



A comprehensive review on analytical and equation derived multivariate chemometrics for the accurate interpretation of the degradation of aqueous contaminants

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ARTICLE INFO

Article history:

Received 11 June 2021

Received in revised form 21 June 2022

Accepted 12 July 2022

Available online 18 July 2022

Keywords:

Pollutant assessment

Chemometrics

Canonical analysis

Ridge analysis

Response surface methodology

Mathematical modeling

ABSTRACT

Preciseness in pollutant analysis and optimizing a process required to remediate wastewater are essential in environmental engineering. The chemometric approach is used to analyze pollutant molecules from actual samples with maximum accuracy quantitatively. Various calibration models like Principal Component Regression, Partial Least Squares, Cluster analysis, Parallel Factor Analysis, and Artificial Neural Networks are employed to compute the pollutant concentration. In this review, the application of chemometrics in aqueous pollutant degradation processes is explained to understand better how accurate and what kind of information can be extracted from the pollutant degradation processes using chemometrics. The reaction rate-determining ability of Multivariate Curve Resolution–Alternating Least Square, a second-order chemometric model, is explained. Understanding the degradation profiles of a mixture of components and analyzing the by-product evolution are benefits of employing chemometrics. This review describes studies where chemometrics and response surface methodology-based techniques are used to gain insights into process optimization and resolve issues on the accurate determination of pollutant concentration profiles. Suitable examples of advanced oxidation methods, namely photocatalytic degradation, and gamma-ray mediated pollutant deterioration, are discussed to understand better the application of Canonical and Ridge analysis. This review gives the readers a good view of various applications of chemometrics in accurate assessment of pollutants in multi-component systems and process optimization of pollutant degradation.

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1. Introduction

Chemometrics, the mathematical modeling of analytical chemistry, is an indispensable methodology for environmental engineering. Environmental engineering usually deals with analyzing environmental samples with many interfering compounds and minimal concentration of the molecule of interest (Mas et al., 2010). Accuracy in quantitating the analyte of interest is essential. Chemometrics helps in overcoming these difficulties by employing various statistical models. Chemometrics classifies molecules' analysis as zero, first, second, and higher-order, based on the analytical method's data. For example, a single wavelength data about a pollutant molecule given by a spectrometer is zero-order data, like shown in Figure S1(a). The instrumental outcomes for various order data are represented in Figure S1. In contrast, first-order data is the spectrum analysis of a pollutant molecule over a wavelength range, second order comprises of spectrum of sample at various time as shown in Figure S1(b). Higher order data includes time and number of sample such that it also encompasses an error component in calibration. Mathematical modeling used to calibrate such outputs from instruments also depends upon the order of data. Different mathematical modeling techniques like Partial Least Squares (PLS) (Moreno-Martin et al., 2018), Classical Least Squares (CLS), Principal Component Regression (PCR), Parallel Factor Analysis (PARAFAC) (Jutaporn et al., 2021), and N-way Partial Least Squares (NPLS) (Patel and Kothari, 2016) are employed to analyze the molecules of interest. In a study by Moreno-Martin et al. the Partial Least Squares (PLS) method was adopted to study silver nanoparticles' spectroscopic behavior in the presence of L-Cysteine (Moreno-Martin et al., 2018). Silvia Mas et al. have explained the different chemometric approaches for analyzing organic contaminants like Pesticides and Poly Aromatic Hydrocarbons in their exploratory environmental studies, toxicity, and quantitative analytical determinations (Lavine and Workman, 2013; Mas et al., 2010). The spectroscopic analysis of silver nanoparticles in natural waters was enumerated based on the PLS method.

In heterogeneous Fenton degradation of a mixture of three different textile dyes, the spectroscopic overlapping of the three distinct peaks of textile dyes in the mixture was resolved, and the accuracy and precision in analyzing the dyes distinctively in the mixture were improvised using Multivariate Curve Resolution with Partial Least Squares (MCR-PLS) chemometric method (Khataee et al., 2016). Because of the ease of implementation and quality of the calibration model given by PLS, it was used on a significant scale compared to MCR, which possesses the disadvantage of rotational ambiguity (Ahmadi et al., 2015). Calibration of pollutant sample analysis data using chemometric models could produce more accurate optimization of process regarding degradation or removal of pollutant molecule. From simple data sets like absorbance, spectrum, and elution time-absorption spectrum of a sample, essential information can be obtained using chemometric methods. Chemometrics poses several advantages in monitoring the change in pollutant concentration over the duration of the environmental degradation process and also helps in identifying end products and intermediate compounds that evolve during the process. Even second-order data like the spectrum of a mixture of contaminants can be assessed without the requirements of calibration and validation of data sets. The role of chemometrics in pollutant analysis and process optimization is shown as a flow diagram in Figure S2. In environmental remediation, degradation of a pollutants comprises of two parts: first, the quantification of the pollutant and second, analyzing the process. Initially the process is studied by analyzing various factors that may affect positively or negatively. The wastewater containing mixture of pollutants are then analyzed using chemometric method to precisely quantitate the pollutants. These two methodologies in combination together with optimizing strategies, employing canonical and ridge analysis, for the remediation process, makes it more mathematically appreciable remediation process with high accuracy.

The pollutant degradation process usually employs many input parameters that need to be optimized. Consider, for example, applying nanoparticles for recalcitrant degradation which involves various parameters to be optimized. Nanoparticles find their application in methods like sonication (Gholami et al., 2020, 2019), catalytic membranes (Safarpour et al., 2015; Vatanpour et al., 2012), and Photocatalysis (Hassandoost et al., 2019; Padmanaban et al., 2016), with potential for pollutant removal. These methods also require optimization of their input factors. Optimization of a process earlier involved using the One Variable at A Time approach or trial and error method, which is a traditional one and consumes a lot of resources and time. It gives the experimenter only the linear effects of the input variables. But therein lay a query, what are the interactive effects of input variables? What is the optimal combination of inputs to obtain a maximum response? The light was thrown on the solutions for these questions during the path of solving a problem posed by Imperial Chemical Industries. George E. P. Box, a statistician, and K. B. Wilson, a Chemist, figured out a way to find the maximum optimal chemical process solution (Draper, 1992). The base for Response Surface Methodology (RSM) originated in 1951 (Box and Wilson, 1951). This statistical optimization is given much importance because of its benefits, like minimizing the time and reducing the experiment requirement.

