Article

Ecological Risk Indicators for Leached Heavy Metals from Coal Ash Generated at a Malaysian Power Plant

Teh Sabariah Binti Abd Manan ^{1,*} , Salmia Beddu ^{2,*}, Nur Liyana Mohd Kamal ², Daud Mohamad ², Zarina Itam ², Taimur Khan ³ , Affiani Machmudah ⁴, Denys Dutykh ⁵ , Wan Hanna Melini Wan Mohtar ⁶ , Hisyam Jusoh ⁷, Fadzli Mohamed Nazri ⁸ , Md Fauzan Kamal Mohd Yapandi ^{9,10} , Siddhartha Pati ^{11,12} , Amirrudin Ahmad ^{1,13} and Nadiah Wan Rasdi ^{1,14}

- ¹ Institute of Tropical Biodiversity and Sustainable Development, Universiti Malaysia Terengganu, Kuala Nerus 21030, Terengganu Darul Iman, Malaysia; amirrudin@umt.edu.my (A.A.); nadiah.rasdi@umt.edu.my (N.W.R.)
- ² Department of Civil Engineering, Universiti Tenaga Nasional, Jalan Ikram-Uniten, Kajang 43000, Selangor Darul Ehsan, Malaysia; Yana_Kamal@uniten.edu.my (N.L.M.K.); Daud@uniten.edu.my (D.M.); iZarina@uniten.edu.my (Z.I.)
- ³ Civil and Environmental Engineering Department, Universiti Teknologi PETRONAS, Seri Iskandar 32610, Perak Darul Ridzuan, Malaysia; taimurkhan7@gmail.com
- ⁴ Industrial Engineering, Faculty of Advanced Technology and Multidisciplinary, Universitas Airlangga, Jalan Mulyorejo, Kampus C, Surabaya 60115, Indonesia; affiani.machmudah@stmm.unair.ac.id
- ⁵ Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, LAMA, 73000 Chambéry, France; Denys.Dutykh@univ-smb.fr
- ⁶ Civil Engineering Department, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, Bangi 43600, Selangor Darul Ehsan, Malaysia; hanna@ukm.edu.my
- ⁷ Geo TriTech, No. 17, Persiaran Perdana 15A, Pinji Perdana, Lahat 31500, Perak Darul Ridzuan, Malaysia; mnhsyam.jusoh@gmail.com
- ⁸ School of Civil Engineering, Engineering Campus, Universiti Sains Malaysia, Nibong Tebal 14300, Penang, Malaysia; cefmn@usm.my
- ⁹ TNB Research Sdn. Bhd. No. 1, Kawasan Institusi Penyelidikan, Jalan Ayer Itam, Kajang 43000, Selangor Darul Ehsan, Malaysia; fauzankamal@tnb.com.my
- ¹⁰ Faculty of Applied Science, Universiti Teknologi Mara, Shah Alam 40450, Selangor Darul Ehsan, Malaysia
- ¹¹ SIAN Institute, Association for Biodiversity Conservation and Research (ABC), Balasore 756001, Odisha, India; patissiddhartha@gmail.com
- ¹² Department of Biotechnology, Academy of Management and Information Technology, Khordha 752057, Odisha, India
- ¹³ Faculty of Science and Marine Environment, Universiti Malaysia Terengganu, Kuala Nerus 21030, Terengganu Darul Iman, Malaysia
- ¹⁴ Faculty of Fisheries and Food Science, Universiti Malaysia Terengganu, Kuala Nerus 21030, Terengganu Darul Iman, Malaysia
- * Correspondence: tehsabariah@umt.edu.my (T.S.B.A.M.); Salmia@uniten.edu.my (S.B.); Tel.: +60-3-89212020 (ext. 6219) (S.B.)

