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ABSTRACT: Zero-valent metals proved high reactivity to adsorb and degrade various contaminants removal. The chemically prepared nZVAl was characterized using UV-Vis spectrum, X-ray diffraction (XRD), and scanning electron microscope (SEM). This investigation explores the adsorption effect of nZVAl powder toward soluble organic compounds exemplified by chemical oxygen demand (COD) standard solution. The effect of different operating parameters was studied to identify the best removal conditions. All variable and covariable data were introduced to build statistical models. The effect of the operating parameter was studied at different pH (3-10), nZVAl dosages (0.1-0.8 g), at different times (5-120 minutes), stirring rate (50-400 RPM), and initial COD concentration (100-800 mg/L). The obtained results displayed that nZVAl is effective in the removal of standard COD solutions, where the removal percentages were 56% and 96% for 800 ± 18.0 and 100 ± 11.8 mg/L COD, respectively, at 10 minutes after using nZVAl dry dosage 0.6 g/L, pH 8, and rate 100 rpm. Also, the effect of nZVAl on other wastewater contaminants removal was studied and compared with Egyptian law for draining wastewater into nonfresh water (drainage-lakes-ponds) No. 48 of 1982 limits. The results of adsorption isotherm and kinetic model of COD fitted well to Freundlich isotherm and pseudo second order, respectively. Nonlinear artificial intelligence neural network (ANN) importance data agree with linear response surface methodologies (RSM) in simulating the adsorption of COD onto nZVAl indicating that the most significant coverable is adsorbent dose. Finally, this study appropriates using nZVAl in highly contaminated wastewater rather than other chemical and biological processes.

KEYWORDS: Chemical Oxygen Demand removal, nZVAl, artificial neural networks, regression analysis, isotherm studies, kinetic studies

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Introduction and Background

Water is the basic source for the development of developing countries.[1] Traditional irrigation processes, fish ranches, nuclear reactors, and electricity stations are highly consuming water and allowing highly contaminated water to pass into water drainage, lakes, and bonds, leading to increased awareness about overcoming the current problem and finding the suitable low-cost solution for it.[2] Nowadays, developing countries depend on water in large projects to secure and save the energy and food supply for the existing and coming generations.[3-5] Theoretical studies were conducted to calculate and expect the amount of consumption in municipal and industrial wastewater in Egypt according to the growth rate and expected that it will reach 7.9 billion cubic meters at 2030, while it was 3.5 billion cubic meters in 1995.[6,7] So, wastewater treatment is the only choice to save water and decrease water consumption, especially in developing countries. Nowadays, there are different nontraditional techniques carried out for wastewater treatment depending on reducing the operation cost and producing high-quality treated water.[8,9] The traditional treatment techniques depend on dilution, physical, and chemical treatment processes, but they are not effective to eliminate a wide range of wastewater contaminants.[10-14] Also, the biological treatment process is ineffective for industrial contaminants removal.[15-17] Different studies proved that nanotechnology is an effective way for wastewater treatment by adsorption and degradation process. One of the important materials is nano zero-valent metals such as nZVI, and other advanced oxidation processes (AOPs) are effective in removing organic and inorganic contaminants via degradation and adsorption process in an efficient and fast way.[18,19] Equation (1) describes the reaction of nano zero-valent iron when contacted with the aqueous solution indicating that the electron transfer process is responsible for its reactivity.[19,20] Also, previous studies describe that nZVAl have a similar character for degradation and adsorption of wide range of wastewater contaminants as in equations (2) and (3).[21] The selection of alternative high-efficiency zero-valent metals depends on the facility of electron transfer and the stability of dissolved metals against precipitation through different pH ranges. Zero-valent aluminum (ZVAl) proved a high thermodynamic driving force (for electron transfer) than ZVI, so this article suggested using nZVAl for wastewater treatment instead of nZVI.[21,22]

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO + OH^- \quad (1)$$

$$Al^0 + 3O_2 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O_2 \quad (2)$$

$$Al^0 + 3H_2O_2 \rightarrow Al^{3+} + 3HO + 3OH^- \quad (3)$$

There are different water quality indicators that can describe the presence of contaminants in an aquatic system, such as dichromate chemical oxygen demand (COD), total 5-day biological oxygen demand (BOD), and selective ultraviolet (UV) scanning spectrum at 254 and 220 nm, which indicates the presence of carbon and nitrogen compounds in direct and indirect ways.[23-25] Mainly, the presence of organic contaminants in high concentrations is accompanied by reduction of dissolved oxygen (DO) concentrations. The oxidizable organic compounds are highly consuming DO levels in water bodies.[26] Final COD in the effluent must be reduced to allow limits to be reused in different purposes.[27-30]

This work attempts to prepare and characterize nZVAl using the same method of preparation of nZVI also, to examine the removal of soluble COD using nZVAl. The relation among COD removal efficiencies and various operating parameters were studied. Nonlinear equations of isotherm and kinetic models were used to predict the suitable model by applying different error functions. Multilayer perceptron (MLP) statistics algorithm was selected to describe the artificial neural network (ANN) model. Linear regression model using the "Enter method" was conducted to estimate the theoretical removal equations for COD and sensitivity of each variable.

Materials and Methods

Chemicals and reagents

All chemicals used in the present work is high-grade chemicals and reagents including aluminum sulfate (purified 99.9%; LOBA Chemie), sodium borohydride ($NaBH_4$, 98% pure; CDH Company), Ethanol (C_2H_5OH 99%, World co. for sub & med industries), potassium hydrogen phthalate (99.5%; ADWIC company), mercuric sulfate (Ex-Pure; Oxford Laboratory reagent company), and potassium dichromate ($K_2Cr_2O_7$, 99.5; Loba Chemie).