Moreover, Box and Wilson's findings were a solution to a practical problem that can be applied over a wide range of experiments in various fields. After the advent of RSM, much research was performed in mathematics, and various mathematical operations were used to enhance the base RSM strategy. Khuri and Mukhopadhyay, explains the evolution of RSM based techniques into three different periods, i.e., Part I (1951–1975), the developmental period of RSM; Part II (1976–1999), the era of an alternative approach to RSM; and Part III (2000–Till now) the modern RSM period (Khuri and Mukhopadhyay, 2010). The main success of RSM is the incorporation of mathematical techniques, most notably statistics, for the optimization process. The influence of maths in RSM does not stop with providing a response equation. The end product of an RSM, i.e., the response equation, can further be manipulated with the help of various other mathematical techniques like Matrices and Determinants and Partial Differential equations. These mathematical techniques further

Table 1

Comparison of recent relevant reviews related to application of chemometrics in water quality with the current review.

S.No.	Recent reviews on the application of chemometrics in environmental applications.	Themes of the reviews	References
1.	Combining Chemometrics and Sensors: Toward New Applications in Monitoring and Environmental Analysis	Focuses on integrating chemometrics with sensors for water quality monitoring	(James et al., 2020)
2.	Chemometrics for environmental monitoring: a review	Summarizes various chemometric methods involved in environmental monitoring	(Madeleine et al., 2020)
3.	Current trends and advances in analytical techniques for the characterization and quantification of biologically recalcitrant organic species in sludge and wastewater: A review	Focuses the integration of chemometrics and the analytical detection of the recalcitrant organic compounds from real-time wastewater and sludge	(Faixo et al., 2021)
4.	Chemometric approach in environmental pollution analysis: A critical review	Comprehends the application of various chemometric tools in the assessment of quality of different environmental matrices (Air, Water, and Soil.)	(Inobeme et al., 2022)
5.	A comprehensive review on analytical and equation derived multivariate chemometrics towards the degradation of emerging water contaminants (This Review)	Gives a detailed insight into the augmentation of chemometrics with RSM-based optimization of pollutant degradation in advanced oxidation systems with suitable case studies.	(Current Review)

interpret results obtained from the response equation in a more precise manner. The two crucial mathematical strategies deployed are the Canonical and Ridge analysis which aid the experimenter in better interpreting the optimal solutions of the system under study.

There are methods by which the removal of contaminants using the advanced oxidation process (AOP) is characterized using the chemometric approach, which will be discussed later in this review. Therein lies a scope where enhancements in the process can be performed using coupled methods of chemometrics and RSM. Speciation of contaminants into different electronic and oxidation states, especially heavy metals, due to environmental variation may make them more stable and could interfere with or hinder the remediation process. It was found that Fe(II) gets converted into Fe(III) complexes due to irradiation in a photo-Fenton's process and hence requires proper radiation spectrum (Kim and Vogelpohl, 1998). Heavy metals in contaminated soil or soil leachates have also existed in different states due to interaction with other components in their environment. In the study by Minkina et al. (2019), the further speciation of Cu^{2+} in Haplic Chernozem was characterized using a first-order derivative spectrum of X-ray absorption near edge structure (XANES) analysis. This study showed that the speciation of Cu^{2+} was due to interaction between the other components present in the soil. This relationship or interaction analysis of the pollutant molecules with different chemical entities present during the AOP process could help strategically modify the process for proper investigation and better remediation. Iron is also found to form Fe-oligomers and Ferrihydrate during oxidation/hydrolysis in the presence of organic matter (Vantelon et al., 2019). This study was performed with the help of Quick-EXAFS combined with the MCR-CLS approach. For these speciation studies, XANES spectroscopy was found useful where it was able to characterize the different forms of Hg as β -HgS (metacinnabar), Hg-cysteine, Hg-bound to tannic acid, and Hg^0 in the bark of *Pinus nigra* (Chiarantini et al., 2017). In this study, the bark is considered a chemically inert adsorbent, helping to analyze the Hg pollution in the surrounding region.

Hence it is essential to understand the speciation of contaminants under different conditions and the suitable method to analyze them. Based on the approach adopted, RSM coupled chemometrics can be used to analyze the optimal exploring regions for other methods. In this context, this review gives insights into the potential use of chemometrics and various simple mathematical modeling techniques in RSM in pollutant removal using AOPs whose comparison is given in Table 1.

2. Chemometric analysis of contaminants

2.1. Use of mathematical model for measurement

Chemometrics is used along with analytical methods like UV-Visible spectroscopy, HPLC, GC-MS, LC-MS, and other hyphenated techniques used in environmental monitoring, reducing noise, and improving precision accuracy in the measurement of environmental contaminants. Chemometrics assist in obtaining information like concentration of single compound in a mixture (Sciscenko et al., 2021), kinetic parameters estimation (Moreira et al., 2022), identify intermediates generated during AOPs (Hemmateenejad et al., 2015). The above mentioned indormation like concentration estimation, kinetics and analysis of intermediates is very much essential in environmental remediation. Using these methods helps to study a remediation process with less requirement for sophisticated equipments or techniques. One of the critical aspects of chemometrics is pre-processing the data obtained from measuring samples using any instrument. The data obtained can be a matrix. Concerning UV-Visible spectral analysis of a sample at a regular interval of time, the matrix of data with rows and columns as wavelength and time respectively, the pre-processing of the data can give results with reduced

Table 2
Methods used to pre-process the obtained experimental data (Garrigues and Guardia, 2020).

