Experimental Investigation and Performance Optimisation of Washing Cycles for Pre-processing of Coal Fly Ash

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Abstract

Coal Fly Ash (CFA), a by-product of thermal power plant combustion, has a profound focus among researchers due to its pozzolanic properties, porosity, wide chemical composition, and thermal stability. While being suitable for many applications (e.g., pozzolanic material, soil stabiliser, and structural fill), CFA is also a potential precursor for synthesising zeolites, broadly used in wastewater treatment. However, pre-processing is crucial due to the heterogeneous nature of CFA. This work focused on pre-processing CFA prior to wastewater treatment through continuous washing cycles at various operating temperatures. To this end, we studied the pH and conductivity of the solution after washing over multiple cycles, Sauter mean diameter, and the mineralogy of the settled CFA. The gathered results were analysed and optimised through response surface methodology. This was done to find the best combination of the number of washing cycles and temperature to remove soluble ions and increase the surface area of CFA particles. The analytical outcome revealed that five washing cycles at 70°C were adequate, with minimal soluble ions and maximum surface area. Evidently, these findings demonstrated significant improvements in the physical and chemical properties of CFA as a precursor for zeolite synthesis. Therefore, we recommend further studies on this front to extend the effective usage of CFA for the synthesis of commercial zeolites to be used for wastewater treatment.

Keywords: Dissolution, Response surface methodology (RSM), Wastewater treatment

1. Introduction

Coal is the world's cheapest, most abundant, and widely distributed fossil fuel. It is considered a non-renewable natural resource, taking millions of years to form [1]. The demand for coal is falling in North America and Europe, while China, India, and other developing countries in Asia continue to dominate the investment market in new mines [2]. Even though the number of coal power stations is declining for the first time on record, three-quarters of the total new coal power plants of 200 GW are being constructed on the Asian continent. With the prevailing production rate throughout the world, it is estimated that there are adequate coal reserves for another hundred years, emphasising coal's significance [1].

Using coal in thermal power plants generates fly ash, bottom ash, flue gas desulphurisation waste (scrubber sludge), fluidised bed boiler waste, and coal gasification ash collectively referred to as

coal combustion residues (CCRs). Out of total CCRs from the boiler, fly ash occupies 65 to 95% and bottom ash 15 to 35% depending on the chemical composition of the parent coal [3].

Coal fly ash (CFA) is the predominant by-product among the CCRs. CFA earns substantial attention in the scientific community for its physicochemical properties as a versatile engineering material. The vital chemical constituents of CFA are SiO_2, SO_3, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, and TiO_2 [4]. Because of the high content of Silica, it has been broadly used as a pozzolan in blending cement. Apart from cement production, CFA applications are widespread, including bricks manufacture, backfill material, soil stabiliser, soil ameliorant, ceramic material production, absorbent, geopolymer production, electromagnetic interference shields, wastewater treatment, and catalyst applications [4], [5].

The applicability of CFA as a potential adsorbent in wastewater treatment is promising. Many researchers have found the usability of CFA in raw and modified forms to treat wastewater [6]. In addition, CFA is available in bulk at a low cost and is recognised as a highly efficient precursor for synthesising zeolites [7]. Pre-processing CFA before any wastewater treatment yields more desirable results than using them in the raw form. In addition, the merits of using pre-processed CFA in synthesising zeolite are acknowledged for enhancing zeolite formation and its adsorption capacity [6].

Pre-processing of CFA is essential as it intrinsically possesses impurities depending on the coal origin and combustion method, hindering the potential application of zeolite in effluent treatment [8]. Sieving, calcination, magnetic separation, acid treatment, and water treatment are widely employed to enhance raw CFA by eliminating impurities in the initial processes [4]. Even though the importance is addressed, there are limited discussions on the efficient and cost-effective methods for pre-processing CFA. To this end, this study aims to pre-process CFA before synthesis, using the washing cycle to alter the physical and chemical properties.

2. Material and methods

2.1 Sample acquisition and initial characterisation

Samples of CFA for the study were collected from the Lakvijaya coal power plant in Norochcholai, Puttalam District of Sri Lanka. The parent coal utilised in the power plant is a bituminous type imported from Indonesia. Two bulk samples were collected through the vessel's discharge using ASTM D2234 and D7430 standards, and one of them was used for further studies. The X-ray Fluorescence results on the identical CFA from previous study is presented in Table 1. The silicon, aluminium, and iron by mass are greater than 70%, and calcium oxide is less than 10%, which characterised the CFA as Class F, according to ASTM C618 standard [9].