Preparation of nZVAl

The preparation process was adapted from the reduction equation of nZVI using drop by drop methods.[14,31] By converting the number of moles in equation (4) to grams, we can dissolve 6.84302 g from $Al_2(SO_4)_3$ in 4/1 (v/v) ethanol/deionized water (100 mL ethanol/25 mL of deionized water). About 4.539 g $NaBH_4$ reducing agent was added into 1000 mL of deionized water. The $NaBH_4$ solution was dispensed into a burette and dropped into the aluminum solution in the rate of 1 drop in 1 second as shown in Figure 1A. A huge amount of H_2 was evolved during the reduction process as in Figure 1B and white solid precipitate appeared after the first drop of $NaBH_4$ solution. The reduction of aluminum salt by the effect of sodium borohydride produced nZVAl. The mix was motivated by adding an excess amount of $NaBH_4$ for an additional 10 minutes to ensure the complete reduction of aluminum ions. Then, the filtration process was applied to separate the white Aluminum nanoparticles from the liquid solution using Whatman filter papers (No. 42, 100 circles, diameter 150 mm, and 2.5 μm pore size) as shown in Figure 1C. The filtrated white Al nanoparticles were washed with 50 mL of absolute ethanol 3 times to prevent the rapid oxidation of nZVAl. Finally, the synthesized Al nanoparticles were dried in an oven at 80°C overnight as shown in Figure 1D. For storage, the layer of ethanol was placed to prevent the oxidation of nZVAl

$$2Al_2(SO_4)_3 + 12NaBH_4 + 36H_2O \rightarrow 4Al^0 + 42\,H_2 + 12B(OH)_3 + 6Na_2SO_4 \quad (4)$$

Batch adsorption studies

The effect of nZVAl into standard COD solution was studied by the batch procedure. The COD removal efficacy was studied with pH range from 3 to 10, different nZVAl dosages from 0.1 to 0.8 g, different stirring rates from 50 to 400 RPM, and different times from 5 to 120 minutes. A known selected weight of nZVAl dry powder 0.6 g was equilibrated with 1 L of different standard COD solutions 100 to 800 mg/L and shacked at 100 RPM for 10 minutes at room temperature. After equilibrium, the standard solutions were filtrated using filter paper No. 1 and the remaining concentrations were measured using dichromate—closed reflux method according to Standard methods for the examination of water and wastewater 23rd edition.[32] The removal percentages were calculated by using equation (5). The sorbed amount of COD was calculated using equation (6).[33]

$$Sorption(\%) = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \quad (5)$$

where C_0 is the initial COD concentration (mg/L) and C_e is the equilibrium COD concentration (mg/L).

$$Q_e\,(\text{mg/mg}) = \frac{(C_0 - C_e)V}{m} \quad (6)$$

where Q_e is the adsorbed COD capacity (mg/mg), V is the volume of used solution (L), and m is the nZVAl dry weight (mg).

Characterization of nZVAl

The prepared nZVAl was examined using UV-Vis spectrum at a range from 190 to 1000 nm, powder X-ray diffraction (XRD) and scanning electron microscope (SEM). The nZVAl sample was placed in XRD at radiation wavelength (Cu-Kα = 1.5418 Å). The bending angles (2θ) ranged from 0° to 80° at a step size of 0.0167°.[34] Also, nZVAl was characterized using an SEM at magnification 80 000.

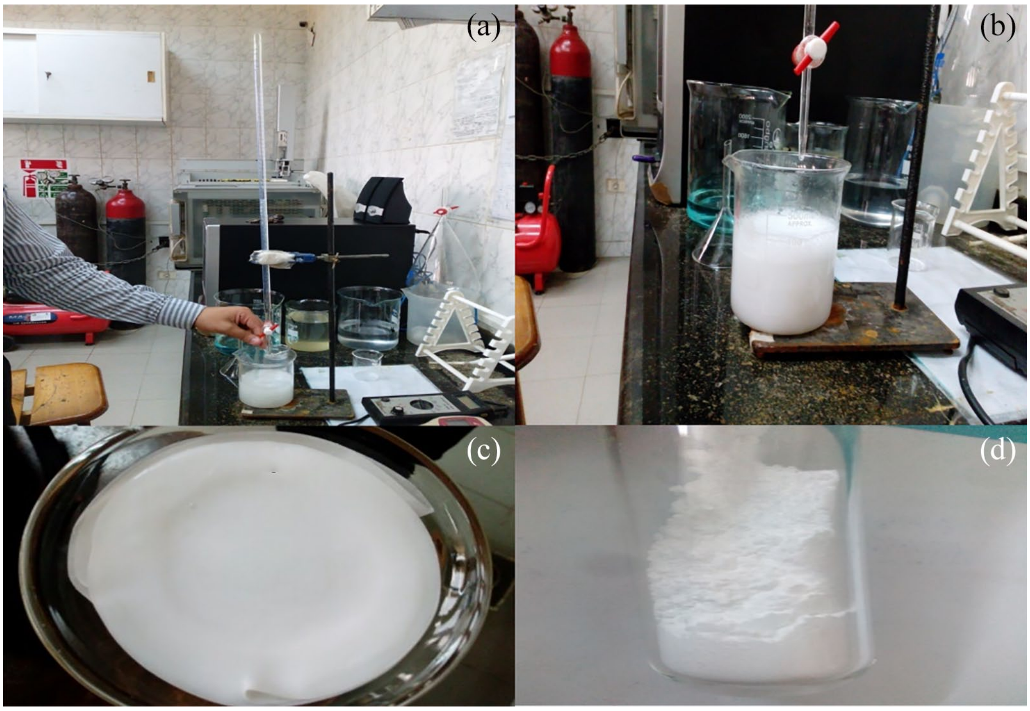

Figure 1. Preparation of nZVAl: (a) White precipitate appears after first drops of $NaBH_4$ solution, (b) Complete reduction of $Al_2(SO_4)_3$ solution at the end of the preparation process and evolve huge amount of hydrogen gas (c) Filtration process using whatman filter paper. (d) Final product of dried nZVAl powder.

Isotherm studies

Different nonlinear models were studied to define the adsorption mechanism of COD into nZVAl. The selected isotherm models were Langmuir, Freundlich, Redlich-Peterson, Sips, Hill, Khan, Koble-Corrigan, Toth, and Jovanovich. The description, as well as the nonlinear equations of these models, is presented in Supplementary Table S1.

Kinetic studies

To determine the suitable time for reaching the equilibrium state, COD solutions were sited in contact with nZVAl at different times at a fixed temperature. The quantity of sorbed COD at time t is known Q_t (mg/mg), which was calculated using equation (7):

$$Q_t = \frac{(C_o - C_t)V}{W} \quad (7)$$

where C_o is the initial COD concentration (mg/L), C_t is the initial COD concentration at time t (mg/L), V is the volume of the solution (L), and W is the weight of nZVAl.