Pre-processing method	Equation used
Transformation	
Logarithmic	$\log_{10}(x_{ij})$
Box-Cox	$x_{ij}^{\lambda} - 1/\lambda$, where λ is the exponent value
Power	x_{ij}^p , where $p = 0.5$ gives the square root
Row pre-processing	
MSC	$x = b_0 + b_{ref}x_{ref} + e$ $x_{corr} = (x - b_0)/b_{ref}$
SNV	$(x_{ij} - \bar{x}_i)/\sigma_i$, where σ is the standard deviation
Normalization	x_{ij}/\bar{x} , where \bar{x} is the estimated value
Column pre-processing	
Mean centering	$(x_{ij} - \bar{x}_j)$
Autoscaling	$(x_{ij} - \bar{x}_j)/\sigma_j$
Pareto scaling	$(x_{ij} - \bar{x}_j)/\sqrt{\sigma_j}$

MSC-Multiplicative Scatter Correction, SNV-Standard Normal Variate.

noise. As provided by (Garrigues and Guardia, 2020), some pre-processing methods employed over that matrix to obtain a low signal-to-noise ratio are shown in Table 2. Preprocessing of the data helps to increase the signal to noise ratio and also pose the advantage of preventing the influence of intense signals over the other. Before subjecting to chemometric modeling, pre-processing the data, i.e., identifying the subintervals of spectra, helps produce more accurate models. For instance, PLS was used to optimize COD determination using UV-Visible spectroscopy in a work by (Li et al., 2018). The optimal spectral regions were first identified using synergy intervals Partial Least Squares (siPLS), and then the PLS model was developed (Jiang et al., 2012). The spectra obtained for a mixture of chemical compounds from various analyses like Fluorescence spectroscopy, Mass spectroscopy, UV-Vis spectrophotometry, and Infra-Red (FTIR) spectroscopy can be resolved into the pure spectra of individual chemical compounds using the chemometric method. (Gu et al., 2018; Lavine and Workman, 2008; Lima et al., 2019; Moura et al., 2019)

The different chemometrics methods that are applied for first-order, second-and higher-order calibrations based on the data availability and the objective are listed in Table 3. In the first order calibration, compounds that interfere with pure spectra of analyte of interest cannot be analyzed but can be detected (Booksh and Kowalski, 1994). The analysis of spectroscopically active interfering compounds can be done using second order calibration. This is a drawback and advantage of first order and second order calibration respectively. The limitation of first order calibration with respect to interfering compounds is that the interfering compound must also be included in the calibration set. On the other hand second order calibration also has the problem of information loss during cube decomposition, shown in Figure S1(c). This occurs when the interfering compound and sample are collinear. Chemometrics has been successfully employed to monitor and measure various contaminants like antibiotics and other pharmaceuticals, pesticides, dyes, heavy metals, etc., in laboratory simulated and real environments. Therefore it finds an important place in pollution monitoring. Table 4 lists the different kinds of pollutant molecules analyzed using the chemometric approach. This table also lists the chemometrics methods that are used with instruments like UV-Spectrophotometer, FTIR, and HPLC, etc., for the analysis of both organic and inorganic pollutants. The chemometric approach is not only limited to pollutant molecules but can also be used to analyze the molecules with many interfering compounds accurately. The limit of detection (LOD), selectivity, and stability parameters for detecting Glucose and H_2O_2 based on chemiluminescent activity were estimated using linear calibration, Relative Standard Deviation (Irani-nezhad et al., 2019).

Comparing the different chemometric methods for quantitative analysis of contaminants from the UV-Visible spectroscopy data would give a good understanding of the potential of chemometrics and its methods. In a work by Mohamed et al. the concentration of a binary mixture of β -lactam antibiotics from spectrophotometric data was determined using CLS and the PCR method. Four different antibiotics namely, ampicillin, amoxicillin, flucloxacillin, and dicloxacillin, are used as binary mixtures in the study. The spectra of pure components, mixture components were analyzed where there was found to be around 71 to 94% spectral overlap for mixtures. The model to determine the individual concentrations of the antibiotics was validated using CLS and PCR method. The percentage detection of antibiotics, where an external sample, i.e., commercially available capsules, were used for testing, with PCR method were 99.44 ± 0.50 , 99.40 ± 0.46 , 100.32 ± 0.30 , and $99.24 \pm 0.60\%$ towards the antibiotic Ampicillin, Flucloxacillin, Dicloxacillin, and Amoxicillin. Similarly, using the CLS method, the percentage detection for the aforementioned antibiotics were 100.28 ± 0.10 , 101.00 ± 0.50 , 100.60 ± 0.20 , and $100.80 \pm 0.34\%$ (Mohamed et al., 2007). A different approach in the usage of chemometrics has been performed by Sajjadi and coworkers, where the standard deviation was used as a parameter to analyze the degradation of ortho- and para-nitro phenols (Sajjadi et al., 2021). Matrix Augmentation-MCR ALS method was employed to perceive the pure spectra of the individual components in presence of spectral overlapping. On comparing the above methods like PCR, CLS, and PLS, PCR method was found to be statistically significant (Galeano Díaz et al., 1997).

Table 3

List of first and second-order calibration methods (Mas et al., 2010).

First-order calibration methods	Second and higher-order calibration methods
<ul style="list-style-type: none"> • Artificial Neural networks (ANN), • Multiple Linear Regression (MLR), • Principal Component Regression (PCR), • Partial Least Squares (PLS), • Projection Pursuit Regression (PPR). 	<ul style="list-style-type: none"> • Absolute Principal Component Analysis (APCA), • Bilinear Least-Squares (BLS), • Factor Analysis (FA), • Generalized Rank Annihilation Method (GRAM), • Multivariate Curve Resolution-Alternating Least-Squares (MCR-ALS), • Parallel Factor Analysis (PFA), • Partial Least-Squares (PLS), • Positive Matrix Factorization (PMF), • Trilinear Decomposition (TLD), • Unfolded Principal Component Analysis (U-PCA), • UNMIX, • Artificial Neural Networks (ANN), • Chemical Mass Balance (CMB), • Cluster Analysis (CA), • Concentration Weighted Trajectory (CWT), • Multi-Dimensional Scaling (MDS), • Principal Component Analysis (PCA), • Polytopic Vector Analysis (PVA), • Potential Source Contribution Function (PSCF), • Classification And Regression Tree (CART), • Residence Time Weight Concentration (RTWC) • Discriminant Analysis (DA), • Nearest Mean Classifier (NMC), • K-Nearest Neighbors (KNN), • Soft Independent Modeling Of Class Analogy (SIMCA)

Table 4

Various pollutant molecules analyzed using different instrumental methods and their chemometric approach.