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Abstract: The application of coal ash (CA) in construction industries has grown rapidly, posing risk to the environment due to heavy metals leaching from the material. This research presents a simulation of ecological risk assessment and model risk indicators (ERI) of leached heavy metals (lead (Pb), copper (Cu), zinc (Zn) and arsenic (As)) from CA (FA: fly ash and BA: bottom ash) via response surface methodology (RSM). The ERI values were based on quantified leached heavy metals from the toxicity characteristic leaching procedure (TCLP-1311) and synthetic precipitation leaching procedure (SPLP-1312). The ecological risk index (R_I) values for TCLP were 10.27×10^0 (FA), 9.91×10^0 (BA) and 12.58×10^0 (FA + BA); whereas R_I for SPLP were 10.34×10^0 (FA), 9.90×10^0 (BA) and 12.61×10^0 (FA + BA). Twenty-nine combinations of operations were evaluated based on Box-Behnken design with ERI as the response variable. The established model risk indicator (i.e., coded and actual factors) of Pb, Cu, Zn and 'As' showed significant model terms that describe their relationship very well, perfectly fit to the corresponding ERI (sum of squares = 0.4160, F value = 682,375.55) with probability of 0.01% for an F-value could occur due to noise. The optimized models were validated with error percentage of less than 5%. The established ERI models showed significant model terms and will be useful for ecological monitoring of CA application in construction industries.

Keywords: coal ash; power plant; heavy metals; ecological risk indicators; ecological risk assessment; Box-Behnken design

1. Introduction

Coal is a geofuel for electric power generation that produces millions of tonnes of CA (i.e., FA and BA) as a by-product of the process [1]. ‘CA’ has the potential to be sustainably reused, promoting green-coal ash technology, and reducing greenhouse gas emissions [2]. The waste should be managed without risking the environment (i.e., water, air, soil, plants, and animals) and human health [3]. Nevertheless, CA contains heavy metals and in the absence of proper waste management, it is a hazardous waste material that poses risk to both the environment and human health [4]. Heavy metals have atomic numbers greater than 20 with relatively high densities and are present in soils at low concentration. However, concrete mixes containing coal ash as a binder may pose risk of leaching heavy metals to the soil leading to adverse environmental and health impacts. The biohazards of heavy metals are due to their bioproperties, such as high toxicity with possibilities of acute and chronic toxicity effects [3,5–7]. Heavy metals are non-biodegradable metal ions that bioaccumulate in living organisms [8,9]. They can deteriorate brain and central nervous system, alter the blood composition, and corrode other vital organs [7,10,11].

There are many recycled products made from CA such as radionuclide stabilizers in roadway pavements [12], adsorbents [13] and coagulants for wastewater treatment [14]. Moreover, it is useful as cement replacement material [15], good for brick production [16] and convenient as aggregate for concrete made from the combination of granite waste and FA [17]. ‘CA’ is also rich in heavy metals making it a premium source for aluminium extraction [14,18,19] as well as a source of rare earth metallic elements (e.g., yttrium, scandium, and 14 elements of the lanthanide series) [1,20–22]. It can also function as an excellent scrubber and fixation reagent for hazardous acidic sludge wastes containing toxic trace elements from the phosphate industry [17]. The reuse of CA as cement replacement material has been long established in the US construction industry [23,24]. FA consists of fine coal ash particles that accumulate in electrostatic precipitators or fabric filter baghouses. Meanwhile, BA consists of coarse granular particles that accumulate at the furnace’s bottom [23,25]. These pozzolans are similar in heavy metals composition [3,10,11,26].

Aquatic organisms (algae, plants, microbes, planktons, crustacean, fish etc.) are biological indicators of water pollution [27–29]. Ecological risk assessment studies are based on toxicity risk of a pollutant to aquatic organisms. It is essential in the current study to determine the risk posed to aquatic organisms by contaminants leached from coal ash like heavy metals. A good study model in this case is the application of microphyte plants of the *Lemna* genus for the bioremediation of wastewater [30].

Literature reports leaching studies focused on sulphate [31], single heavy metals such as mercury (Hg) [32] or a combination of heavy metals [31,33–35], ammonia [36] and a combination of heavy metals and trace elements [37]. Researchers used standard procedures known as US EPA method 3501A (SW 846) [32,38], 1311 [32], 1312 [36], and 3052 [37] to study metal leaching. The US EPA method 3501A is a digestion method that uses nitric acid to extract analyte from sediments, sludges, soils, and oils. Meanwhile, US EPA method 3502 is also an extraction method that employs microwave-assisted acid digestion of siliceous matrices, and organic matrices and other complex matrices and is not appropriate for regulatory applications that require the use of leachate preparations as stated in method 3501A. Standard methods for leaching tests are the US EPA toxicity characteristic leaching procedure (TCLP-1311) and the synthetic precipitation leaching procedure (SPLP-1312). Detection of heavy metals can be done via inductively coupled plasma optical emission spectroscopy (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS) and atomic absorption spectrophotometry (AAS) [39,40]. ‘ICP-OES’ is generally used for total

dissolved solids (TDS) or suspended solids. 'ICP-MS' cannot be used to measure arsenic, mercury, and some other toxic metals with very low regulatory limits.