To explore the suitable kinetic models which illustrate the kinetics of COD removal mechanism at different times, the pseudo first order (PFO); pseudo second order (PSO); Avrami, Elovich, and intraparticle nonlinear models were calculated. The description, as well as equations of these models, exists in Supplementary Table S2.[35-39]

Validation of adsorption isotherms and kinetics. The error functions were identified as the suitable isotherm and kinetic models that can describe the mechanism of the adsorption process, and the 5 error equations exist in Supplementary Table S3.[40]

Quality control

All trials were directed triplicate during this research, and the average results are reported along with the standard deviations. Blank samples without any nanoparticles were run along with the tests. The analytical grade [A] glassware was used during the experiments and the deviation was added in uncertainty calculations with combined uncertainty of 0.001; the uncertainty for the mass standard was added by calculating the SQRT of power 2 of uncertainty from calibration certificate of balance with combined uncertainty 0.0118. Also, the uncertainty of prepared standard (potassium dihydrogen phosphate) was calculated by SQRT of summation power 2 of repeatability, purity, mass, and glassware with combined uncertainty 0.006. Finally, the budget uncertainty was calculated by the same techniques after adding the uncertainty from the calibration curve. The budget combined uncertainty in COD determination was 0.0411. The expansion of combined uncertainty was 2 to represent 95% from results and the expanded uncertainty was 0.082. All used instruments were calibrated before the measurements. Microsoft office 2016, Origin pro-2016, and SPSS statistics 22 were used for all statistical investigates.[41]

Statistical analysis

Response surface methodology. The response surface methodology (RSM) results were carried out by using linear regression

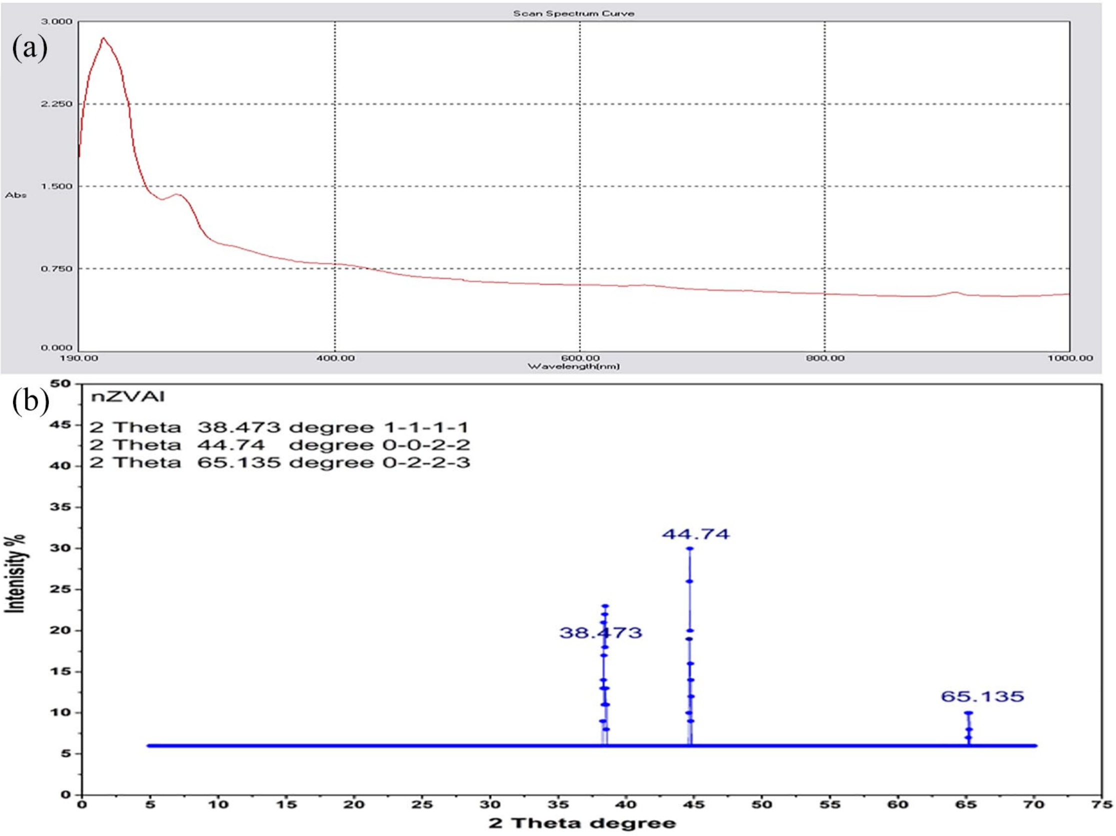

Figure 2. (A) UV scanning spectrum and (B) X-ray powder for nZVAl nanoparticles. UV indicates ultra violet.

enter method to show a simultaneous confidence band for response surface. The model displays the outline of RSM for COD removal percentages against different covariables as in equation (8).

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_5 x_5 + \beta_6 x_6 \quad (8)$$

where Y is the predicted response of COD removal percentages (%); x_1 is the pH range (3 to 10); x_2 is the adsorbent nZVAl dose (0.1-0.8 g); x_3 is the contact time 5-120 minutes; x_4 is the stirring rate (50-400 RPM); x_5 is the COD concentration (100-800 mg/L); β_0 is the model intercept; and β_1, β_2, β_3, β_4, and β_5 are the linear coefficients of x_1, x_2, x_3, x_4, and x_5, respectively.

Neural network structure. An ANN using MLP was established to expect COD removal percentages, which involve input, output, and hidden layers. The adsorption obtained data from the 5 covariables are located in the input layer. All presented data are divided into standard training, validation, and testing values and plotted by the SPSS system. The selected type of artificial networks models is multi-layer perceptron, and it is one of the most regularly used network styles.

Results and Discussions

Characterization of nZVAl

Figure 2A of UV scanning spectrum shows that there are no significant peaks during scanning spectrum from the duration between 190 and 1000 nm indicating that the aluminum sample is free from oxides and hydroxides.[42,43]

Figure 2B of the XRD result shows 3 main peaks at $2\theta = 38.473°$, $44.74°$, and $65.135°$ indicating the formation of pure aluminum powder and showing agreement with the other previous studies.[44]

Figure 3 shows the SEM figure of nZVAl before any treatments. The powder nZVAl showed an irregular surface with size ranging from 34 to 50 nm as many pores increase its ability to adsorb a huge amount of sorbed COD materials to the inner nZVAl.[45]

All characterized results agree with previous preparations of a commercial product of nZVAl.[46]

Effect of operating parameters

pH effect. The effect of pH was studied (pH 3, 4, 5, 6, 7, 8, 9, and 10) for standard COD concentration 400 ± 5.11 mg/L using 0.6 g nZVAl dosage, contact time 10 minutes, and rate 100 RPM, and the final COD concentrations were reduced to (180, 168, 156, 136, 116, 108, 112, and 148 mg/L) and the removal percentages were (55%, 58%, 61%, 66%, 71%, 73%, 72%, and 63%), respectively, as shown in Figure 4A. The effect of pH shows maximum removal efficiency at pH 8 in slightly alkaline media, and this maybe because of different reasons. First, the effect of point of zero charge (PZC) and the PZC of Aluminum lie in alkaline media and PZC of acid-washed ZVAl is between 7.2 and 8.[47] At the point of zero, the surface