Type of pollutant	Instrument used for pollutant detection/quantification.	Chemometric methods used	Reference
Pharmaceuticals (Detection of Pharmaceuticals in Malaysian aquatic environment)	LC-MS/MS	<ul style="list-style-type: none"> • Cluster analysis • Discriminant analysis • Principal component analysis 	Al-Odaini et al. (2012)
Dyes (Acridine Orange and Auramine O)	UV-Visible Spectrophotometer	<ul style="list-style-type: none"> • Partial least squares (PLS) 	Hassaninejad-Darzi et al. (2017)
Dyes (Methylene Blue, Crystal Violet, Bright Green and Methyl Orange)	UV-Visible Spectrophotometer	<ul style="list-style-type: none"> • Partial Least Squares Regression 	Besegatto et al. (2021)
Tryptophan and Tyrosine	Excitation Emission Fluorescence Spectroscopy	<ul style="list-style-type: none"> • Generalized rank annihilation method (GRAM) 	Kumar (2020)
Heavy metals (Soil samples collected from Ganges Alluvial Plain)	Atomic Absorption Spectroscopy	<ul style="list-style-type: none"> • Principal component analysis • Cluster analysis 	Devi and Yadav (2018)
Atrazine, Desloratadine, Paracetamol, β -esterdiol, Ibuprofen, Carbamazepine, Sulfamethoxazole, and Ethynylesterdiol	FTIR transmission spectroscopy	<ul style="list-style-type: none"> • K-nearest neighbor analysis • Partial Least Squares • Ordinary Least Squares 	Quintelas et al. (2020)

2.2. Use of chemometrics towards pollutant quantification in wastewater treatment

A simple chemometric analysis is a linear regression used to analyze the concentration profile of a pollutant molecule. Concentration profiles analyzed at various time intervals during a remediation process made by calibration models help fit the data to study the kinetics of the process. First-order kinetics is represented using Eqs. (1) and (2).

$$r = k \times S \quad (1)$$

$$\ln \left(\frac{C_0}{C_t} \right) = kt \quad (2)$$

Where r is the reaction rate, k is the rate constant (unit – 1/s), S is the concentration of the reactant, t is time, C_0 is the initial reactant concentration, and C_t is the concentration of the reactant at time t . Apart from these equations, various kinetics models have been employed based on the process being carried out to calibrate the kinetic estimation perfectly. Moghadam et al. used chemometric models of ANN and PLS to assess the presence of ascorbic acid, uric acid, and dopamine

spectrophotometrically (Moghadam et al., 2011). In this study, the mixture was analyzed using chemometrics whereby their reaction rate with common reactant was utilized for analysis. The chemometric modeling was based on the kinetics of oxidation of those molecules using tris (1, 10-phenanthroline) and iron (III) complex (ferritin, $[\text{Fe}(\text{phen})_3]^{3+}$). Feed Forward Artificial Neural Network was found to best model the analysis from the kinetic modeling. Chemometric modeling of pollutant analysis can be coupled with RSM to optimize the process and simultaneously estimate the kinetics of degradation. Kaur et al. used the Central Composite design to optimize textile wastewater's electro-oxidation process (Kaur et al., 2020). CCD design employs a multivariate analysis to model the process and enumerate the response equation. This study used the MCR-ALS modeling to resolve the process's kinetics in presence of the intermediates produced during the process. In addition MCR-ALS modeling was applied over the design developed using RSM so that kinetics of degradation can be estimated in optimized condition. The general model used for ALS is shown in Eq. (3).

$$D = CS^T + E \quad (3)$$

In the above equation, D represents the data matrix, C represents the concentration spectral profile, S represents the pure spectra profile, and E represents the experimental error (Hemmateenejad et al., 2015). For estimating kinetic parameters, MCR-ALS is found helpful because it does not require initial calibration and validation, and constraints like non-negativity, unimodality, and correlation constraint can be applied to reduce the ambiguity of the results obtained from the model (Azzouz and Tauler, 2008; Kalejahi et al., 2014).

Case study 1: Nikou and Samadi-Maybodi (2020) performed adsorption of a mixture of dyes, namely amaranth (AM) and sunset yellow (SU), using amine-functionalized Fe-MIL-101 Metal-Organic Framework (MOF). PCR analysis was used to quantify the individual dyes present in the mixture more accurately since spectral overlap was observed when the solution has mixture of dyes. The generalized linear model obtained using PCR is shown in Eq. (4), where C represents the concentration, A represents the spectra, b represents the regression coefficient, and E_c represents the error. Based on the PCR analysis, the dyes' concentration profiles were generated and utilized for estimating the optimal parameters using the Box-Behnken design.

$$C = A \times b + E_c \quad (4)$$

To perform the PCR analysis, two sets of samples were prepared, which included a calibration set (24 samples with a combination of AM and SU at different concentrations from 0 to 20 mg L^{-1}) and a validation set (7 samples with a combination of AM and SU at a different concentration from 0 to 14 mg L^{-1}). The calibration set is used to create a model using PCR, whereas the validation set is used to check the model's predictability. From the PCR analysis, based on the results obtained from the validation set, it was found that the chemometric method employed showed good predictability in accurately measuring the concentration of dyes with R^2 values greater than 0.995. Moreover, the PCR model generated were characterized using figure of merit using mean recovery, coefficient of determination (R_{pred}^2), Relative Error of Prediction (REP), root mean square error of prediction (RMSEP), sensitivity (au L mg^{-1}), selectivity, and limit of detections (mg L^{-1}) and the values were 101.85, 0.997, 3.066, 0.242, 0.69, 0.92, and 2.55 for AM and 102.10, 0.996, 3.047, 0.241, 0.77, 0.90, and 2.23 for SU respectively. The % recovery, R_{pred}^2 , REP, and RMSEP were calculated using the equations (5, 6, 7, and 8):

$$\% \text{Recovery} = \frac{C_{i,\text{pred}}}{C_{i,\text{act}}} \times 100 \quad (5)$$

$$R_{\text{pred}}^2 = 1 - \frac{\sum_{i=1}^n (C_{i,\text{act}} - C_{i,\text{pred}})^2}{\sum_{i=1}^n (C_{i,\text{act}} - \bar{C})^2} \quad (6)$$

$$\text{REP} = \frac{100}{\bar{C}} \times \left[\frac{\sum_{i=1}^n (C_{i,\text{act}} - C_{i,\text{pred}})^2}{n} \right]^{\frac{1}{2}} \quad (7)$$

$$\text{RMSEP} = \left[\frac{\sum_{i=1}^n (C_{i,\text{act}} - C_{i,\text{pred}})^2}{n} \right]^{\frac{1}{2}} \quad (8)$$

A lower REP value and an RMSEP value closer to zero depict the accuracy of the prediction of the concentration of individual dye from the dye mixture using the PCR method. From this study, it is evident that chemometrics helps calibrate the pollutant and optimize the remediation process. Using a chemometric approach in a process also helps obtain maximum information using the data obtained from simple instruments rather than relying on expensive methods and complex instruments.