Table 1: Composition of the studied CFA [9].

Mineral ash analysis (%)	ASTM Standard	Results
SiO_2	D4326	55.38
Al_2O_3	D4326	23.96
Fe_2O_3	D4326	8.12
CaO	D4326	4.96
MgO	D4326	1.26
Na_2O	D4326	0.38
K_2O	D4326	1.26
P_2O_5	D4326	0.33
TiO_2	D4326	1.18
Mn_2O_4	D4326	0.18
SO_3	D1757	2.28
Undetermined		0.71
Total		100.00

2.2 Washing cycles

Experiments were designed to understand and optimise the number of washing cycles and temperature, keeping other variables

(i.e., stirring time, stirring speed, and ratio between distilled water and CFA) constant. Sixteen individual samples of each 100 g were separated. Precisely measured 100 g of CFA (using electronic mass balance from OHAUS Discovery) and 500 ml of ultra-pure water from the AUTOSTILLTM Freshman-4 water system were initially added to the 1 L Teflon beaker. The beaker containing the solution was kept on a magnetic stirrer (AM4 from VELP), agitated for 15 minutes, and allowed to settle for another 15 minutes. After settling, the top samples were skimmed using a clean glassware. The solution samples were poured into an airtight container and bottom samples were separated. This entire process is interpreted as "one washing cycle" and illustrated descriptively in Fig. 1.
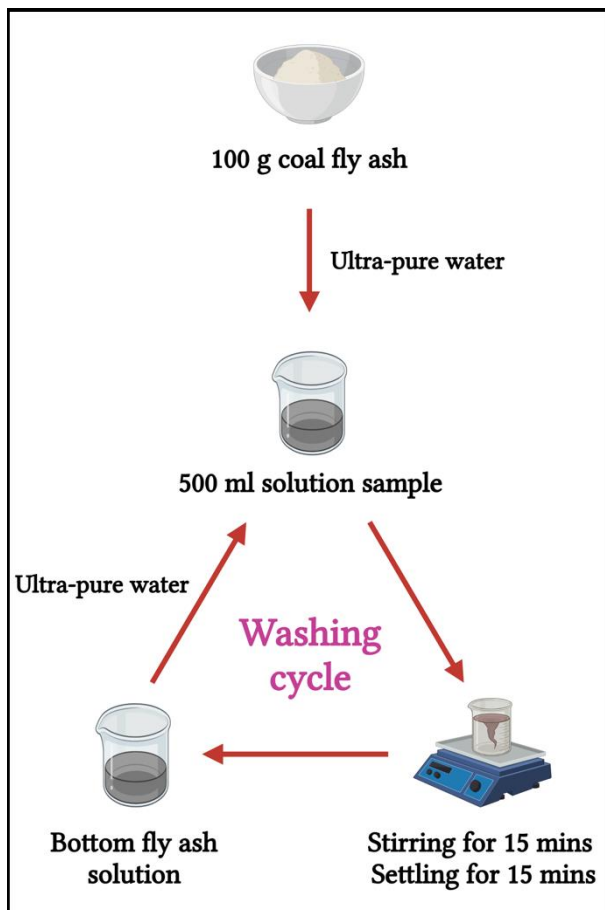

Figure 1: Design of experiment for a single washing cycle experiment.

At the end of every washing cycle, the bottom layer was refilled with ultra-pure water until it reached the 500 ml level. This process continued for 1, 3, 5, and 7 washing cycles at that constant temperature to understand the effects of the number of washing cycles. Further, the same set of experiments (i.e., 1, 3, 5, and 7 washing cycles) was performed at room temperature, 45°C, 65°C, and 90°C to understand the effect of temperature during washing cycles.

2.2   Final characterization

Collected top samples and bottom samples were oven dried at 105°C and 120°C for 24 hours, respectively. The representatives from bottom samples were analysed for size distribution using the HMK-CD2 Laser particle analyser to obtain the Sauter mean diameter (i.e., surface area-weighted mean diameter - D[3,2]). Further, the mineralogy phases were obtained using the Rigaku Ultima IV X-ray Diffractometer. The pH and conductivity of the effluent solution were measured using a Hach SensION-1 pH meter and a Hach HQ40D digital conductivity meter.

