HF washing) |
| Humic acid (%) | 62.10 | 89.18 | 62.90 | 87.44 |
| K ₂ O (%) | 0.02 | 0.02 | 0.06 | 0.06 |
| Cl (%) | 0.03 | 0.01 | 0.08 | 0.02 |
| Lead (ppm) | 24 | <0.01 | 51 | <0.10 |
| Cobalt (ppm) | 14 | <7.62 | 13.40 | <8.14 |
| Arsenic (ppm) | 5.0 | <2.0 | 5.0 | <3.0 |

Ghani et al., 2021).

2.7. Development of RSM model

2.7.1. Response surface methodology

The influence of operating conditions such as; concentration (M) X₁, time (min) X₂ and pH X₃ on the extraction efficiency of HA (%) was investigated using a Box-Behnken design (Y). Statgraphics Centurion 15.2.11.0 version 8.0 was used for developing a three-factor experimental matrix. A total of 15 experimental having 3 central points were designed to conduct experiments for coal sample 1 and coal sample 2 separately. For the two selected coal samples (sample 1 and sample 2). Three coded ranges; low (−1), center (0) and high (+1) were nominated from the subsequent preliminary experimentation (Table 3). A quadratic equation (Eq. (2)) was employed for the approximation of resulting HA percentage extraction (Rashid et al., 2021b).

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i=1}^k \sum_{j=i+1}^k \beta_{ij} x_i x_j \quad (2)$$

where Y is the predicted extraction efficiency of HA (%), coefficient β₀ is the constant and β_{ii}, β_{ij} are the regression-based coefficients. To compare independent variables and HA extraction efficiency used in this study a second-degree polynomial equation was employed (Eq. (2)). To assess the significance of each regression coefficient on HA extraction efficiency, analysis of variance (ANOVA) was carried out.

3. Results and discussion

3.1. Optimization for HA extraction conditions

To study the effect of operating conditions on the extraction process a preliminary study was performed for their initial screening. To achieve this, the impact of process variables namely, KOH concentration (2, 2.5, 2.75 and 3.0) M, extraction time (120, 180, 240 and 360) mins, pH (1, 1.25 and 1.50) respectively on the percentage extraction of HA was examined.

3.2. Effect of sample to extractant ratio

The impact of sample to extractant ratio (sample loading) on the HA extraction was investigated by making individual samples of 1:5, 1:10,

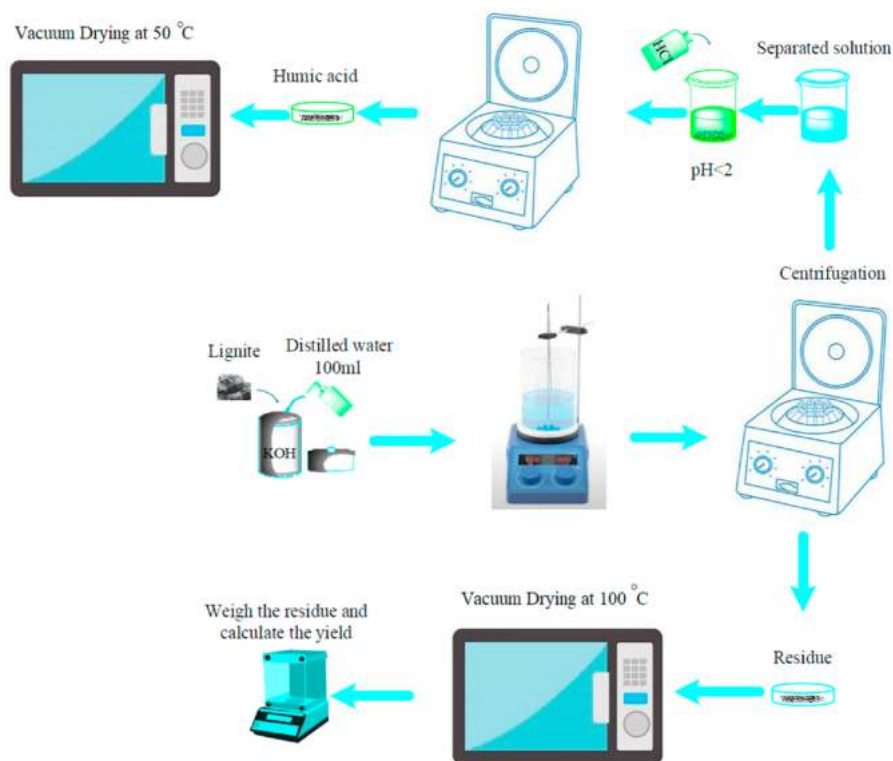


Fig. 1. The proposed methodology scheme for the humic acid extraction.

Table 3

Three coded ranges selected for RSM-based optimization studies.

| Factors | Symbol | Coded levels | | |
|-------------------------|--------|--------------|------|------|
| | | -1 | 0 | +1 |
| Molar concentration (M) | X_1 | 2.0 | 2.75 | 3.5 |
| Time (min) | X_2 | 120 | 180 | 240 |
| pH | X_3 | 1.0 | 1.25 | 1.50 |

1:15 and 1:20 extractant ratio. A slight difference in extraction percentage of HA was observed between the extraction ratios of 1:5 and 1:10 respectively. However, it was observed that extraction of HA was reduced to 25–60% by increasing the ratio to 1:20. Based on these observations it is suggested that the recommended optimal sample to extractant ratio is either 1:5 or 1:10 for HA extraction from humic substances (Zara et al., 2017). This may be explained in light of literature as; the sample to extractant ratio of <1:10 causes the lignite sample and KOH mixture to have a lower cohesive energy, which lowers the HA extraction. Moreover, KOH ion kinesis is decreased as the viscosity of the lignite sample and KOH mixture increases at a sample to extractant ratio of >1:10. Therefore, the 1:10 sample to extractant ratio is advised by the International Humic Compounds Society (IHSS) because it yields the highest proportion of HA when extracted from humic compounds (Fatima et al., 2021). For the present study 1:10 ratio was selected for easy handling of the sample during the experimentation process.

3.3. Effect of KOH concentration

Humic Acid extraction was studied using four different KOH molar concentrations (2, 2.25, 2.5, 2.75 and 3) M respectively (Fig. 2). Individual 50 gm of coal samples (coal sample 1 and coal sample 2) were loaded with 250 mL of KOH solution with various molar concentrations (2, 2.25 2.50, 2.75, 3 and 3.5) M respectively to investigate the effect of KOH molar concentration on HA extraction. (Fig. 2 (a)) depicts that HA extraction increased significantly with an increase in KOH molar

concentration from 2 to 3 M. As expected, increasing the KOH molar concentration from 3 to 3.5 M resulted in a decrease in % extraction of HA (Cheng et al., 2019). This could be attributed to the reason that with an increase in KOH concentration lignite comes completely in contact which leads to the complete oxidation reaction (de Souza and Bragança, 2018). However, this increase in HA extraction rate no longer increases when the KOH concentration reaches a certain concentration of 3–3.5 M. This may be due to the reason that the intermolecular interactions holding fulvic acids to HA were disrupted and enhanced by increased KOH concentration (Asing et al., 2009). Possibly ester-type linkages or H-bonding are one of them which alter the fulvic acid and HA ratio (Cheng et al., 2019; Asing et al., 2009; de Souza and Bragança, 2018). Consequently, less HA was precipitated after the alkali extract was acidified which is in accordance with the reported literature (Asing et al., 2009). Considering the results of the current experiments, KOH concentration in the range of (2.75, 3 and 3.5) M was carefully chosen for further optimization studies. This could prevent the need for using excessive solvent during the HA extraction process.