Case study 2: Kalejahi et al. used both the chemometric approach (MCR-ALS) and RSM to simultaneously remove organic dyes, namely Crystal Violet (CV), Methylene Blue (MB), and Malachite Green (MG), using Fenton's process (Kalejahi et al., 2014). This study gives an excellent insight apart from the spectral overlap that exists due to different components in solution, i.e., a mixture of dyes, which is the interference in the spectra due to another component generated during the process. This component is the by-product generated during the degradation process, which could be spectrophotometrically active and un-calibrated. In this case, the author used the MCR-ALS technique to resolve the

spectra into their individual dye components and determine their kinetic degradation profile. The data matrix obtained for the MCR-ALS process to fabricate the degradation profile was decomposed into orthogonal, transverse of the orthogonal, and diagonal matrices using the Singular Value Decomposition (SVD) method. This analysis gave the result of an additional component apart from three dyes, that exist in the system, which is the by-product. The advantage of using chemometrics in this study is that it helps in analyzing the concentration of the components even without prior calibration and validation since second-order data is used, which is also called a second-order advantage (Booksh and Kowalski, 1994) and also helps in simultaneous quantification of a by-product that evolves during the process, which is usually done using techniques like gas chromatography, mass spectrometry, and high-pressure liquid chromatography. The model constructed using the MCR-ALS technique to determine the concentration of individual dyes from the dye mixture was validated using Prediction Residual Error Sum of Squares (PRESS). In this study, PRESS values were closer to zero, i.e., 0.12, 0.08, and 0.09, for determining the concentration of CV, MG and MB dyes, respectively. Lower PRESS values indicate a very less error in the prediction and validate the model predicted. Therefore there arises a scope for using MCR-ALS for the determination of individual dye concentration from a mixture of dyes and the concentration by-products formed during the degradation process.

Case study 3: Similar insights were obtained in a study by Hammateenejad et al. where starch coated CdSe quantum dots were used to degrade cationic dyes (Hemmateenejad et al., 2015). The dyes were quantified using UV-Vis spectrophotometry. Eq. (3) is used as a soft model to fabricate the data matrix. D represents an augmented matrix in the model because the matrices were categorized into submatrices based on the eight different pH used. Hence the matrix consists of two hundred spectra at five hundred and one wavelengths resulting in a matrix of order ($r \times c$) 200×501 .

On the other hand, the matrices C and S are of order ($r \times n$) and ($n \times c$), respectively. The n represents the number of components found using the SVD method. The benefit of using the chemometric method is that number of components enumerated by this method helped identify one reaction intermediate and two products along with the two reactants. It also gave insight into how these components behave in response to pH. The concentration of components 2 and 3 increased with an initial increase in pH and remained constant with further increase. Components 4 and 5 were found to decrease with an increase in pH, which is considered to be the products evolved. Component 1 appeared during the initial time and declined with an increase in time, suggesting it to be an intermediate compound. Thus, chemometrics helps know the number of components produced during the process and helps understand their behavior concerning the process parameters.

2.3. Modeling the speciation of pollutants

Speciation of a pollutants mostly metals occurs via interaction with other acids or humic substances present in water or soil matrix. Speciation of pollutants, mainly the heavy metals, involve the complexation with other anions or chelating agent (Xu et al., 2022). The pollutants take different oxidation states upon interaction. Insights about the speciation of pollutants help to develop good treatment strategy. There are models which helps to analyze and understand the speciation of pollutants based on their chemical reaction nature in the environment. One such model is Windermere Humic Aqueous Model (WHAM) (Tipping, 1994). Using the WHAM Tipping et al. analyzed the different speciation of metal ions in seawater, river and estuarine water (Tipping et al., 1998). Twiss et al. used MINEQL+ and MINTEQA2 softwares to compute the chemical speciation of metals (Twiss et al., 2001). This software estimates the speciation of metals using database and the equilibrium of metal and metal complexes at experimental condition. A parsimonious model was developed by Lofts, whereby the speciation of metal can be modeled using simple parameters of the soil (Lofts, 2022). This model is termed as POSSMs i.e., ParsimOniouS Speciation of Metals in soils, developed based on the metals that are geochemically active and solution phase composition.

2.4. Benefits of using chemometrics over conventional analysis methods

So far, the discussion of the application of chemometrics in different environmental remediation processes gives a clear thought that quality information can be obtained with the help of elementary data. Initially, it was not possible through conventional methods like simple concentration quantification and reaction rate prediction. The vital benefit of using chemometrics is resolving the pure spectra of the components present as a mixture, where a spectral overlap exists (Khataee et al., 2016). This aspect is least considered in the conventional approach, where the absorbance of a dye at its λ_{\max} is taken as such, even though a spectral overlap occurs. One of the aspects that chemometrics is appreciated for is their ability to construct the pure and concentration spectra to reactant species and by-products and to intermediates that are generated. Constraints can also be applied to chemometric modeling to compute the compounds along with interfering compounds (Bayat et al., 2020). These benefits are found less in conventional or rather the usual method of pollutant quantification.

3. Use of mathematical and equation modeling toward process optimization

The optimization of processes is performed using software like Design Expert and Minitab, which provides the user with an equation that predicts the process and gives some optimal solutions. The solutions it offers may or may not be feasible experimentally or economically. Additional mathematical implications may help the researcher obtain more clarified results on the experiment performed. The software's response equation mostly comes under a second-order polynomial equation, upon which fundamental mathematical implications like partial differentiation, matrix construction and manipulation, and eigenvalues production can be performed.