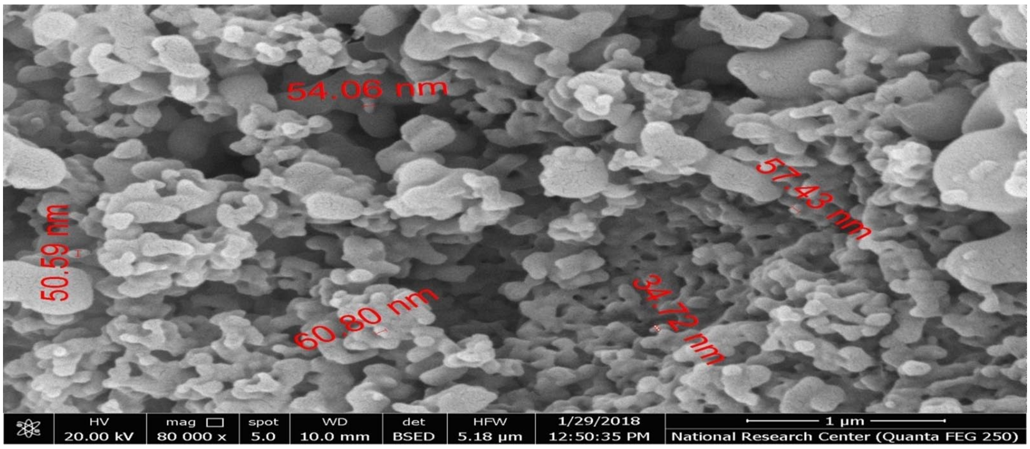

Figure 3. SEM analysis for the prepared nZVAl nanoparticles with the scale of 1 μm. SEM indicates scanning electron microscope.

was ideal for physical adsorption process because low steric in the nZVAl surface. Second, at high acidic media, the small amount of metal was dissolved by the effect of acid leading to losing a huge number of vacant sites and that affected the adsorbent dose capacity.[2] The high alkaline solution with an excess of OH^- ions effects on adsorption activities of nZV-metal through the steric effect of negative charge.[48,49] There are different studies conducted with COD removal using different sorbent materials and showed that the effective pH values ranged from 7.5 to 8 showing agreement of the obtained resu lts.[19,50-55] Also, different pH values can affect the surface charge for any chemical adsorption process as present in Figure 6A. At lower pH, the surface of nZVAl was charged with positive; at neutral pH, the nZVAl surface can eliminate both positive and negative contaminants; and at high pH, the surface of nZVAl was covered with a negative charge.[56]

nZVAl dose effect. The effect of dry nZVAl dosages was studied for standard COD concentrations 400 ± 5.11 mg/L at pH 8 using nZVAl dosages (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8 g) for 10 minutes with stirring rate 100 RPM, and the removal efficiency was (43%, 47%, 54%, 62%, 67%, 73%, 80%, and 88%), respectively, for the selected nZVAl doses as shown in Figure 4B. The results displayed that the minimum effective dosage was 0.6 g. The COD removal efficiency was increased with dose due to increasing the vacant site for adsorption and free electrons for degradation process.[57] Zero valence metals act as good electron donor and can be used for wastewater treatment using AOP.[19] Different studies conducted with COD removal using different sorbent materials and doses showed high-efficiency properties for the reduction of COD concentrations using different operating conditions. El-Naas et al[55] studied "Reduction of COD in refinery wastewater through adsorption on date-pit activated carbon" for 3 different wastewater concentrations between 900 and 3500 mg/L using 20 g/L from sorbent material, and the result showed that activated carbon dosages can adsorb a huge amount of COD at first 30 minutes.[55] Walker et al[58] studied "Treatment of hazardous shipyard wastewater using dolomitic sorbents" and showed the ability of dolomite with the particle size ranging from 0 to 38 μm to reduce the initial 3300 mg/L of COD concentration to 820 mg/L after 24 hours time at pH 7.5[58] Laohaprapanon et al. in 2010 studied "Removal of Organic Pollutants from Wastewater Using Wood Fly Ash as a Low-Cost Sorbent" using dose 160 g/L with diameter less than 1 mm for COD removal with removal efficiency of 37% for initial COD concentration 49 360 at room temperature at time less than 20 minutes.[59]

Contact time effect. The effect of contact times was studied for standard COD concentration 400 ± 5.11 mg/L, using 0.6 g of nZVAl dose, at different times (5, 10, 15, 20, 25, 30, 60, and 120 minutes) and pH 8, and 100 RPM stirring rate and the removal percentages were (65%, 73%, 74%, 75%, 75%, 76%, 78%, and 79%), respectively, as shown in Figure 4C. From the obtained results, the removal efficiency increased by increasing time, and the minimum effective time was 10 minutes. Figure 6B showed the relation between COD uptake and removal percentages at different times and indicated that the effective time was determined at the first crosslink between the 2 curves at 10 minutes. Farag et al[14] studied the adsorption of COD using nZVI, and the obtained results indicated that the minimum effective time was 20 minutes.[14]. Nassar et al[60] studied "Treatment of olive mill based wastewater by means of magnetic nanoparticles: Decolourization, dephenolization, and COD removal" and the effective time for COD removal was 30 minutes.[60]

Effect of stirring rate. The effect of stirring rate was studied for standard COD concentration of 400 ± 5.11 mg/L using 0.6 g of nZVAl dose at time 10 minutes at different stirring rates of 50, 100, 150, 200, 250, 300, 350, and 400 RPM at pH 8, and the removal efficiency was 71%, 73%, 72%, 73%, 73%, 74%, 74%, and 74%, respectively, as shown in Figure 4D. The results showed that the optimal stirring rate was 100 RPM and it was in agreement with previous data.[38,57,61] There is a slight increase in removal percent according to stirring rate relative to chemisorption reaction.[38] In the case of physical adsorption process,