3.4. Effect of time

Once the optimal KOH concentration has been determined, the effect of extraction time (120, 180, 240 and 360) mins was investigated for coal sample 1 and coal sample 2 respectively. It was observed as the time increased, HA extraction increased nearly linearly before showing a decline in extraction till the attainment of equilibrium at 240 min for coal sample 1 and coal sample 2 respectively (Fig. 2(b-c)) indicating that maximum HA is extracted after reaching equilibrium (Rashid et al., 2018). This phenomenon of reduced HA extraction with prolonged extraction time could be attributed to the reason that HA could easily decompose and degrade at extended extraction times (Cheng et al., 2019; Li and Yuan, 2021). Larger time periods correspond to more energy usage and financial consequences. Thus, a time range of 120–240 min was chosen for additional optimization studies.

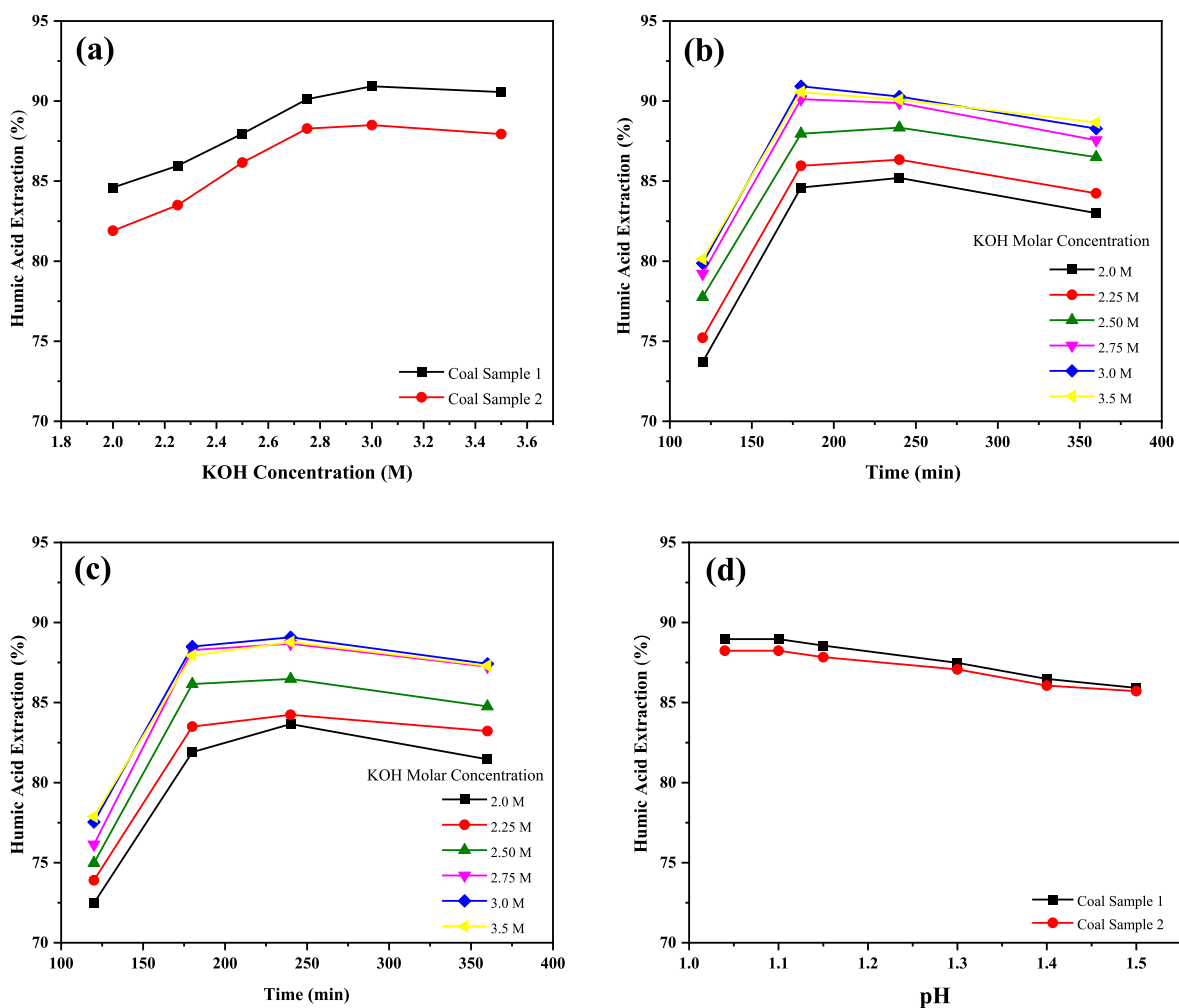


Fig. 2. Effect of operating parameters on humic acid extraction; (a) Effect of KOH concentration, (b) Effect of time using coal sample 1, (c) Effect of time using coal sample 2 and (d) Effect of pH on different coal samples.

3.5. Effect of pH

To investigate the effect of pH on HA precipitation six individual experiments were performed using optimum conditions (3 M, 240 min). Humic acid was precipitated from the humic substance (alkaline extracts) by dropwise addition of HCl at constant stirring. The pH of the samples was lowered to about 1, and the final pH values attained were 1.5, 1.4, 1.3, 1.15, 1.1 and 1.04 at room temperature. For the separation of the precipitated humic acid from soluble fulvic acid (supernatant), the suspension was centrifuged at 1200 rpm for 30 min. It is evident from Fig. 2(d) that high pH had a negative effect on the HA extraction also HA extraction was increased at lower pH values. A possible description for the higher HA extraction at lower pH may be due to the reason that HA is composed of a mixture of weak aliphatic (carbon chains) and aromatic (carbon rings) organic acids. These organic acids (aliphatic and aromatic) are insoluble in water under acidic conditions but soluble in alkaline conditions (Bedrock et al., 1995). HA consists of a fraction of humic substances that precipitate out from the aqueous solution when the $\text{pH} < 2$ because it is insoluble at low pH whereas the fulvic acid remains in the supernatant solution (Zhang et al., 2017; Bedrock et al., 1995). The effective pH in the range of 1–1.5 was chosen for additional optimization studies based on the findings of the current experiment.

3.6. Statistical analysis

Based on the results of the initial experimentation a Box-Behnken

design was employed to determine the effects of three independent variables namely, concentration (M) X_1 , time (min) X_2 and pH X_3 , on the extraction of HA (Y). The experiments for coal sample 1 and coal sample 2 were conducted individually. A complete design matrix was used with 15 sets of experiments (including 3 center points). Based on initial screening experiments three selected levels coded as low (−1), center (0) and high (+1) for coal sample 1 and coal sample 2 are listed in Table 3. Table 4 and Table 5, illustrate the trials produced matrix design for coal sample 1 and coal sample 2 using the Box-Behnken design. A randomized experimental sequence was used to explain how the independent factors affected the observed response (Rashid et al., 2018, 2021b). The following polynomial expression was utilized to relate the HA percent extraction to other independent variables (Eq. (3)).

$$y = \beta_0 + \sum_{i=1}^k \beta_{ixi} + \sum_{i=1}^k \beta_{iixi^2} + \sum_{i=1}^k \sum_{j=i+1}^k \beta_{ijxixj} \quad (3)$$

where Y is the predicted extraction efficiency of HA (%), coefficient β_0 is the constant and β_{ii} , β_{ij} are the regression-based coefficients. A second-degree polynomial equation based on Eq. (3) was utilized to associate HA extraction with other independent variables.