3.1. Role of partial differentiation

Partial differentiation is an advantageous method to interpret the character of a contour plot obtained through optimization software. Both the first order and second partial derivatives help in this scenario. First-order derivatives provide the contour graph's stationary points. In contrast, the second-order partial derivative gives information about the geometric characteristic, i.e., the contour's maximum, minimum, or minimax character. The geometric aspect can also be estimated using canonical analysis, which we will deal with in the next part.

Consider a second-order response equation,

$$Y = \beta_0 + \sum_{i=1}^3 \beta_i X_i + \sum_{i=1}^3 \sum_{j=1}^3 \beta_{ij} X_i \times X_j + \sum_{i=1}^3 \beta_{ii} X_i^2 \quad (9)$$

Upon differentiating the eqn (9) for the individual factor variables, i.e., finding of $\frac{\partial y}{\partial x_i}$ Where $i = 1, 2, 3$, etc., equating it to zero gives the contour's stationary point.

Then finding of second-order partial derivatives, i.e., $\frac{\partial^2 y}{\partial x_i^2}$ where $i = 1, 2, 3$, etc, and $\frac{\partial^2 y}{\partial x_i \partial x_j}$ helps in figuring out the geometrical characteristic of the contour graph. Let us see this method with an example.

Consider a second-order polynomial equation with three different variables, $y = f(x_1, x_2, x_3)$. The following steps help in finding the nature of this equation.

Step 1. Find $\frac{\partial^2 y}{\partial x_1^2}, \frac{\partial^2 y}{\partial x_2^2}, \frac{\partial^2 y}{\partial x_3^2}, \frac{\partial^2 y}{\partial x_2 \partial x_3}, \frac{\partial^2 y}{\partial x_3 \partial x_1}, \frac{\partial^2 y}{\partial x_1 \partial x_2}$, which are A, B, C, F, G, H.

Step 2. Find $AB - H^2$, which is equal to $\begin{vmatrix} A & H \\ H & B \end{vmatrix}$ and denoted as D_1

Step 3. Find $\begin{vmatrix} A & H & G \\ H & B & F \\ G & F & C \end{vmatrix}$ which is denoted as D_2

The obtained response equation can be interpreted as maximum if $A < 0, D_1 > 0, D_2 < 0$. In the case of minimum, the condition is $A > 0, D_1 > 0, D_2 > 0$. A saddle or minimax exists if the results fit under neither minimum nor maximum.

3.2. Role of canonical analysis

The canonical analysis is a kind of transformation performed to an equation with the help of matrices. Similar to the results produced by second-order partial differentiation, Canonical analysis provides insight into the nature of a contour plot with eigenvalues' help. The steps to perform Canonical analysis are as follows,

Step 1. Find the Hessian matrix or the B matrix shown in eqn (10). The Hessian matrix is constructed as follows for a second-order polynomial equation with three different variables. Here x_{11} corresponds to the coefficient of x_1^2 term and x_{12} corresponds to the coefficient of $x_1 x_2$ term.

$$B = \begin{bmatrix} x_{11} & \frac{x_{12}}{2} & \frac{x_{13}}{2} \\ \frac{x_{21}}{2} & x_{22} & \frac{x_{23}}{2} \\ \frac{x_{31}}{2} & \frac{x_{32}}{2} & x_{33} \end{bmatrix} \quad (10)$$

Step 2. Find $|\hat{B} - \lambda I| = 0$

The above equation gives the values of λ . If all the eigenvalues are positive, then the contour is a minimum. Else if all the eigenvalues are negative, then the contour is a maximum. Saddle occurs if eigenvalues with mixed signs are obtained.

Step 3. Convert the polynomial response equation into the canonical equation, eqn (11), as given below.

$$\hat{y} = \hat{y}_s + \lambda_1 w_1^2 + \lambda_2 w_2^2 + \lambda_3 w_3^2 \quad (11)$$

In the above equation, \hat{y}_s is the response obtained at a stationary point, λ_1, λ_2 , and λ_3 are the eigenvalues.

3.3. Role of ridge analysis

When the stationary point is a saddle or the point lies outside the experimental region, ridge analysis helps find the best feasible solutions, either maximum or minimum, based on the requirements within the operating domain. Ridge analysis also works on matrix manipulations. The steps involved in performing ridge analysis are as follows,

Table 5

Use of canonical and ridge analysis for optimization in various fields.

S.No	Field	Research work	References
1.	Food Technology	Food quality check, production of edible oils and gels, Food processing, extraction of compounds from a natural food source	Ortega-García et al. (2005), Roopa and Bhattacharya (2008), Sumithra and Bhattacharya (2008), Tiwari et al. (2008), Tiwari and Bhattacharya (2014) and Wang et al. (2017)
2.	Bioprocess Technology	Production of metabolites, Production of enzymes, optimization of media components	Dayananda et al. (2005), Leite et al. (2012), Li et al. (2007), Munder et al. (2020), Pasma et al. (2013), Sarada et al. (2002) and Yu et al. (2008)
3.	Environmental Engineering	Degradation of contaminants, detection of contaminants	Franceschi et al. (2002), Hazime et al. (2013), Li et al. (2010), Sudarjanto et al. (2006) and Tukai et al. (2002)
4.	Extraction	Solvent mediated, Microwave-assisted, Solid-phase extraction, Ultrasonication	Derrien et al. (2017), Eh and Teoh (2012), Jang et al. (2014), Mihaela (2007) and Prouteau et al. (2004)
5.	Synthesis of Compounds	Chemical way of synthesis, Enzymatic way of synthesis	Behij et al. (2011), Chen et al. (2002), Liu and Zhang (2011) and Liu et al. (2007)

Step 1. Find $(\hat{B} - \mu I)x = -\frac{1}{2}b$, where b is a single column matrix whose elements are coefficients of linear terms in the response equation.

Step 2. Upon solving the above matrix equation, we get $x = f(\mu)$.

Step 3. Substitute the values of μ based on the following criteria. If the required region should be of maximum response, substitute the value of μ greater than the maximum eigenvalue, i.e., $\mu > \lambda_{\max}$. Conversely, if the required region should be of minimum response, then $\mu < \lambda_{\min}$ must be chosen. The values obtained are the maximum or the minimum response value within the sphere whose center is the design origin, and the radius (no unit) is given by the square root of the sum of the squares of the maximum or minimum value obtained.

The ridge analysis helps find solutions with various combinations of variables that are most feasible for the process to be operated with either maximum or minimum response.