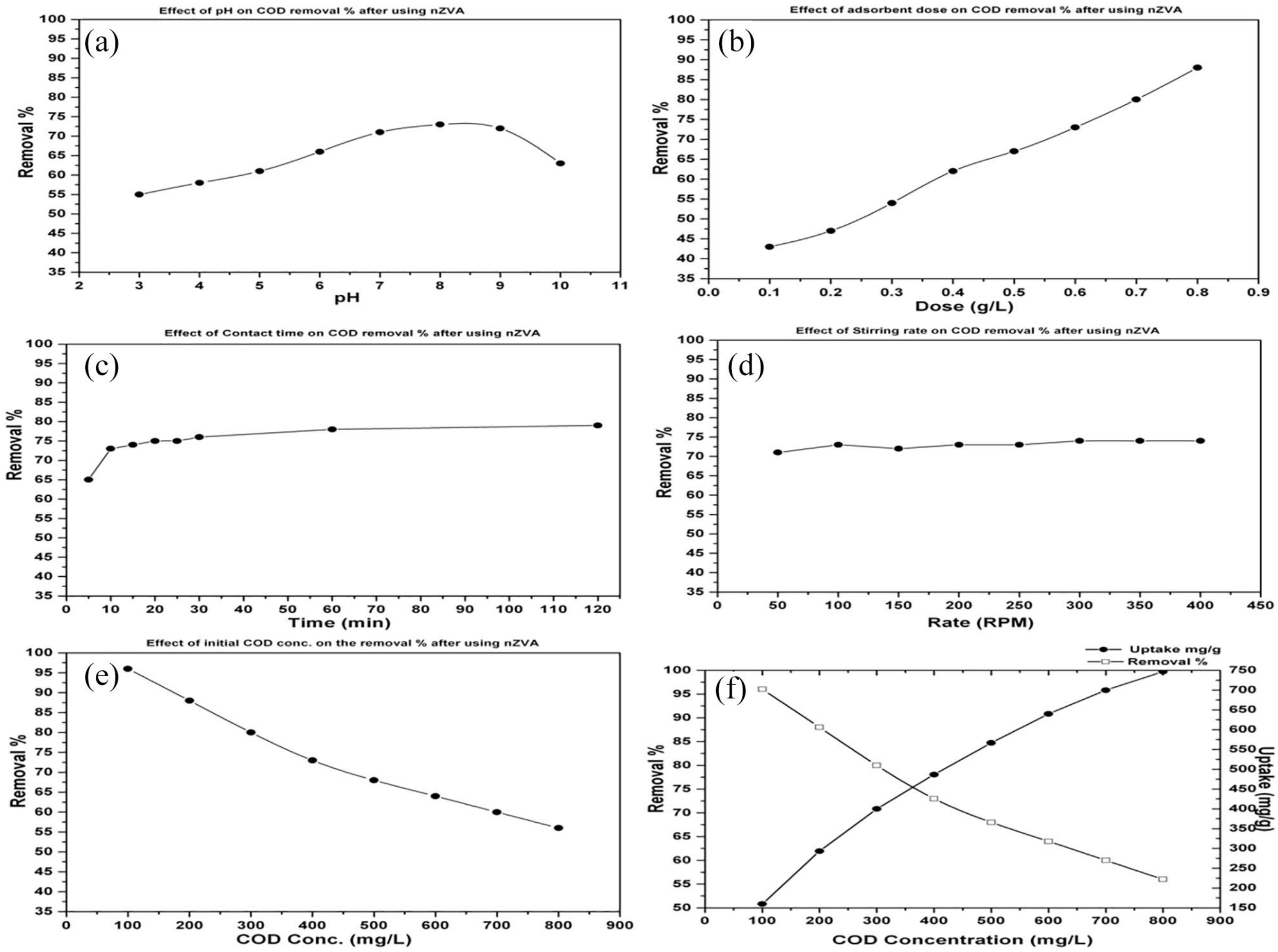

Figure 4. The effect of operating parameter on COD using nZVAl: (A) pH, (B) adsorbent dose, (C) contact time, (D) stirring rate, (E) initial COD concentration, and (F) uptake concentration for the selected dose. COD indicates chemical oxygen demand.

the stirring rate effect is an effective parameter to distribute all adsorbent molecules into all sorbent sites. In the case of chemical adsorption, it depends on the attraction between positive and negative charges, and in many cases, the stirring rate effect is not effective. P.S.O kinetic mechanism indicated that the desorption of COD onto nZVAl mechanism is chemically rated controlling. Also, the Freundlich model describes heterogeneous adsorption surface and reversible adsorption process and that occur in the chemisorption process. By using linear regression analysis and nonlinear statistical algorisms analysis to determine the significance operating variables and the importance of each covariable, the results indicated that the stirring rate effect is not a significant parameter for COD removal using nZVAl with P value $>.05$ equal .583, and the importance of stirring rate is 6.4% as listed in Tables 4 and 5, respectively.

Effect of standard COD concentrations. The effect of standard COD concentration on the removal efficiency was studied using nZVAl dosage of 0.6 g at the time limit of 20 minutes, pH 8, and 100 rpm for initial COD concentrations 400 ± 5.11 mg/L (100, 200, 300, 400, 500, 600, 700, and 800 mg/L) and the removal efficiency was 96%, 88%, 80%, 73%, 68%, 64%, 60%, and 56%, respectively, as shown in Figure 4E. The results showed that a significant decrease in removal percent with concentration is due to high competition in the vacant sorbent sites.[62] Figure 4F shows the uptake results for COD adsorption onto 0.6 g of nZVAl dose and indicates that the suitable COD concentration for the selected nZVAl dose is 360 mg/L. C.P. Devatha et al.[62] studied "Green synthesis of iron nanoparticles using different leaf extracts for treatment of domestic waste water," and the removal efficiency of COD was 82% after using FeNPs for initial COD concentration of 448 mg/L, and dose of 25 mL for dosage 1 g/L at pH from 6.5 to 8.[62]

Adsorption studies

Figure 5A describes relations between different nonlinear adsorption models. The obtained results signifying that the Freundlich isotherm is the most suitable can describe the adsorption mechanism of COD onto the surface of nZVAl, as shown in Table 1. The Freundlich model describes heterogeneous adsorption surface and reversible adsorption process, and the multilayer adsorption process can occur in the surface of sorbent materials. Also, Freundlich concept displayed that the mechanism of the adsorption process

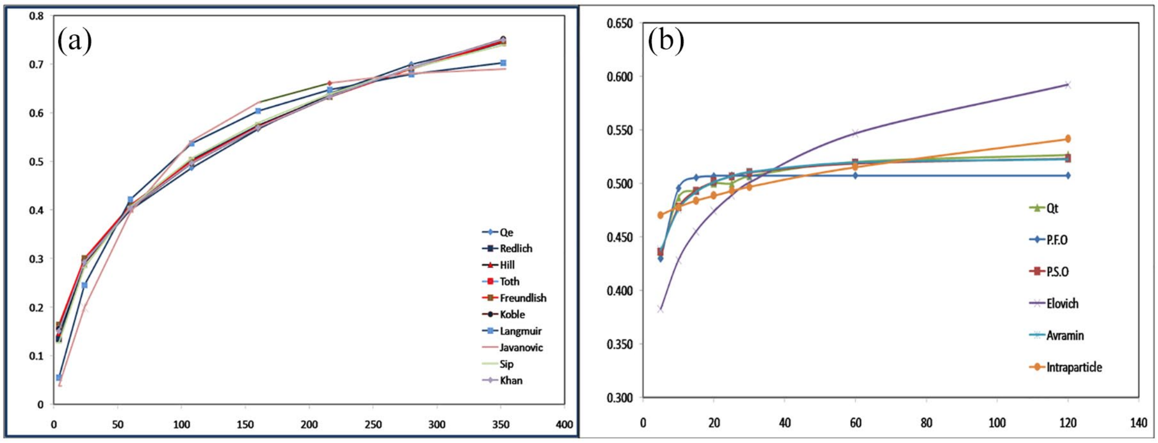

Figure 5. Nonlinear isotherm and kinetic studies for COD removal using nZVAl. COD indicates chemical oxygen demand.