Table 4

The generated matrix design of the experiments using the Box-Behnken model for HA extraction from Coal sample 1.

| Run | Molar concentration | Time | pH | HA extraction (%) | |
|-----|---------------------|----------------------|---------------------|-------------------|-------------|
| | X ₁ (M) | X ₂ (min) | X ₃ (pH) | Experimental | Box-Behnken |
| 1 | 2.75 | 180 | 1.25 | 87.48 | 87.48 |
| 2 | 2.75 | 240 | 1.50 | 85.92 | 85.98 |
| 3 | 2.00 | 240 | 1.25 | 84.60 | 85.94 |
| 4 | 3.50 | 180 | 1.00 | 87.92 | 89.32 |
| 5 | 2.75 | 120 | 1.50 | 72.70 | 73.62 |
| 6 | 3.50 | 180 | 1.50 | 85.92 | 86.33 |
| 7 | 2.00 | 180 | 1.50 | 84.92 | 83.51 |
| 8 | 2.00 | 120 | 1.25 | 71.34 | 71.82 |
| 9 | 2.75 | 240 | 1.00 | 89.88 | 88.95 |
| 10 | 3.50 | 120 | 1.25 | 77.76 | 76.42 |
| 11 | 2.75 | 180 | 1.25 | 87.48 | 87.48 |
| 12 | 2.00 | 180 | 1.00 | 86.92 | 86.50 |
| 13 | 2.75 | 180 | 1.25 | 87.48 | 87.48 |
| 14 | 3.50 | 240 | 1.25 | 87.48 | 86.99 |
| 15 | 2.75 | 120 | 1.00 | 76.70 | 76.63 |

Table 5

The generated matrix design of the experiments using the Box-Behnken model for HA extraction from coal sample 2.

| Run | Molar concentration | Time | pH | HA extraction (%) | Molar concentration |
|-----|---------------------|----------------------|---------------------|-------------------|---------------------|
| | X ₁ (M) | X ₂ (min) | X ₃ (pH) | Experimental | Box- Behnken |
| 1 | 2.0 | 120.0 | 1.25 | 68.05 | 68.56 |
| 2 | 2.0 | 180.0 | 1.5 | 81.58 | 79.98 |
| 3 | 2.0 | 240.0 | 1.25 | 82.45 | 84.09 |
| 4 | 2.75 | 180.0 | 1.25 | 85.28 | 85.28 |
| 5 | 3.5 | 240.0 | 1.25 | 86.18 | 85.67 |
| 6 | 2.75 | 120.0 | 1.0 | 73.14 | 73.18 |
| 7 | 3.5 | 120.0 | 1.25 | 75.88 | 74.24 |
| 8 | 2.75 | 180.0 | 1.25 | 85.28 | 85.28 |
| 9 | 3.5 | 180.0 | 1.5 | 83.44 | 83.99 |
| 10 | 3.5 | 180.0 | 1.0 | 85.45 | 87.04 |
| 11 | 2.75 | 120.0 | 1.5 | 68.78 | 69.86 |
| 12 | 2.75 | 180.0 | 1.25 | 85.28 | 85.28 |
| 13 | 2.75 | 240.0 | 1.0 | 87.86 | 86.77 |
| 14 | 2.75 | 240.0 | 1.5 | 83.28 | 83.23 |
| 15 | 2.0 | 180.0 | 1.0 | 84.35 | 83.79 |

Table 6

Analysis of variance (ANOVA) for coal sample 1 and coal sample 2 for HA extraction.

| Source | Mean Square | | Df | F-Ratio | | P-Value | |
|--------------------------------------|---------------|---------------|----|---------------|---------------|---------------|---------------|
| | Coal sample 1 | Coal sample 2 | | Coal sample 1 | Coal sample 2 | Coal sample 1 | Coal sample 2 |
| X ₁ : Molar concentration | 15.9613 | 26.3538 | 1 | 7.91 | 9.44 | 0.0374 | 0.0277 |
| X ₂ : Time | 304.798 | 363.421 | 1 | 151.14 | 130.15 | 0.0001 | 0.0001 |
| X ₃ : pH | 17.8802 | 23.5298 | 1 | 8.87 | 8.43 | 0.0309 | 0.0337 |
| X ₁ ² | 3.93621 | 2.66769 | 1 | 1.95 | 0.96 | 0.2212 | 0.3733 |
| X ₂ ² | 139.766 | 146.083 | 1 | 69.30 | 52.31 | 0.0004 | 0.0008 |
| X ₃ ² | 0.00279231 | 1.94077 | 1 | 0.90 | 0.70 | 0.9718 | 0.4425 |
| X ₁ X ₂ | 3.1329 | 4.2025 | 1 | 1.55 | 1.50 | 0.2678 | 0.2745 |
| X ₁ X ₃ | 0.1100 | 0.1444 | 1 | 0.07 | 0.05 | 1.0000 | 0.8291 |
| X ₂ X ₃ | 0.0004 | 0.0121 | 1 | 0.00 | 0.00 | 0.9893 | 0.9501 |
| Total error | 2.0167 | 2.7924 | 5 | | | | |
| Total (corr.) | 493.665 | 578.379 | 14 | | | | |

$$\begin{aligned}
 \text{HA extraction (Sample 1)} = & -8.26806 + 15.5189 X_1 + 0.771375X_2 \\
 & - 5.0X_3 - 1.83556 X_1^2 - 0.0196667 X_1X_2 \\
 & + 0.0 X_1X_3 \\
 & - 0.00170903 X_2^{2+} + 0.000666667X_2X_3 \\
 & - 0.44 X_3^2
 \end{aligned} \tag{4}$$

$$\begin{aligned}
 \text{HA extraction (Sample 2)} = & -27.7994 + 13.5644X_1 + 0.808556X_2 \\
 & + 20.0133X_3 - 1.51111 X_1^2 \\
 & - 0.0227778 X_1X_2 + 1.01333X_1X_3 \\
 & - 0.00174722 X_2^{2-} - 0.00261725 X_2X_3 \\
 & - 11.6X_3^2
 \end{aligned} \tag{5}$$

Where the coded independent variables are X₁, X₂ and X₃, the quadratic (squared) effects are X₁², X₂² and X₃² and the interaction effects are X₁X₂, X₁X₃ and X₂X₃. Table 6 depicts the results of the analysis of variance (ANOVA) which was performed to find the significance of operating parameters effecting the HA % extraction at a P-value of 0.05. According to Rashid et al. (2021b), the linked coefficient fits the model more significantly when the p-value is less than 0.05 (Rashid et al., 2018, 2021b). It was observed that quadratic and linear effects of time (X₂) were the most significant for HA extraction. As they showed about 99.92% of significant level with the p-values ≤0.0008. Additionally, p-values (<0.05) for the linear effect of concentration (M) X₁ and pH X₃ are also significant for both coal sample 1 and coal sample 2 that are 0.0374 and 0.0309 respectively. The remaining coefficients showed no significant effects on HA extraction.

To justify the standing of the model, non-significance of these coefficients and their effects cannot be neglected, because R² for HA extraction shows up to 97.957% variability of the response (Fu and Mazza, 2011). The analysis of ANOVA showed that the response (HA Extraction) is influenced by the parameters in the order of extraction time > Molar Concentration > pH. The experimental HA extraction values were 97.95% in agreement with the model-predicted values, as shown by the coefficient of determination (R²) of the model, which was 0.97957. For the model's validation, experiments were run under predicted optimal conditions (Table 7). Table 8 shows that the presently developed model (Eq. (3) and (4)) for coal sample 1 and coal sample 2 showed an overall standard error of estimation of 1.4201 and 1.671. Which justifies the existing model's accuracy and applicability for extracting HA from Pakistani lignite coal. The findings demonstrated that the mathematical model could accurately predict HA extraction (Rashid et al., 2021b).