4. Augmentation of canonical and ridge analysis with RSM for a more accurate process optimization

Canonical and Ridge analysis provides a more clear picture of the geometry of the response surface. The canonical analysis provides information about the contour without its reference. Gaining knowledge about a response surface when there are factors more than three is difficult, wherein a canonical analysis provides a better understanding of the surface. Many of the response surfaces obtained may give a visualization that could end in erroneous interpretation about the process (Taylor et al., 2012). Reducing a second-degree polynomial response equation into a canonical form helps the researcher find the factors that maximize or minimize the response. This simple mathematical modeling also provides information about the stationary points' location and the type of surface obtained, either a maximum or minimum or minimax (Šibaliija and Majstorović, 2015). The use of canonical and Ridge analysis in the optimization of a process does provide not only the researcher about the location of optimal operating solution(s) but also some insights to carry out the process in a different way of input combination so that the same optimization is achieved with some additional benefits (Myers et al., 2016). The canonical analysis gives the results by placing the origin of the response surface in the stationary point. The signs of the eigenvalues tell about the kind of response surface obtained and tell us about the direction, forward or reverse, in which one must move to obtain a required response.

Table 5 represents the usage of Canonical and Ridge analysis in various domains and the subdomains in which its application has been found. Apart from the areas listed in the table, canonical and ridge analysis are used in the field of Plant biotechnology (Belščak-Cvitanović et al., 2017), electrophoresis (Arroyo-Manzanares et al., 2019), and mechanical engineering (Cinar et al., 2016). Supplementary figure S3, represents the percentage of articles that used canonical and ridge analysis for optimization at three different time intervals, i.e., from 2000 to 2020. Canonical and Ridge analysis was effectively used in researches related to bioprocess, food technology, and extraction. In chemical engineering, the use of these mathematical models is less compared to other fields. The exploitation of these mathematical models in this field gives many profitable solutions that benefit optimization. Canonical and Ridge analysis is more frequently used in the field of food processing and technology. Other areas that were found to use these mathematical modeling include electrophoresis, plant and agriculture technology, pyrolysis, animal husbandry, and neuroscience. When the stationary point obtained using a canonical analysis lies remote to access, a ridge analysis helps identify the optimal responses within the region. The results of ridge analysis are appreciable from both empirical and theoretical points of view. The results obtained from ridge analysis help the experimenter to carry out the experiments at a reasonable cost.

Table 6
Ridge analysis of removal of RR120 using TiO₂/UV system.

Coded radius	Estimated response (Color removal %)	TiO ₂ concentration (g/L)	Dye concentration (mg/L)	UV intensity (mW/cm ²)
0.0	76.1	1.50	75.0	6.0
0.1	78.9	1.53	71.8	6.4
0.2	81.7	1.57	68.0	6.8
0.3	84.7	1.59	63.8	7.1
0.4	87.9	1.61	59.4	7.4
0.5	91.2	1.62	54.8	7.6
0.6	94.8	1.63	50.0	7.8
0.7	98.6	1.63	45.2	8.1
0.8	102.6	1.63	40.4	8.3
0.9	106.9	1.62	35.5	8.5
1.0	111.4	1.62	30.7	8.7

4.1. Use of canonical and Ridge analysis: Case studies on environmental application

The canonical and Ridge analysis have an extensive application in the modeling process, enabling better process control. Though it has various applications, the importance of this analysis is highly significant in environmental applications. Most of the environmental processes involve many parameters to work with based on the types of an operation used. Each parameter's significance towards the optimized treatment target creates an arena of opportunities to employ canonical and Ridge interpretation. Two case studies were taken from the reported literature. The results were discussed and compared with the outputs generated using the SAS program.

Case Study 1 Iyoung Cho and Kyung-Duk Zoh have studied and modeled the Photocatalytic degradation of azo dye (RR120) in TiO₂/UV system. The advantage of canonical and Ridge analysis (Cho and Zoh, 2007) over the response surface modeling was justified. Three factors, (X₁) TiO₂ Concentration, (X₂) Dye concentration, (X₃) UV intensity, and two responses (Y₁) Color removal % and (Y₂) TOC removal %, were taken, and they framed models using Central composite design. The obtained model equations (uncoded form) were Eqs. (12) and (13)

$$\begin{aligned} \text{Color removal \%} = & 69.84 - 8.55x_1 - 0.82x_2 - 12.48x_3 + 3.18x_1^2 + 0.004x_2^2 - 0.43x_3^2 + 0.12x_1x_2 \\ & + 0.0001x_1x_3 - 0.05x_2x_3 \end{aligned} \quad (12)$$

$$\begin{aligned} \text{TOC removal \%} = & -15.78 + 53.96x_1 - 0.23x_2 + 7.36x_3 - 12.8x_1^2 - 0.0013x_2^2 - 0.48x_3^2 \\ & - 0.06x_1x_2 + 0.167x_1x_3 + 0.003x_2x_3 \end{aligned} \quad (13)$$

As there were three factors, keeping one factor constant for each graph, three response surfaces for (Y₁) response and three response surfaces for (Y₂) response were obtained; a total of six response surfaces were obtained as mentioned above. Using Canonical analysis, the response surfaces of (Y₁) response were saddle, and the response surfaces obtained for (Y₂) response were maximum. The optimal solutions were also found using Canonical analysis, they were X₁ = 1.63 g/L, X₂ = 45.2 mg/L, X₃ = 8.1 mW/cm², for saddle Y₁ response and X₁ = 1.92 g/L, X₂ = 34.7 mg/L, X₃ = 8.5 mW/cm², for maximum Y₂ response and the points were also located within the experimental ranges. Ridge analysis was used to predict the responses. The estimated response for color removal using ridge analysis at various coded radius is shown in Table 6. From the maximum ridge analysis it is found that there is a 31.69% increase in dye removal when the TiO₂ concentration and UV intensity is increased by 7.41% and 31.03% respectively. Since the concentration of dye gives a negative effect, 59.07% decrease in dye concentration increased the color removal by 31.69%. This individual effect of the factors has been calculated upon changing the maximum ridge radius in contour from 0.0 to 1.0. The predicted responses were 100% Color removal (Y₁) and 67.3% TOC removal (Y₂). These predicted results were on par with the experimental results: 98 ± 2% Color removal and 66 ± 3% TOC removal. Therefore the detailed study on canonical and Ridge analysis would provide a lot of interesting information from the basic experimental data, which helps in efficient process control.