2.3   Analysis of results

The gathered experimental data was analysed and optimised through the response surface methodology (RSM) to find the effective washing cycles. In addition, numerical optimisation was performed by considering the importance and scale of process responses to get optimal results through washing cycles. A user-defined custom design was evaluated by using the experimental data for the three responses of the washing cycle process; pH and conductivity of solution and Sauter mean diameter of the bottom sample. Whilst some model terms that may have been inconsequential were ignored, and models with fewer terms were chosen for a reasonable representation of the experimental data. A minimal pH for a neutral solution, minimal conductivity for maximum removal of soluble ions, and maximum Sauter mean diameter for increased exposure of surface area of particles were assigned to optimise the washing cycle and temperature combination for the pre-processing of CFA. The numerical optimisation finds a point

that maximizes the desirability function (D_f). For several responses and factors, all goals combine into one D_f. Finally, a solution with higher D_f was chosen as the optimal condition for CFA pre-processing. The final model generated the responses in terms of graphical representations of the parameter shown by contour plots that gave their relative influence on the D_f and an optimum parameter combination.

3. Results and discussion

3.1 Variation of pH value

Fig. 2. illustrates the pH trend with increasing washing cycles and temperature.
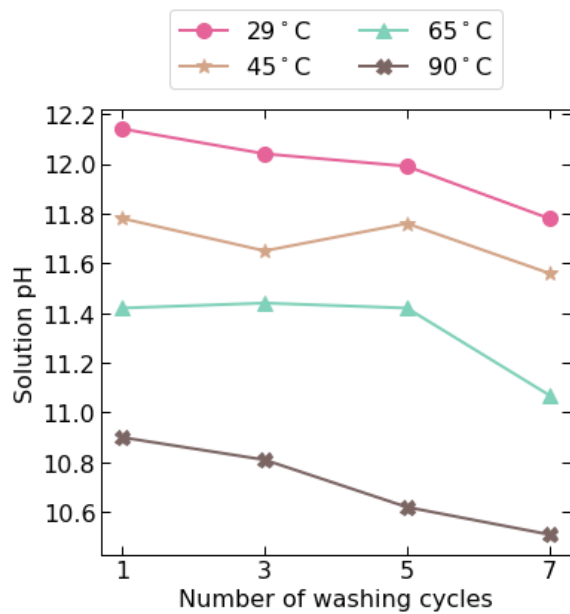
Figure 2: Temperature dependency of solution pH with different washing cycles (rpm =900).

The solution possesses alkaline characteristics throughout the entire washing cycle at varying temperatures. It has been explicitly seen that the value of pH in the solution decreases with the increasing washing cycle for a constant temperature. This phenomenon results from a continuous discharge of soluble alkaline components, i.e., K_2O, Na_2O, MgO, and CaO, during every washing cycle and has been previously identified in different studies (e.g., [6]). Additionally, the temperature increase stresses the equilibrium condition of the alkaline components and causes the equilibrium to shift to the right. Thus, the

solubility increases as the temperature increases in the experimental runs. However, the resulting trends in the pH indicate a decreasing pH with an increase in temperature. This discrepancy could be attributed to the increased solubility of acidic components, i.e., P_2O_5 and SO_3, from the CFA sample. The solubility of acidic components may have caused this phenomenon.

The maximum pH value of the solution sample was 12.14, which was attained after the first washing cycle at room temperature (29°C). A minimum pH value of 10.51 was attained on the solution sample after seven washing cycles at 90°C. This observation further justifies the influence of the washing cycle and temperature on the pH value of the solution and the dissolving of alkaline components.

3.2 Variation of conductivity value

Fig. 3. illustrates the conductivity trend with increasing washing cycles and temperature.
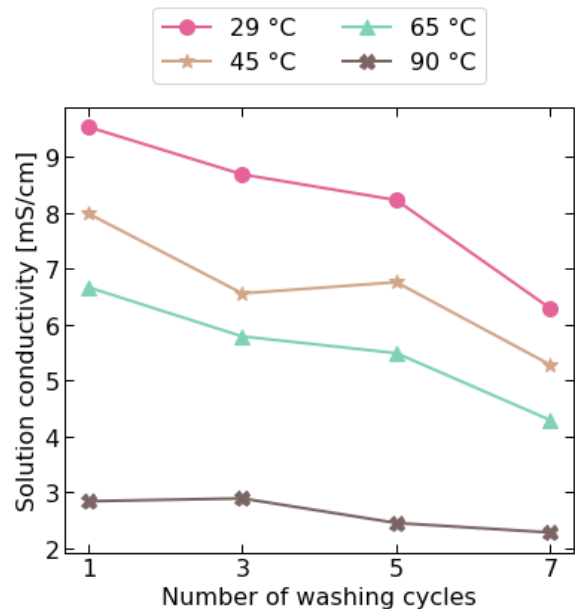

Figure 3: Temperature dependency of solution conductivity with different washing cycles (rpm = 900).