3.7. Interaction effects of process variables

RSM was used to investigate the impacts of the three process variables (concentration, time, and pH) on HA extraction. Two variables

Table 7

Predicted optimal conditions for model's validation and HA extraction efficiency for coal sample 1 and coal sample 2.

| Lignite coal | HA extraction (%) | Optimum operating conditions | | | HA extraction (%) |
|---------------|-------------------|--|---------------------------|------------------------|-------------------|
| | Observed values | Molar concentration X ₁ (M) | Time X ₂ (min) | pH X ₃ (pH) | Predicted values |
| Coal sample 1 | | 3.28 | 180 | 1.09 | 89.32 |
| Coal sample 2 | | 3.11 | 180 | 1.00 | 87.04 |

Table 8

Comparison of standard error attained from RSM for HA extraction from coal sample 1 and coal sample 2.

| Error prediction | Coal sample 1 | Coal sample 2 |
|------------------|---------------|---------------|
| R ² | 0.9795 | 0.97586 |
| RMSE | 4.784 | 4.907 |
| MAE | 0.6186 | 0.724 |
| SEE | 1.4201 | 1.6710 |

were assessed at a time while keeping other variables constant at central level. To determine the interaction effects of any two variables on the response (HA extraction) three-dimensional response surface and contour plots were plotted. According to the linear and quadratic coefficients, the sequence of variables that affect the HA extraction was extraction time > molar concentration > pH. The detail is discussed in the following section.

3.7.1. Interaction effect of extraction time and molar concentration

Fig. 3 depicts a response surface graph (3D plot) of HA extraction. By maintaining pH at a constant value of 1, the interaction between the effects of extraction time and molar concentration on HA extraction is displayed (since at this pH, practically all coal samples showed the same trend in HA extraction efficiency). The plot's trend specifies that HA extraction increased with longer extraction times and higher molar concentrations until plateauing at 180 min and 3 M for coal sample 1 and coal sample 2, respectively. This shows that HA % extraction

remained constant as the maximum amount of HA is being extracted at equilibrium. This indicates that increased molar concentration and time did not result in additional extraction efficiency improvements. Similar trends in the interaction effect of extraction time and molar concentration on HA extraction efficiency have been reported in the literature (Asing et al., 2009; de Souza and Bragança, 2018). Fig. 4 displays the 2D contour graphs of HA extraction. It is clearly depicted that the maximum projected value represented by the surface area is contained in a small elliptical area in the contour plot. The circular or elliptical shapes of the contour plots reflect the relevance of the variables (Rashid et al., 2021b; Govarathanan et al., 2015; Selvankumar et al., 2017). The presence of an elliptical contour plot amongst time and molar concentration suggests that the variables and their interaction effects are significant.

3.7.2. Interaction effect of molar concentration and pH

The interaction effect of molar concentration and pH on HA extraction efficiency was non-significant. From ANOVA analysis (Table 6) it can be seen that their quadratic coefficients had non-significant effects on the extraction of HA ($P > 0.05$). The response surface and contour plots of HA extraction are plotted in Figs. 5 and 6. The interaction effect of molar concentration and pH on HA extraction at a constant time of 180 (mins) are reflected. The non-significant interactions between the related variables are indicated by the circular contour plots of molar concentration and pH in Fig. 6 (Rashid et al., 2021b; Dana et al., 2020; Govarathanan et al., 2014).

3.7.3. Interaction effect of time and pH

Fig. 7 illustrates the interaction effect of time and pH on HA extraction at a constant molar concentration of 3 M (response surface plots). It is evident that with an increase in extraction time HA extraction increases, while for pH the response was the opposite phenomenon. From the current study, long extraction times and high pH levels are unfavorable for HA extraction, as they subsequently result in declining HA extraction. The increased HA extraction at reduced pH (acidic medium) could be explained in light of literature as in an acidic solution, hydrogen is linked to the functional groups on the surface of the HA. The resulting solution (Lignite coal sample + KOH) is an alkaline extract containing a humic substance. Upon addition of HCL H⁺ ions attached to humic molecules get attached to OH⁻ ions, which leads to an excessive protonation process. As previously postulated, due to this protonation the hydrophobic property of HA in acidic media allows the chains to agglomerate like micelles to lower the system's free energy. (Bedrock et al., 1995). This coiled configuration results in the complete expulsion of water around the molecules resulting in insoluble behaviour of HA at lower pH and thus HA precipitates out as shown on SEM analysis

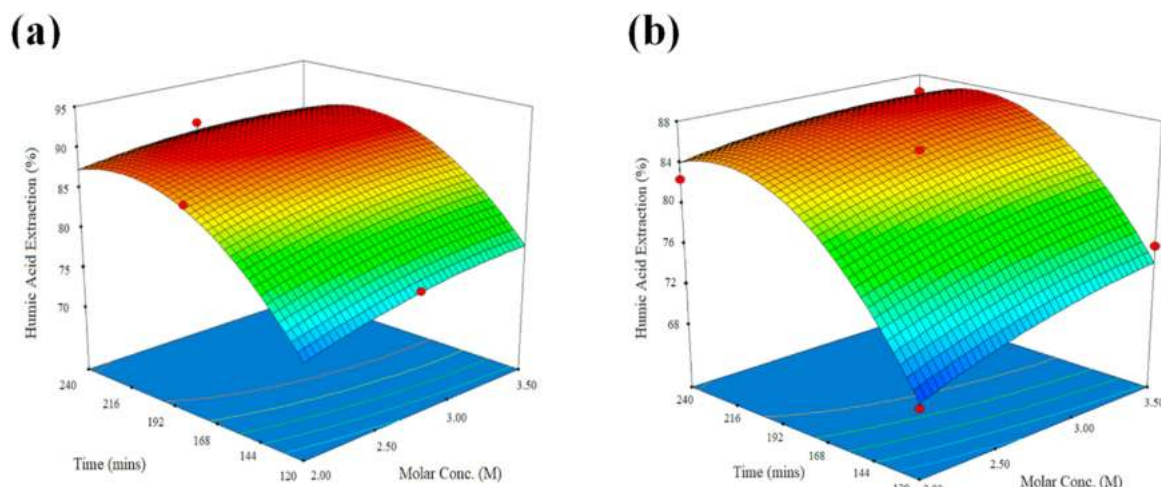


Fig. 3. The response for HA extraction as a function of molar concentration and time for (a) coal sample 1 and (b) coal sample 2 at fixed pH.

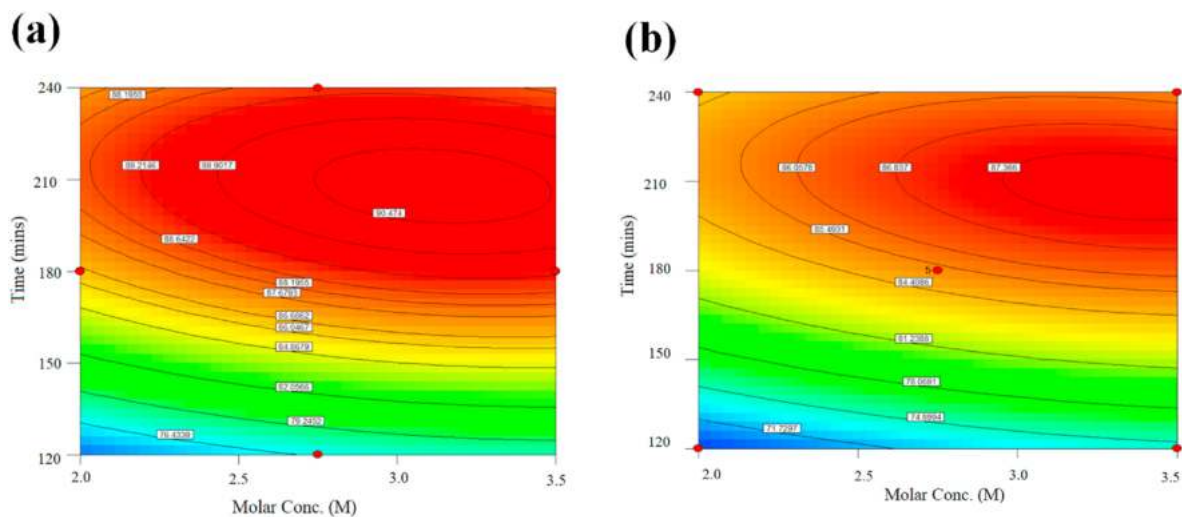


Fig. 4. Contour plot for HA extraction as a function of molar concentration and time for (a)Coal sample 1 and (b) Coal sample 2 at fixed pH.