Case Study 2: Canonical and Ridge analyses were utilized to estimate the degradation of Cefaclor, a β-lactam antibiotic, using gamma irradiation (Yu et al., 2009). Cefaclor concentration and Gamma-ray dose were given as input factors X₁ and X₂, respectively. The responses were the reduction of Cefaclor concentration (Y₁) and Cefaclor removal efficiency (Y₂).

The signs of eigenvalues, shown in Table 7, show that both the responses are saddle. Hence a ridge analysis for a maximum response would give better optimization solutions for Cefaclor degradation. From maximum ridge analysis, shown in Table 8, the optimal condition obtained for a better reduction in Cefaclor concentration was 25 mg/L of Cefaclor and 350 Gy of gamma irradiation. Cefaclor concentration of 21 mg/L and gamma irradiation of 565 Gy gives a good removal efficiency of 98.35%. The maximum ridge analysis shows that, maximizing the gamma ray dosage by 30.42% and reduction of Cefaclor concentration by 48.41% increases the reduction of Cefaclor concentration and removal efficiency by 88.33% and 26.98% respectively.

Table 7
Stationary point and Canonical analysis results.

Factors	Y ₁ (Reduction of Cefaclor concentration)		Y ₂ (Cefaclor removal efficiency)	
	Stationary point (coded)	Eigenvalue	Stationary point (coded)	Eigenvalue
X ₁ (Cefaclor concentration)	8.9	7.63	1.7	5.9
X ₂ (Gamma-ray dose)	3.5	−0.08	0.4	−42.28
Result	The response surface is a saddle		The response surface is a saddle	

Table 8
Consolidated ridge analysis for responses Y₁ and Y₂.

Coded radius	X ₁	X ₂	Y ₁	Y ₂
	Cefaclor concentration (mg/L)	Gamma ray Dose (Gy)	Reduction of Cefaclor concentration (mg/L)	Removal efficiency (%)
0.0	19.5	350.0	2.05	89.3
0.1	19.06	381.8	2.92	93.7
0.2	18.43	410.2	3.95	97.5
0.3	17.59	433.6	5.12	100.9
0.4	16.61	451.5	6.44	104.0
0.5	15.55	465.1	7.91	107.0
0.6	14.45	475.6	9.54	110.0
0.7	13.35	484.2	11.32	113.0
0.8	12.25	491.3	13.25	116.0
0.9	11.15	497.5	15.33	119.1
1.0	10.06	503.0	17.56	122.3

5. Comparative analysis towards the enhanced interpretation

Here software indicates the use of statistical software that performs optimization using RSM. Most of the study of interest on RSM ends in the response equation, contour plots, and the software's optimal solutions. There exist an elixir of solutions that provide a detailed picture of the response elements obtained. Canonical analysis can be performed using both software, like Maple and SYSTAT (Baheti et al., 2013), SAS, R-Program, and paperwork. Canonical analysis tells the optimal solution is maximum or minimum, or a saddle is a simple mathematical calculation. If a saddle occurs, it also means the remoteness of the stationary point to the origin. Ridge analysis yields the optimal solutions within the increasing radii from the origin, either a maximum or minimum, which lies within the experimental domain. These solutions provide an alternative to the stationary point solution that lies remote to the explored domain. This can be explained so that a change in the concentration of initial reactants for a product production that is optimal and economically profitable can be obtained using ridge analysis. Hence Canonical and Ridge analysis acts as a converting factor between empirical calculations to operational enhancement.

6. Challenges and future recommendation

- Knowledge gap in understanding the application of Canonical and Ridge analysis in enhancement of results obtained through RSM should be addressed among scientific community.
- Incorporation of chemometrics in basic research methodology will help reducing the errors in experimentation and increases the validity of research.
- Using chemometrics in pollutant remediation helps researcher to work on degradation of mixture of pollutant synthesized in lab, instead of using real samples, and analyze them with maximum precision.
- In remediation processes like AOPs, the solution conditions are highly dynamic, where the physical conditions like temperature, pH, and ionic strength vary which leads to the formation of various by-products. With the help of chemometrics, the possible compounds present in the reaction mixture can be elucidated and absolute kinetic parameters can be determined. An example for this kind of analysis could be the work performed by Sajjadi et al. where the MCR-ALS method was coupled with RSM to analyze the pure spectra of individual components in binary mixture of ortho- and para nitrophenol (Sajjadi et al., 2021).

7. Conclusion

This review gives insight into effective pollutant quantification and process optimization using simple mathematical methodologies. Mathematical tools like chemometrics and response surface methodology-based optimization help effectively quantify contaminants and optimize the remediation process, respectively. Chemometrics help in pollutant monitoring in the presence of many interfering compounds, which ease the quantification of the desired contaminant in

real wastewater samples. Different statistical and software packages are available to perform chemometrics analysis of results obtained through quantifying instruments like UV–Vis spectrophotometer, HPLC, Atomic Absorption Spectroscopy, and LC/GC–MS. The instrumental software coupled with chemometrics packages helps environmental researchers to quantitate the concentration of the contaminants accurately in the real wastewaters. Response surface methodology tools have limitations in addressing the gap in finding the optimal solutions within the selected range in some cases. Manual errors may also occur while interpreting response surfaces. Therefore, the importance of simple mathematical tools like partial derivatives, Canonical analysis, and Ridge analysis in resolving these problems was discussed.

Chemometrics can help in complete understanding of the AOPs like photocatalytic degradation, electro-catalytic oxidation process, sulphate activation and gamma irradiation, where intermediates and by-product monitoring is quite tricky and also requires higher-end instrumentation.

CRedit authorship contribution statement

Harish Kumar Rajendran: Data curation, Writing. **Mohammed Askkar Deen Fakrudeen:** Data curation, Writing. **Ragavan Chandrasekar:** Data curation, Writing. **Siara Silvestri:** Review & editing. **Mika Sillanpää:** Supervision. **Padmanaban Velayudhaperumal Chellam:** Review & editing, Conceptualization, Supervision.

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.

Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.eti.2022.102827>.

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