The conductivity of the solution results from the concentration of ions removed from the CFA sample. The conductivity increments with the concentration of ions in the solution, their mobility, and the

temperature of the solution. A few noticeable patterns can be observed in Fig. 4. i.e., with the increase in the washing cycle, the conductivity of the solution decreases. It implies the reduced removal of ions from the CFA samples. Despite this, increasing temperature decreases the conductivity, which is uncharacteristic (refer to Section 3.1). It is a rather contradictory result and may be due to the high concentration of ions in the solution hindering the mobility of ions. This urges further detailed studies and characterisation of solution samples. Heedless of this, the conductivity gradient decreases with increasing washing cycle and temperature. Moreover, at 90°C, a minimal decline in conductivity is recognised. It shows the near complete removal of soluble ions from the experimental environment.

The maximum conductivity value of the solution sample was 9.54 mS/cm, obtained after one washing cycle at room temperature (29°C). A minimum conductivity value of 2.28 mS/cm was reached on the solution sample after seven washing cycles at 90°C.

3.3 Variation of Sauter mean diameter

Fig. 4. illustrates the diameter trend with increasing washing cycles and temperature.
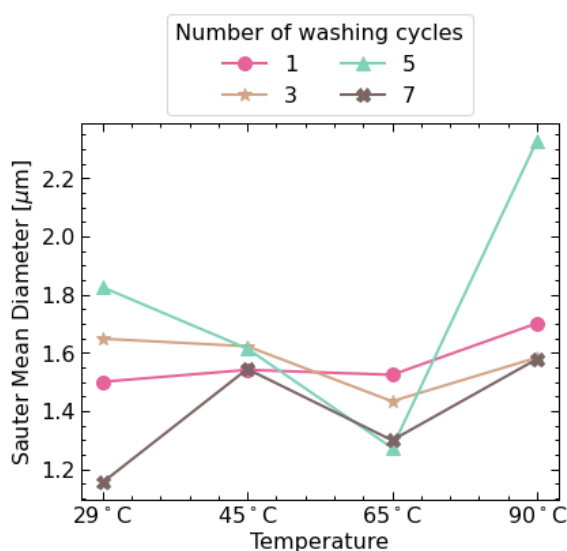

Figure 4: Temperature dependency of Sauter mean diameter with different washing cycles (rpm = 900).

Yielding a higher Sauter mean diameter during the washing cycle is crucial as it determines the probability of particle interaction and exposure to the surface area of individual elements for better synthesis [10]. However, coagulation and flocculation of particles during the continuous washing cycle were unavoidable, resulting in decreased diameter from 29°C to 65°C. Further, the diameter increases as temperatures rise from 65°C to 90°C for 1, 3, and 5 washing cycles. However, the diameter varies as the temperature rises over the course of seven washing cycles. This result is attributed to an uncertain dynamic environment inside the experimental setup, probably dissolving or interrupting the causes that lead to particle bonding.

Additionally, the findings show that between 29°C and 45°C, Sauter mean diameter increased from 1 to 5 washing cycles and decreased from 5 to 7 washing cycles. However, the Sauter mean diameter decreases between 65°C and 90°C with increasing washing cycles until the fifth cycle. At 65°C, an increase in diameter was seen from 5 to 7 washing cycles. Nevertheless, at 90°C, this tendency could not be seen.

3.4 X-ray diffraction (XRD)

The XRD pattern of the top dried sample of pre-processed CFA, which was collected after one cycle of washing at room temperature, is depicted in Fig. 5.