Table 1. The results of nonlinear adsorption models.

	REDLICH-PETERSON (1)		HILL (2)		SIPS (3)		KHAN (4)		TOTH (5)	
Constants	*Kr*	0.120	*QH*	4.366	*Qs*	1.719	*Qk*	0.063	*Kt*	0.902
	Br	0.000	*nH*	0.398	*Ks*	0.002	*Bk*	3.483	*at*	55.814
	G	0.686	*KD*	49.945	*Bs*	0.502	*Ak*	0.652	*t*	0.902
ERRORS										
Chi error	0.006		0.0019		0.0103		0.0010		0.2258	
ERRSQ	0.001		0.0005		0.0019		0.0003		0.0203	
HYBRD	0.005		0.0017		0.0085		0.0010		0.0897	
MPSD	0.029		0.0082		0.0463		0.0041		0.4848	
ARE	0.261		0.1641		0.3494		0.1432		1.1475	
EABS	0.077		0.0535		0.1013		0.0454		0.3349	
Error sum	0.380		0.2300		0.5177		0.1950		2.3030	
	Koble-Corrigan (6)		Javanovic (7)		Freundlich (8)		Langmuir (9)			
Constants	*A* *B* *D*	0.095 0.000 0.353	*Qm* *Kj*	0.695 0.014	*Kf* *n*	0.102 2.952	Q_0 *b*		0.814 0.018	
ERRORS										
Chi error	0.0005		0.4544		0.0011		0.2258			
ERRSQ	0.1002		0.0340		0.0005		0.0203			
HYBRD	0.0005		0.1408		0.0011		0.0897			
MPSD	0.0017		0.7162		0.0028		0.4848			
ARE	0.0942		1.4435		0.1330		1.1475			
EABS	0.0397		0.4283		0.0561		0.3349			
Error sum	0.2368		3.2172		0.1946		2.3030			

depends on binding energy between adsorbed COD molecules and nZVAl.[63] The adsorption energy decreased gradually until vanishes with complete adsorption process (ie, the attraction energy between charged molecules decreased due to consuming nZVAl surface charge). Table 2 shows the result of experimental *Qe* and Calculated *Qe* after applying

Table 2. Shows calculated and experimental *Qe*.

EXPERIMENT *QE* (MG/G)	CALC. *Qe* (1)	CALC. *Qe* (2)	CALC. *Qe* (3)	CALC. *Qe* (4)	CALC. *Qe* (5)	CALC. *Qe* (6)	CALC. *Qe* (7)	CALC. *Qe* (8)	CALC. *Qe* (9)
160.0	133.8	146.7	127.2	150.8	54.4	155.0	37.9	**163.7**	54.4
293.3	292.6	289.1	281.9	292.3	244.8	291.5	198.7	**300.4**	244.8
400.0	409.7	404.5	407.4	404.1	421.8	402.7	395.4	**409.7**	421.8
486.7	502.4	498.9	506.0	496.6	536.8	495.5	542.0	**500.0**	536.8
566.7	573.7	572.3	579.1	569.8	603.6	569.2	621.0	**571.2**	603.6
640.0	633.9	634.4	638.2	632.8	647.0	632.7	661.0	**632.3**	647.0
700.0	690.6	692.4	691.3	692.8	678.8	693.3	680.9	**690.4**	678.8
746.7	744.3	747.1	739.2	750.4	702.7	751.6	689.6	**746.1**	702.7

Note: Bold values represents the selected calculated model and the actual result.

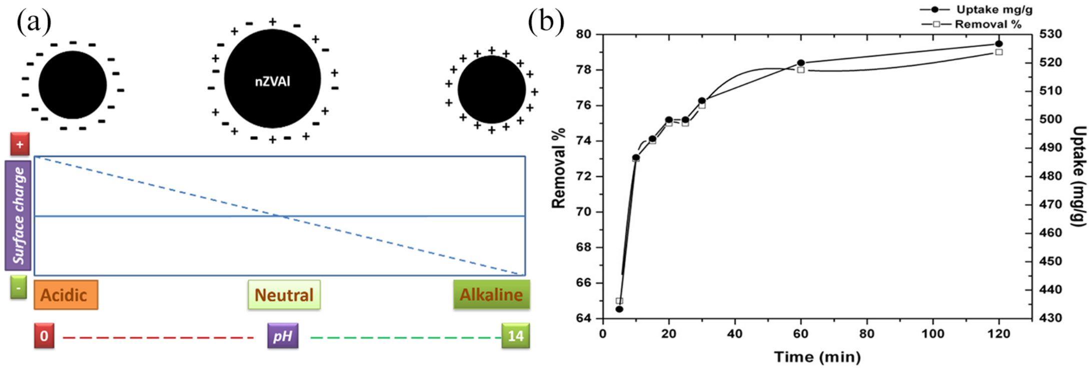

Figure 6. (A) The effect of pH on nZVAl surfaces. (B) The relation between COD uptake and the removal percent at different times.

model constants, showing small deviation between all concentration results.

Kinetic studies

Figure 5B describes kinetic relations between different nonlinear models. The obtained results indicated that the pseudo-second-order is the preferred kinetic model with the minimum summation errors 0.057 as shown in Table 3, indicating that the desorption of 400 mg/L COD concentration onto 0.6 g nZVAl surface depended on both concentration and dosage together, and the P.S.O model constants were well-fitting for describing the kinetics. P.S.O kinetic mechanism indicated that the desorption of COD onto nZVAl mechanism is chemically rated controlling. Also, it indicated that the electrons are covalently exchanged or shared between sorbate and sorbent, meaning that the reaction is chemisorptions.[37,64] At the optimum pH, the surface of nZVAl was charged with both positive and negative charges and can receive both cationic and anionic contaminants as shown in Figure 6A. So, the removal efficiency of COD into nZVAl mainly depends on dose, concentration, and pH, and this is in agreement with linear regression analysis where the *P* value for them was .000.