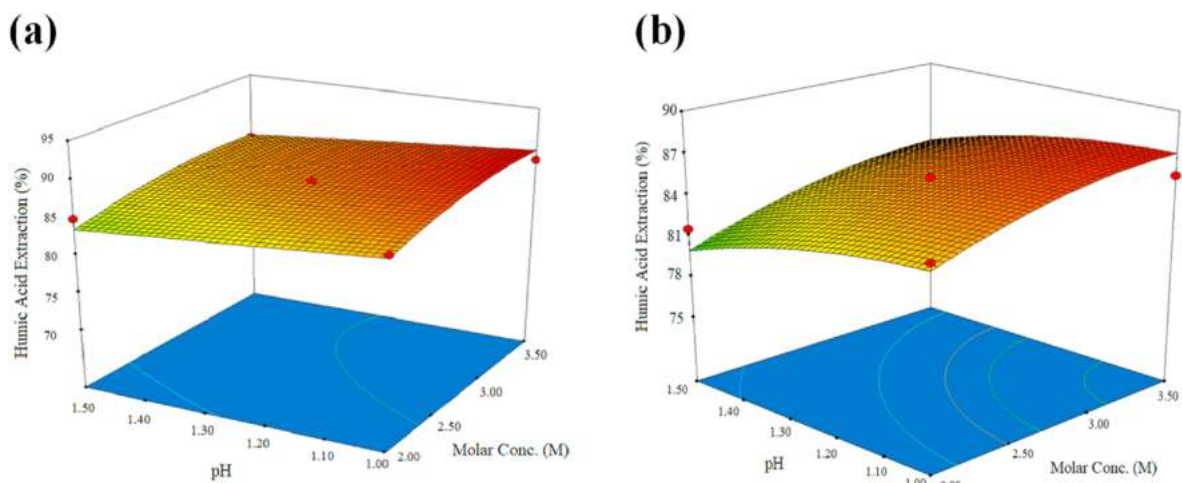


Fig. 5. The response for HA extraction as a function of pH and molar concentration for a) Coal sample 1 and (b) Coal sample 2 at a fixed time.

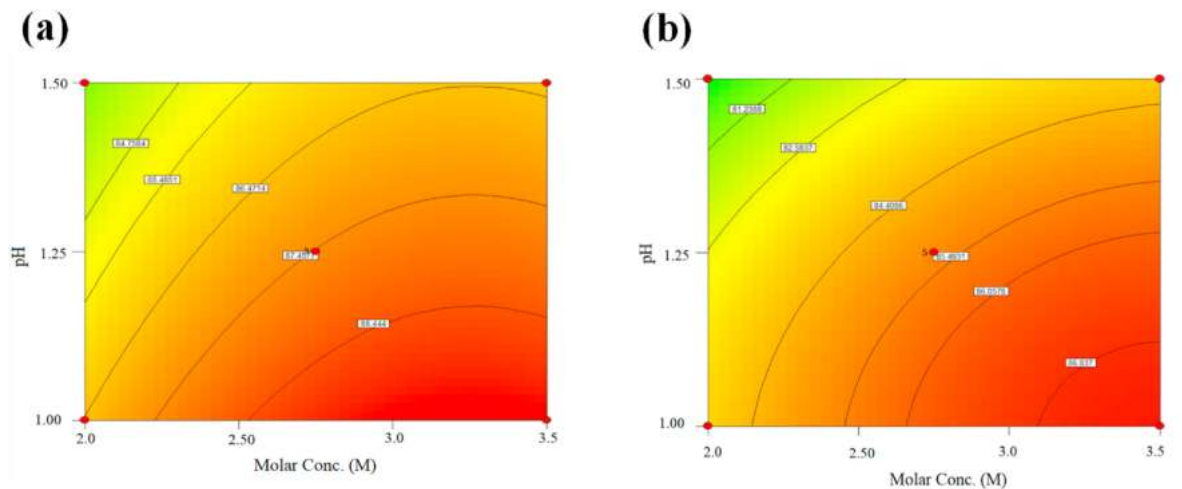


Fig. 6. Contour plot for HA extraction as a function of pH and molar concentration for a) Coal sample 1 and (b) Coal sample 2 at a fixed time.

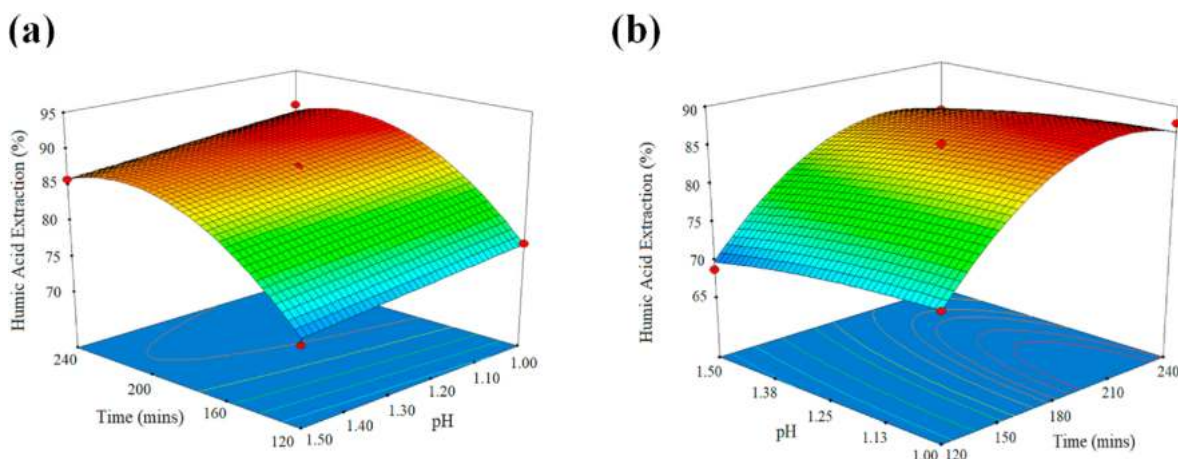


Fig. 7. The response for HA extraction as a function of pH and time for (a) Coal sample 1 and (b) Coal sample 2 at fixed molar concentration.

(Fig. 10) (de Souza and Bragança, 2018). Conversely, the decrease in HA extraction with prolonged extraction time could be considered the main attribute of the equilibrium conditions (Rashid et al., 2018). Therefore, based on the above results reduced pH with suitable extraction times is suggested for optimum HA extraction. Fig. 8 shows an elliptical contour plot of time and pH, demonstrating the significant interactions among the variables (Dana, 2019).