The alkaline substances, i.e., calcite ($CaCO_3$) and sodium nitrate ($NaNO_3$), are accountable for the principal diffraction peaks of the top sample of pre-processed CFA after one washing cycle. The pH of the residual solution decrease once alkaline substances are removed, as seen in Fig. 2. More washing cycles dissolve soluble alkaline components, eventually causing a pH drop. The remaining solution's conductivity also dropped as the number of washing cycles was raised with the removal of the ions. This further validates the

observed trends of pH and conductivity with increased washing cycles.
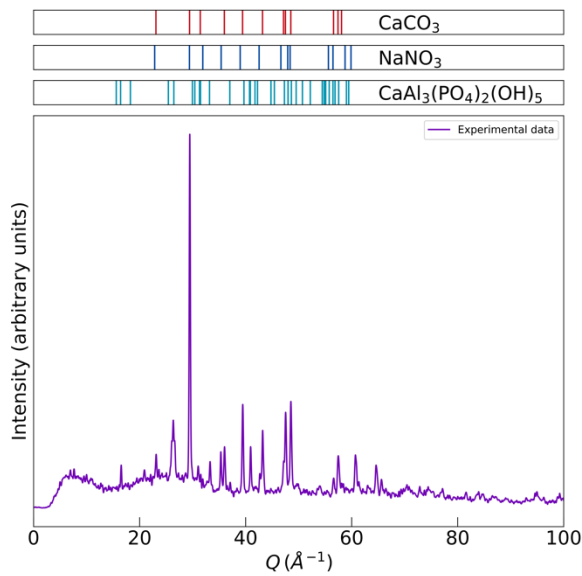

Figure 5: XRD pattern of the top dried sample.

3.5 Numerical optimisation

Contour plots of D_f and all the responses for varying washing cycles and temperatures after 16 experimental runs are depicted in Fig. 6. Highest D_f for the recommended constraints (refer to Section 2.2) is 0.798. The solution with the highest D_f is available around the five-washing cycles at 90°C, as illustrated in Fig. 7.

On the other hand, the practical application of the washing cycle at 90°C exhibits unusual behaviour with an increasing number of washing cycles. The volatile component of the CFA starts to evaporate while producing irritating gas bubbles. This behaviour of CFA made the experiment challenging to conduct in an open environment. Therefore, it is highly recommended to use proper laboratory kits during the practicals. Furthermore, the identical phenomenon is observed in another batch of CFA from the same powerplant. Therefore, restrictions on the temperature were adjusted, and the optimal number of washing cycles was determined.

Five-washing cycles display the highest D_f during the whole temperature range (refer to Fig. 7.). This observation is highly correlated with optimising the surface area. From the trends of pH and conductivity, it is evident that increasing washing cycles and temperature would lead to minimal pH and conductivity. Whereas the Sauter mean diameter did not show such a uniformity. In addition, the Sauter mean diameter of five-washing cycles has a steep gradient that may influence the selection of washing cycles in this study. Therefore, it is recommended to perform pre-processing of CFA with five-washing at 70°C (D_f of 0.55), considering practical implications.