Response surface methodology

The effect of operating parameters such as dose, pH, contact time, stirring rate, and concentrations were placed in the linear regression variable models against the removal percentages. A positive effect of the independent variable "pH," "dose," and "contact time" on COD removal was observed to be significant ($P < .05$). In addition, a significant effect ($P < .05$) was noticed for the independent variable "initial concentrations." However, insignificant effect ($P > .05$) was determined for the linear term of "stirring rate" as shown in Table 4. The coefficient of determination between measured data and simulated results (R^2) and adjusted R^2 were listed in Table 4. The high R^2 value suggested that the reliability of the proposed model was .872. Equation (8) showed all regression models (significant and insignificant):

$$Y_{COD} = 31.925 + 2.960x_1 + 62.103x_2 + 0.073x_3 + 0.005x_4 - 0.053x_5$$

where Y is the predicted response of different wastewater contaminant removal efficiency (%); x_1 is pH (3-10); x_2 is adsorbent dose (0.1-0.8 g); x_3 is contact time (5-120); x_4 is

Table 3. The results of different kinetic models.

	P.F.O	P.S.O	ELOVICH	AVRAMI	INTRAPARTICLE
Constants	$Q_e = 0.507$ $K_1 = 0.376$	$Q_e = 0.521$ $K_2 = 1.805$	$\alpha = 4.390$ $\beta = 15.175$	$Q_e = 0.523$ $K_{av} = 0.953$ $N_{av} = 0.400$	$K_{id} = 0.008$ $C_i = 0.452$
ERRORS					
Chi error	0.002	0.000	0.028	0.000	0.004
ERRSQ	0.001	0.000	0.013	0.000	0.002
HYBRD	0.002	0.000	0.027	0.000	0.004
MPSD	0.003	0.000	0.055	0.001	0.009
ARE	0.126	0.038	0.541	0.047	0.183
EABS	0.064	0.018	0.265	0.023	0.086
Error sum	0.197	**0.057**	0.928	0.072	0.289

Note: Bold values represents the selected minimum error.

Table 4. *t* statistics and *P* values for coefficients of a linear regression model.

RSM MODEL (ENTER METHOD)							
Model summary	R	0.943					
	R^2	0.888					
	Adjusted R^2	0.872					
	Standard error of the estimate	3.786					
ANOVA	F	54.113					
	Model significance	0.000					
Coefficients		Term	Estimate	Standard error	*t*-Ratio	Prob > |*t*|	Effect*
	Constant	β_0	31.925	5.489	5.816	.000	Significant
	pH	β_1	2.960	0.509	5.818	.000	Significant
	Dose	β_2	62.103	5.088	12.205	.000	Significant
	Contact time	β_3	0.073	0.032	2.285	.029	Significant
	Stirring rate	β_4	0.005	0.008	0.555	.583	Insignificant
	Concentration	β_5	−0.053	0.006	−9.303	.000	Significant

Abbreviation: ANOVA, analysis of variance; RSM, response surface methodologies.
Standard error, the error of the estimated difference between the means; *t*-Ratio, the *t*-ratio for the test of whether the estimated difference between the means is zero; Prob > |*t*|, the *P* value for the test.
*The significant levels at the 83% level ($P < .05$) were considered to have a greater impact on the response.

the stirring rate (50-400 RPM); and x_5 is the concentration (100-800 mg/L); β_0 is the model intercept and β_1, β_2, β_3, β_4, and β_5 are the linear coefficients of x_1, x_2, x_3, x_4, and x_5, respectively.

Artificial neural network

Artificial neural networks were trained using the MLP model 6-3-1 for COD removal using sample training and testing without excluding any results with total runs 40 listed in Table 5. The training process is a procedure by which the linking between weight and bias is upgraded over a nonstop process of simulations as shown in Figure 7 and listed in Table 5. Results displayed that there is a small deviation between the predictive values and normalized value as shown in Figure 7B and 7C. Also, there is a small error between the residual and predictive values (−7.2% + 2.5%) as shown in Figure 7C signifying ANN

Table 5. Case processing summary for a neural network model using MLP.

CASE PROCESSING SUMMARY		
Parameter	COD removal ANN	
	N	**%**
Sample training	32	80.0
Sample testing	8	20.0
Valid	40	100.0
Excluded	0	
Total	**40**	
NETWORK INFORMATION		
Input layer	Covariates	5 (pH, dose, stirring rate, time, and concentration)
	Number of units	5
	Rescaling method for covariates	Normalized
	Activation function	MLP: Hyperbolic tangent
Output layer	Dependent variables	Removal %
	Number of units	1
	Rescaling method for scale dependents	Standardized
	Activation function	Identity
	Error function	Sum of squares
MODEL SUMMARIES		
Training	Sum of squares error	.807
	Relative error	.052
	Stopping rule used	One consecutive step(s) with no decrease in error
Testing	Sum of squares error	.074
	Relative error	.005
INDEPENDENT VARIABLE IMPORTANCE		
	Importance	Normalized importance
pH	.174	40.8%
Dose	.426	100.0%
Contact time	.105	24.6%
Stirring rate	.027	6.4%
Concentration	.268	62.7%

Abbreviation: ANN, artificial neural network; COD, chemical oxygen demand; MLP, multilayer perceptron.
Note: Bold values represents the total number of training and testing result.

model's success to describe the adsorption of COD onto the nZVAl. Figure 7D arranges the importance of each covariable, indicating that the effect of the dose is the most effective covariable with normalized importance percentage of 100%, showing agreement with adsorption isotherm, operating parameter data, and RSM data.

Application of Using nZVAl for Wastewater Treatment

In Al-Sanafin wastewater treatment plant, Alsharqia, Egypt, with design capacity of 6000 m^3 per day and actual capacity of 3000 m^3per day, the applied Rotating Biological Contactor (RBC) wastewater treatment plant (WWTP) cannot pass Egypt law for draining wastewater No. 48 of 1982 into Qaliob drain as given in Table 6. By applying the optimum conditions of pH 8, dosage 0.6 g/L, contact time 10 minutes, and stirring rate 100 RPM to the same row sample, the treated sample can pass the law especially for COD and BOD as in Table 6.