3.8. Characterization of extracted HA

3.8.1. Functional groups identification

In order to better understand the findings, FTIR spectroscopy was performed to confirm the chemical structure of the extracted HA from coal sample 1 and coal sample 2 (Fig. 9). FTIR spectroscopy is widely utilized to determine the functional groups and structural properties of HA at specific vibrations. The validation of functional groups using qualitative FTIR analysis such as aromatic substitutions, aliphatic structure, hydrogen bond regions and O-containing groups was conducted from 4000 to 500 cm^{-1} range values (Wang et al., 2017; Li and Yuan, 2021). Generally, the FTIR bands of lignite and HA have common characteristics and distinctive vibrations, even though the intensity of the bands varies depending on the lignite source and the extraction solvent used (de Souza and Bragança, 2018). The FTIR spectra of the present HA extracted from coal samples 1 and 2 are compared (Table 9) with that of HA extracted from lignite coal described by Asing et al.

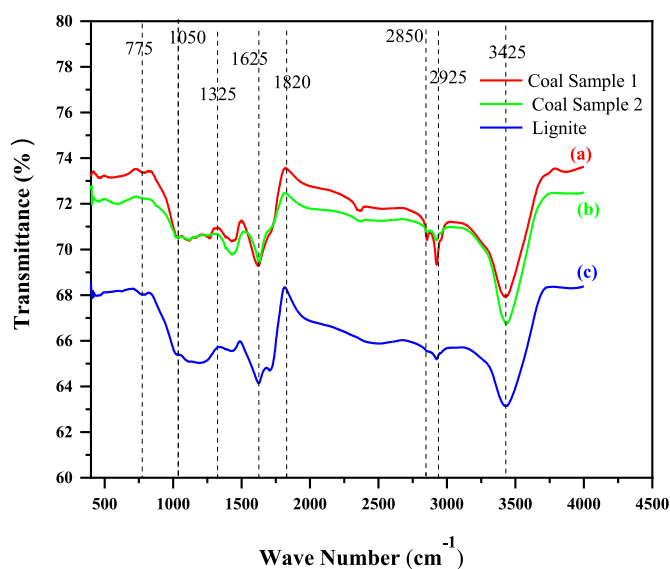


Fig. 9. Comparison of FTIR spectrum of (a) Coal sample 1, (b) Coal sample 2 and (c) Lignite.

(2009); Wang et al. (2017), this verifies the HA backbone is present in

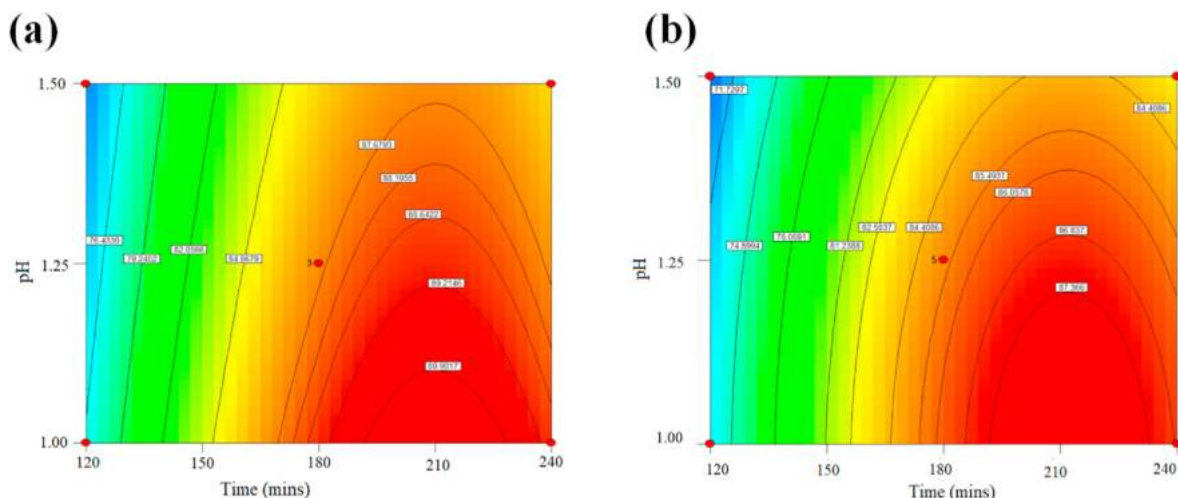


Fig. 8. Contour plot for HA extraction as a function of pH and time for (a) Coal sample 1 and (b) Coal sample 2 at fixed molar concentration.

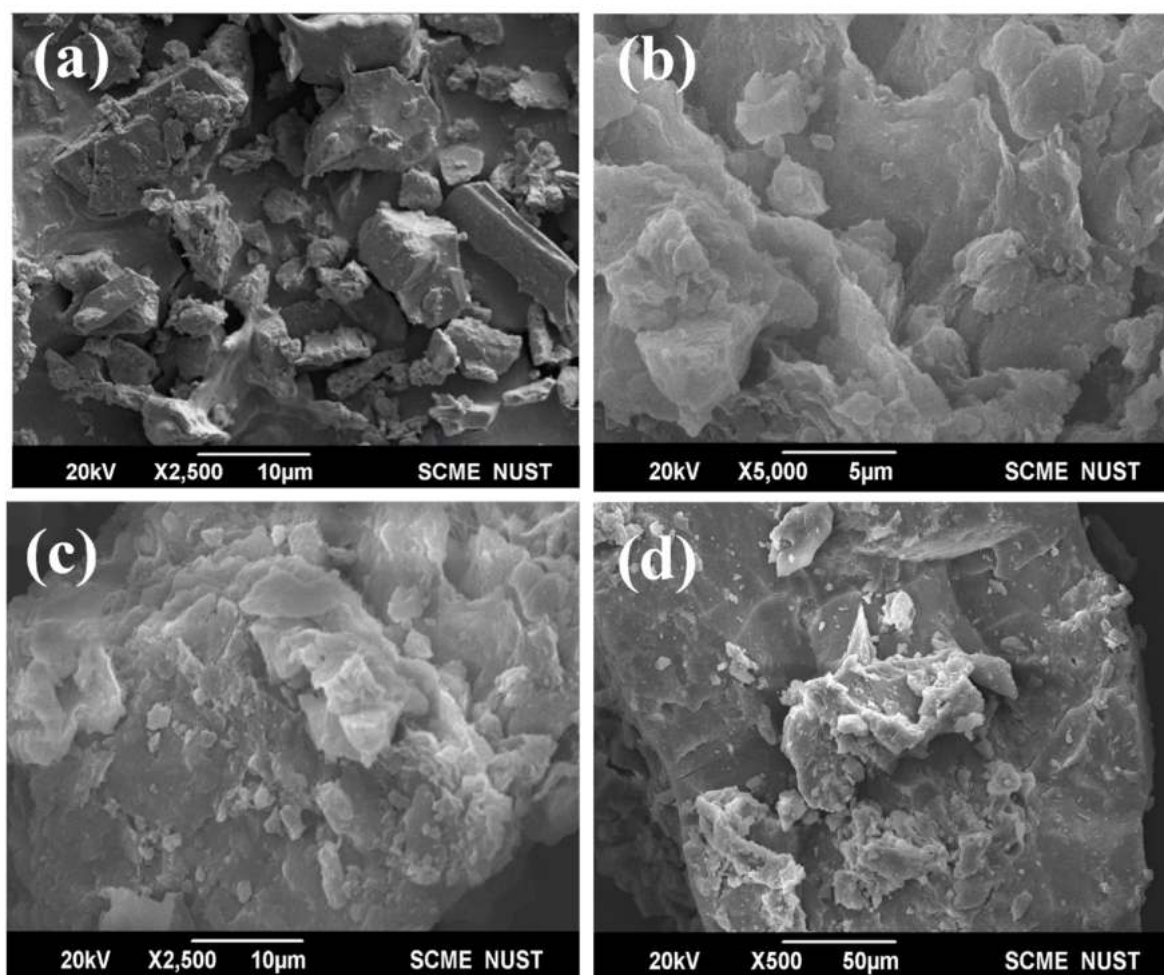


Fig. 10. Scanning electron microscopy (SEM) analysis of (a) Lignite particles, (b), (c) and (d) Extracted HA particles.