4. Conclusions and recommendations

The present research aimed to understand and demonstrate the influence of pre-processing of CFA by altering the physical and chemical properties using continuous washing cycles. The experimental runs were designed in accordance with the objectives of optimising the pH and conductivity of the solution and the Sauter mean diameter of the bottom samples. Most interestingly, the study showed that increasing washing cycles and increasing temperatures will be significantly effective as a pre-processing technique to remove the soluble components from CFA and reduce the pH to neutral. Response surface analysis revealed that the five-washing cycles at 70°C were affirmed to be effective considering the practical restrictions. The removal of soluble ions, reduction of CFA particle size, and neutral pH may contribute to a better synthesis of zeolites. The generalisability of these results is subject to certain limitations. For instance, the initial composition of CFA is diverse, and the presence of certain elements could affect the D_f of the washing cycles at recommended settings. Therefore, large randomised controlled trials with different sources of CFA could provide more robust evidence. Further, the in-depth understanding of many uncharacteristic behaviours of CFA with the increasing temperature prompted numerous questions that need further investigation.
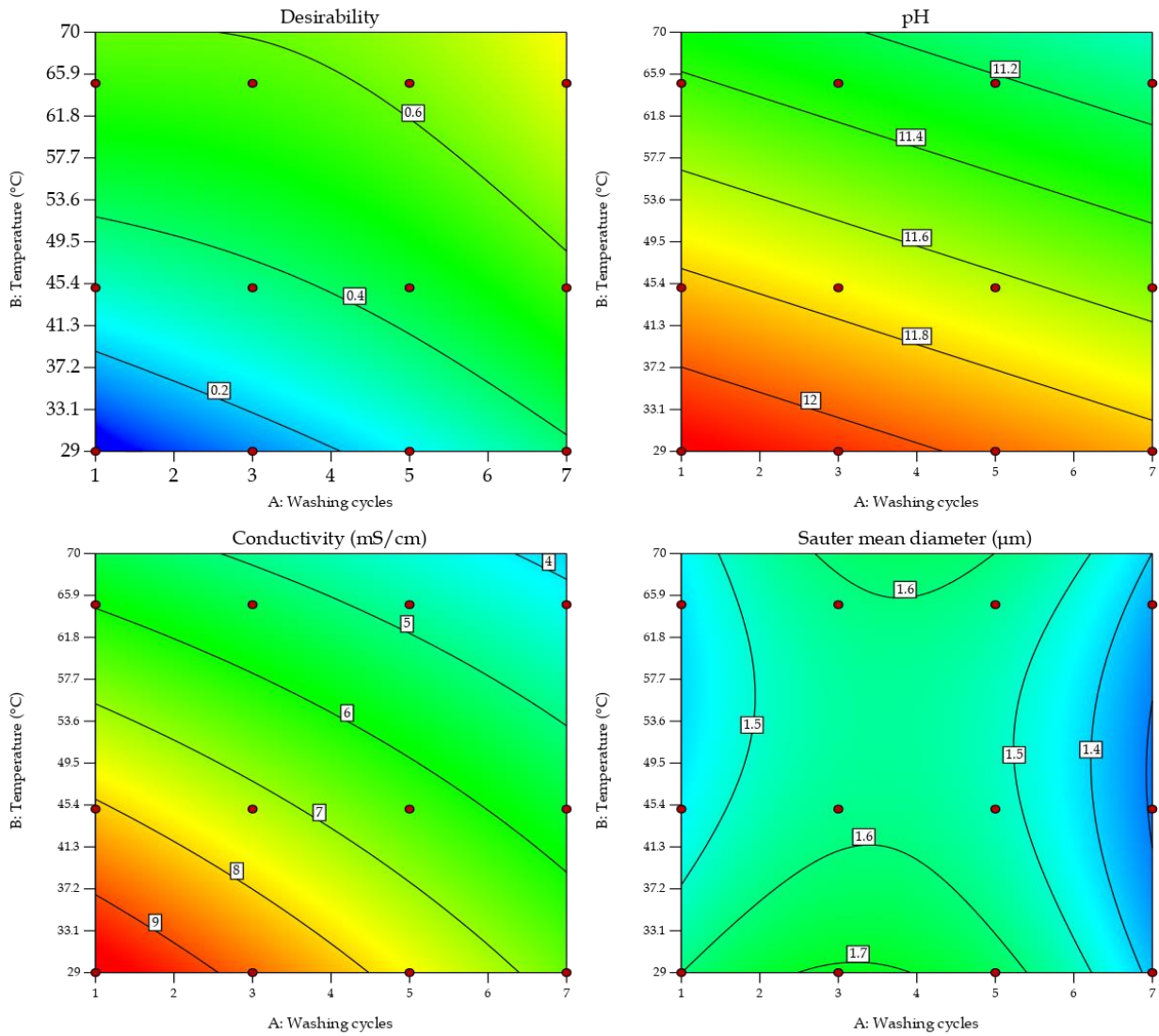
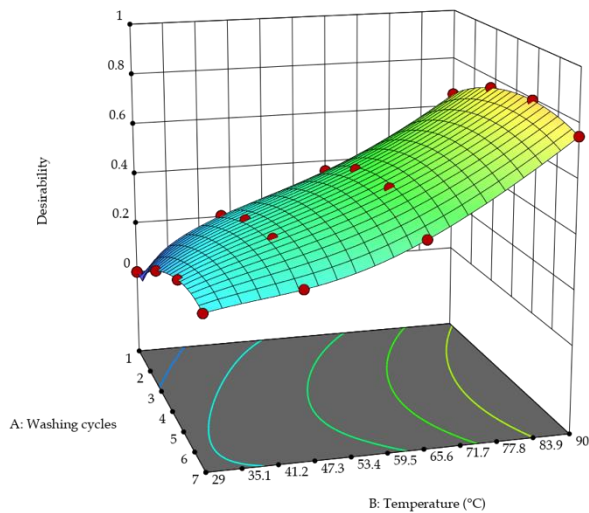**Figure 6: Contour plots of desirability function (D_f), pH, conductivity, and Sauter mean diameter.**

Figure 7: Response surface for the washing cycles and temperature dataset.

Acknowledgement

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