Conclusions

This study investigated the effect of nZVAl to adsorb and degrade organic matters for aqueous solution. The maximum

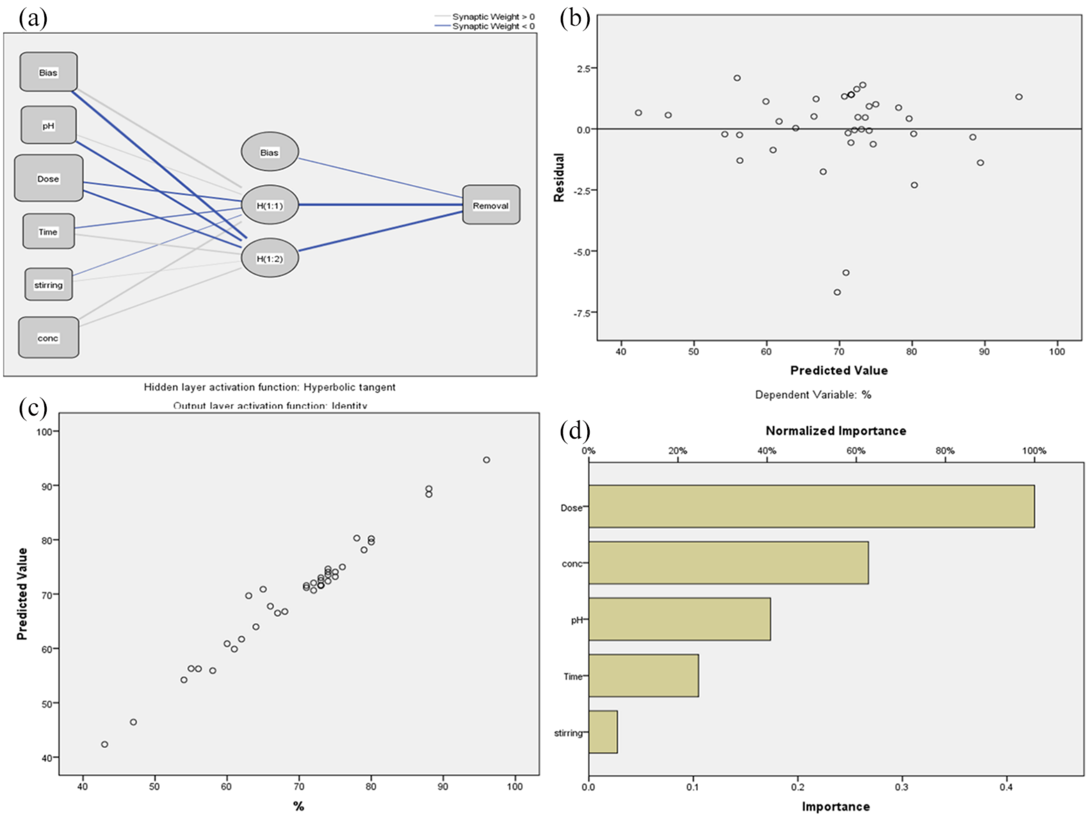

Figure 7. (A) COD multilayer perceptron (MLP) neural network. (B) The relation between predictive removal percent and residual. (C) The relation between true and predictive values. (D) Normalized importance and importance for each variable. COD indicates chemical oxygen demand.

Table 6. The comparative treatment results of Al-Sanafin, Alsharqia, Egypt, activated sludge WWTP, and nZVAl.

PARAMETER	UNIT	RAW WASTEWATER	BEFORE TREATMENT	AFTER NZVAL TREATMENT	LIMITS ACCORDING TO LAW NO. 48 OF 1982
pH	–	7.33	7.92	8.03	6-9
Turbidity	NTU	22.68	9.87	2.89	–
TDS	mg/L	688	695	690	2000
COD	mg/L	543	198	73	80
BOD	mg/L	341	115	28	60
UV_{254}	$C\,m^{-1}$	2.322	0.960	0.312	–
UV_{220}	$C\,m^{-1}$	2.863	1.210	1.789	–
TSS	mg/L	367	146	44	60
Ammonia (NH_3)	mg/L	14.83	7.86	9.65	–
Nitrate (NO_3)	mg/L	1.26	2.2	1.12	–
Nitrite (NO_2)	mg/L	1.1	0.5	0.8	50
TKN	mg/L	31.6	16.77	21.2	–
TN	mg/L	33.8	19	23.1	–
Total phosphorous	mg/L	3.56	3.1	1.98	–
Sulfide	mg/L	2.99	1.1	0.55	1

(Continued)

Table 6. (Continued)

PARAMETER	UNIT	RAW WASTEWATER	BEFORE TREATMENT	AFTER NZVAL TREATMENT	LIMITS ACCORDING TO LAW NO. 48 OF 1982
CN	mg/L	0.201	0.015	0.006	–
Fe	mg/L	0.836	0.386	0.006	3.5
As	mg/L	0.060	0.003	0.011	0.05
Pb	mg/L	0.092	0.008	0.0004	0.1
Cr	mg/L	0.098	0.0001	0.0026	0.1
Cu	mg/L	0.106	0.0210	0.001	0.5
Total organochlorine pesticides	µg/L	1.783	0.920	0.086	–
Total organophosphorus pesticides	µg/L	0.583	0.370	0.006	–
Presumptive test of total coliform	Count/100 mL	430 000	7900	700	5000

Abbreviation: BOD, biological oxygen demand; COD, chemical oxygen demand; TDS, total dissolved solids; TKN, total Kjeldahl nitrogen; TN, total nitrogen; TSS, total suspended solids; UV, ultraviolet; WWTP, wastewater treatment plant.

removal percentage was 96% achieved for 100 mg/L-COD, at 10 minutes, with 0.6 g/L of nZVAl dosage, at pH 8, and with stirring rate 100 rpm. The obtained isotherm results indicated that the Freundlich isotherm and pseudo second-order kinetic model are the most suitable isotherm and kinetic models. The created ANN is effective in predicting the performance of nZVAl onto COD removal with the relative error of 0.052. Linear regression analysis by using RSM showed that all variables were significant with a P value less than .05 except the effect of stirring rate with a P value of .583, and the R^2 of 0.888 indicated the reality of the models and agreement with experimental data. So, the RSM equation can be used to predict and describe the theoretical removal of COD using nZVAl at different operating parameters without using experimental works.

Author Contributions

ASM contributed in preparation of nZVAl, characterization of nZVAl, operating parameters analyzing, application of real wastewater sample, writing and reviewing. RSF contributed in kinetic, isotherm studies, writing and reviewing. MME contributed in Error functions analyzing, writing and reviewing. LAM contributed in estimated RSM removal equation by applying linear regression analysis, writing and reviewing.
SMR contributed in ANN modeling by applying nonlinear MLP statistical algorithms, writing and reviewing.

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Supplemental Material

Supplemental material for this article is available online.

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