Table 9

Band assignments for Humic acid extracted from coal sample 1 and coal sample 2 for FTIR spectra.

| Wavenumber | Coal (Wang et al., 2017; Asing et al., 2009) | Coal Sample 1 | Coal Sample 2 | Band assignment |
|---------------------------|--|---------------------------|---------------------------|---|
| Band (cm^{-1}) | Band (cm^{-1}) | Band (cm^{-1}) | Band (cm^{-1}) | |
| (3450–3400) | 3422 | 3425 | 3425 | Valence vibration of OH group bounded by intramolecular H bonds |
| (2940–2700) | 2931 | 2925 | 2925 | C–H stretching of CH_2 |
| (2940–2700) | 2910 | 2850 | 2850 | Aliphatic C–H stretching |
| (1900–1800) | 1802 | 1820 | 1820 | C=O stretching mainly of COOH + ketones |
| (1625–1600) | 1629 | 1625 | 1625 | Vibration of mainly aromatic C=C + H bonded conjugated ketone (C=O) |
| (1350–1250) | 1367 | 1325 | 1335 | Symmetric deformation vibration of C–H of C– CH_3 |
| (1170–950) | 1040 | 1050 | 1050 | Deformation stretching of C=O chiefly of COOH |
| (900–600) | 727 | 730 | 730 | C–H surface deformation and vibration |

the fingerprint regions. The valence vibration of O–H group in the aromatic and aliphatic regions of HA appears at 3450 cm^{-1} – 3400 cm^{-1} (Das et al., 2015).

The alcoholic and amides N–H non-bonded groups show a deep absorption band at 3425 cm^{-1} , confirming the presence of these groups. The Aliphatic C–H stretching in HA appears at 2940 cm^{-1} , 2700 cm^{-1} . The strong peak at 1802 cm^{-1} indicates the existence of keto C=O or carboxyl C=O groups. The strong absorption peak at 1625 cm^{-1} – 1600 cm^{-1} is attributed to the skeletal vibration of the aromatic rings. The C=C stretching of aromatic groups appears 1625 cm^{-1} while the C–H vibration appears at 727 cm^{-1} . It can be seen from Fig. 9 that at 1625 cm^{-1} sharp edge loop band prominently indicates the presence of the C = C stretch (aromatic ring). Additionally, at 1325 cm^{-1} the presence of symmetrical stretching of COO^- groups is observed. The weakest peak at 1050 cm^{-1} , and 730 cm^{-1} indicates amines (RH_2) of different order (Asing et al., 2009). The two extracted HA spectra show all of the specific peaks, this confirms that the original structure of HA was not disrupted (Rodríguez et al., 2014). From the results, it is evident that humic acids have an aromatic structure and contain aliphatic side chains. The successful extraction of HA from samples of lignite coal may be confirmed by comparing the FTIR spectra of HA and the current extracted HA which are very closely resembling each other (Table 9) (Wang et al., 2017; Asing et al., 2009).

3.8.2. Surface microstructure analysis

The microstructure of lignite coal samples and extracted HA samples were studied by scanning electron microscopy (SEM) (Khalid et al.,

2022). The results are presented in Fig. 10. The SEM study sufficiently demonstrated substantial physical changes showing that the produced HA possessed some structural and morphological changes (Fatima et al., 2021). The microstructures shown in SEM images of HA pose sheet structures, fibres and short rods that form a network, and are primarily dependent on the pH and their synthesis and production conditions (Wang et al., 2017). Fig. 10 depicts the microscopic images of lignite and extracted HA samples. It can be clearly seen from Fig. 10(a) that the lignite particle size and shape are not consistent and homogenous. On the other hand, extracted HA particles have a smooth, non-porous and loose sponge-like appearance (Fig. 10 (b-d)) (Fatima et al., 2021). At higher magnification (5000×) (Fig. 10(b)) it can be seen that aggregated particles with globular-like structures and heterogeneous porosity are present.

4. Conclusion

In this study, two lignite coal samples belonging to Lakhra (Pakistan) were selected to extract humic acid using 2.5, 3.0, and 3.5% KOH solutions. The fixed parameters used in this study were KOH Concentration, extraction time and pH respectively. Effective model development of response surface methodology and (RSM) has been presented for optimizing HA extraction from Pakistani lignite coal. Optimizing the best process conditions resulted in the highest HA extraction efficiency of 89.32% and 87.04% for coal samples 1 and 2 respectively. The results of RSM for coal sample 1 ($R^2 = 0.9795$, RMSE = 4.784) and coal sample 2 ($R^2 = 0.9758$, RMSE = 4.907) showed that the model is well suited for HA extraction efficiency predictions. Coal sample 1 is relatively clean as reflected in the low ash, arsenic and lead contents resulting in higher HA extraction efficiency. From the findings in the present work, it can be concluded that HA extraction efficiency is significantly influenced by metallic impurities and pH. The FTIR analysis endorsed the presence of carboxylic, ketonic, aromatic and aliphatic functional groups in HA indicating that HA was successfully extracted from lignite coal. FTIR results also showed the absence of metallic impurities in the extracted HA. In future, the RSM model can be generalized to predict the extraction efficiency for different lignite sources with different properties. The present work is very helpful for a better design of future clean systems for the environment. This research could lead to the development of HA-based industry and can enhance its application in a variety of fields, which includes pharmaceuticals, agronomy, environmental protection and bio-based industry.

Credit author statement

Tazien Rashid, Tayab Ali Joya: Data curation, Investigation, Formal analysis, Methodology, Software, Supervision, Resources, Writing – original draft. **Mazura Jusoh, Eder C. Lima:** Conceptualization, Visualization, Writing – original draft, Resources, Validation, Supervision. **Shengfu Zhang, Tahir Rasheed:** Visualization, Software, Formal analysis, Resources. **Farooq Sher:** Software, Resources, Writing – original draft, Administration, Funding acquisition, Submission, Reviewing and Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgements

The authors are grateful for the financial support from the International Society of Engineering Science and Technology (ISEST), UK. The authors are also grateful for the financial support from the Higher Education Commission (HEC), Pakistan.

References

- Al-Atta, A., et al., 2022. Supercritical Water Oxidation of Phenol and Process Enhancement with in Situ Formed Fe₂O₃ Nano Catalyst, vol. 29, pp. 61896–61904, 41.
- Asing, J., Wong, N., Lau, S., 2009. Optimization of extraction method and characterization of humic acid derived from coals and composts. *J. Trop. Agric. Food Sci.* 37 (2), 211–223.
- Bedrock, C.N., et al., 1995. Effect of pH on precipitation of humic acid from peat and mineral soils on the distribution of phosphorus forms in humic and fulvic acid fractions. *Commun. Soil Sci. Plant Anal.* 26 (9–10), 1411–1425.
- Chen, P., et al., 2022. Hydrothermal synthesis of similar mineral-sourced humic acid from food waste and the role of protein. *Sci. Total Environ.* 828, 154440.
- Cheng, G., et al., 2019. Extraction of humic acid from lignite by KOH-hydrothermal method. *Appl. Sci.* 9 (7), 1356.
- Ciarkowska, K., et al., 2017. Comparative effects of lignite-derived humic acids and FYM on soil properties and vegetable yield. *Geoderma* 303, 85–92.
- Dana, M., et al., 2019. Optimization of a continuous ultrasound assisted oxidative desulfurization (UAOD) process of diesel using response surface methodology (RSM) considering operating cost. *Chin. J. Chem. Eng.* 28 (5), 1384–1396.
- Dana, M., et al., 2020. Optimization of a continuous ultrasound assisted oxidative desulfurization (UAOD) process of diesel using response surface methodology (RSM) considering operating cost. *Chin. J. Chem. Eng.* 28 (5), 1384–1396.
- Das, T., et al., 2015. Characterizations of humic acid isolated from coals of two Nagaland Coalfields of India in relation to their origin. *J. Geol. Soc. India* 86 (4), 468–474.
- de Souza, F., Bragança, S.R., 2018. Extraction and characterization of humic acid from coal for the application as dispersant of ceramic powders. *J. Mater. Res. Technol.* 7 (3), 254–260.
- Doskočil, L., et al., 2018. Spectral characterization and comparison of humic acids isolated from some European lignites. *Fuel* 213, 123–132.
- El-Aour, A.n.A., et al., 2006. Influence of the osmotic agent on the osmotic dehydration of papaya (*Carica papaya* L.). *J. Food Eng.* 75 (2), 267–274.
- Fatima, N., et al., 2021. Extraction and chemical characterization of humic acid from nitric acid treated lignite and bituminous coal samples. *Sustainability* 13 (16), 8969.
- Fu, D., Mazza, G., 2011. Optimization of processing conditions for the pretreatment of wheat straw using aqueous ionic liquid. *Bioresour. Technol.* 102 (17), 8003–8010.
- Ghani, M.J., et al., 2021. Characterization of humic acids produced from fungal liquefaction of low-grade Thar coal. *Process Biochem.* 107, 1–12.
- Govarthanan, M., et al., 2014. Statistical optimization of alkaline protease production from brackish environment *Bacillus* sp. SKK11 BY SSF using horse gram HUSK. *Prep. Biochem. Biotechnol.* 44 (2), 119–131.
- Govarthanan, M., et al., 2015. Response surface methodology based optimization of keratinase production from alkali-treated feather waste and horn waste using *Bacillus* sp. MG-MASC-BT. *J. Ind. Eng. Chem.* 27, 25–30.
- Ifitikhar, M., et al., 2022. Bioinspired Engineered Nickel Nanoparticles with Multifunctional Attributes for Reproductive Toxicity, vol. 311, 136927.
- Khalid, A.D., et al., 2022. Functional Bioinspired Nanocomposites for Anticancer Activity with Generation of Reactive Oxygen Species, vol. 310, 136885.
- Kurniati, E., et al., 2018a. Humic acid isolations from lignite by ion exchange method. *J. Phys. Conf.* 953 (1).
- Kurniati, E., et al., 2018b. Humic acid isolations from lignite by ion exchange method. *In: Journal of Physics: Conference Series.* IOP Publishing.
- Lamar, R.T., Talbot, K.H., 2009. Critical comparison of humic acid test methods. *Commun. Soil Sci. Plant Anal.* 40 (15–16), 2309–2322.
- Lamar, R., Olk, D., mayhew, L., Bloom, P.R., 2014. A new standardized method for quantification of humic and fulvic acids in humic ores and commercial products. *J. AOAC Int.* 94 (3), 1–10.
- Li, Y., Yuan, S., 2021. Influence of addition of KOH on the yield and characteristics of humic acids extracted from lignite using NaOH. *SN Appl. Sci.* 3 (1), 47.
- Lu, M., et al., 2020. The NMR and Spectral Study on the Structure of Molecular Size-Fractionated Lignite Humic Acid, 100004.
- Maran, J.P., et al., 2017. Ultrasound assisted extraction of bioactive compounds from *Nephelium lappaceum* L. fruit peel using central composite face centered response surface design. *Arab. J. Chem.* 10, S1145–S1157.
- Mercali, G.D., et al., 2011. Evaluation of water, sucrose and NaCl effective diffusivities during osmotic dehydration of banana (*Musa sapientum*, shum.). *LWT—Food Sci. Technol.* 44 (1), 82–91.
- Nazarbek, U., Abdurazova, P., Raiymbekov, Y., 2022. Extraction and characterization of humic acid based on coal mining waste. *Chem. Eng. Technol.* 45 (6), 1133–1140.
- Ozdemir, M., et al., 2008. Optimization of osmotic dehydration of diced green peppers by response surface methodology. *LWT—Food Sci. Technol.* 41 (10), 2044–2050.
- Rashid, T., et al., 2016. Dissolution of kraft lignin using Protic Ionic Liquids and characterization. *Ind. Crop. Prod.* 84, 284–293.
- Rashid, T., et al., 2018. Enhanced lignin extraction from different species of oil palm biomass: kinetics and optimization of extraction conditions. *Ind. Crop. Prod.* 116, 122–136.

- Rashid, T., et al., 2021a. Evaluation of current and future solvents for selective lignin dissolution—A review. *J. Mol. Liq.* 321, 114577.
- Rashid, T., et al., 2021b. Enhanced lignin extraction and optimisation from oil palm biomass using neural network modelling. *Fuel* 293, 120485.
- Rehman, A., et al., 2022. Cellulose Acetate Based Sustainable Nanostructured Membranes for Environmental Remediation, vol. 307, 135736.
- Rodríguez, F.J., Schlenger, P., García-Valverde, M., 2014. A comprehensive structural evaluation of humic substances using several fluorescence techniques before and after ozonation. Part I: structural characterization of humic substances. *Sci. Total Environ.* 476–477, 718–730.
- Sabar, M.A., et al., 2020. Evaluation of humic acids produced from Pakistani subbituminous coal by chemical and fungal treatments. *Fuel* 278, 118301.
- Sarlaki, E., et al., 2019. Extraction and purification of humic acids from lignite wastes using alkaline treatment and membrane ultrafiltration. *J. Clean. Prod.* 235, 712–723.
- Selvankumar, T., et al., 2017. Process optimization of biogas energy production from cow dung with alkali pre-treated coffee pulp. *3 Biotech* 7 (4), 254.
- Sher, F., et al., 2020. Thermal and Kinetic Analysis of Diverse Biomass Fuels under Different Reaction Environment: A Way Forward to Renewable Energy Sources, vol. 203, 112266.
- Skulcova, A., et al., 2017. UV/Vis Spectrometry as a Quantification Tool for Lignin Solubilized in Deep Eutectic Solvents, vol. 12, 2017.
- Tazien, R., et al., 2021. Enhanced lignin extraction and optimisation from oil palm biomass using neural network modelling. *Fuel* 293, 120485.
- Wang, C.-F., et al., 2017. Characterization of humic acids extracted from a lignite and interpretation for the mass spectra. *RSC Adv.* 7 (33), 20677–20684.
- Ye, T., et al., 2022. Effects of potassium fertilization on crops yield, potassium uptake, and soil potassium fertility in rice-oilseed rape cropping systems. *Arch. Agron Soil Sci.* 68 (7), 873–885.
- Zara, M., et al., 2017. Extraction and characterization of humic acid from Pakistani lignite coals. *Energy Sources, Part A Recovery, Util. Environ. Eff.* 39 (11), 1159–1166.
- Zhang, S., et al., 2017. Characterization of pH-fractionated humic acids derived from Chinese weathered coal. *Chemosphere* 166, 334–342.
- Zhang, Y., et al., 2019. Simulation of particle mixing and separation in multi-component fluidized bed using Eulerian-Eulerian method: a review. *Int. J. Chem. React. Eng.* 17 (11).