Cho et al. studied the leaching property of a single heavy metal, mercury (Hg) (method 3501A and TCLP-1311) from FA, BA, sludge, and phosphor powder generated from municipal waste incinerators in Korea [32]. The ranges of Hg content were 11,847 to 23,795 µg/Kg (FA) and 8 to 521 µg/Kg (BA) (method 3501A). The concentrations of leached Hg from municipal waste incinerators were 0.8 to 242.9 µg/L (FA) and 0.1 to 0.7 µg/L (BA) [32].

Roessler et al. presented the leaching of total ammonia nitrogen (TAN) (SPLP-1312) posed by the ammoniated coal FA. The TAN concentrations released from leaching test exceeded 0.02 mg TAN/L (US EPA) [36]. The classification was made into three groups: group A (low NH₃), B (high NH₃) and C (50% group A + 50% group B). The percentages of TAN were 58% (0.15 mg TAN/L), 66% (8.55 mg TAN/L), and 65% (3.61 mg TAN/L) for group A, B, and C accordingly [36].

Mokhtar et al. studied selected trace element behaviour in a coal-fired power plant in Malaysia for the assessment of abatement technologies for air pollution control (method 3052) [37]. The leached elements and heavy metals were As: <7.0 mg/L (not detected), Be: 1.4–3.7 mg/L, cadmium (Cd): <0.3 mg/L (not detected), Cr: <1 mg/L (not detected), Cl: 95.29 mg/L, F: 56 mg/L, Hg: <0.01 mg/L (not detected), Ni: 48.4 mg/L, Pb: <2 mg/L (not detected) and Se: <6 mg/L (not detected) [37].

Flues et al. [34], Hosseini et al. [33], Komonweeraket et al. [31], and Xiang et al. [35] presented leached heavy metal content based on different approaches. Flues et al. [34] studied speciation of heavy metals in coal and ashes (method 3501A-SW 846) at their origin pH (coal: pH 5.3, BA: 9.9, cyclone ash (Cyc): 12.1, bag ash (Bag): pH 11.9) from Figueira coal power plant, Brazil. The cyclone and bag ashes were FA type. Flues et al. used liquid extraction with an organic solvent, ethylenediaminetetraacetic acid (EDTA), for their sample. The percentages of leached heavy metals were >70% for As, >55% for Mo and the remaining were 30 to 50% for Mn, Zn, Cd, and Pb [34].

Hosseini et al. studied the leaching properties of weathered Victorian brown coal fly ash upon pH changes (using ammonium chloride and hydrochloric acid) and durations from 30 to 60 min. The leached concentrations of Ca and Mg ranged from 70% (pH 3.0) to 85% (pH 0.5) while other heavy metals leached from 15% (pH 3.0) to 70% (pH 0.5) [33].

Komonweeraket et al. studied leaching characteristics of heavy metals from coal fly ash mixed soils based on modified leaching test (pH static test) under the influence of pH (pH 1.5 to 13) and detection was done using ICP-OES [31]. The ranges of heavy metal concentrations were from 12 (pH 11.7) to 80 mg/L (pH 10.4) (As), 575 (pH 10.4) to 3621 mg/L (pH 12.4) (Barium, Ba), 14,960 (pH 6.1) to 246,300 mg/L (pH 12.4) (Ca), 0.4 (pH 6.1) to 1.29 mg/L (pH 8.1) (Cd), 3290 (pH 11.7) to 24,650 mg/L (pH 12.4) (Mg), 2.1 (pH 10.4) to 39 mg/L (pH 6.1) (Selenium, Se) and 968 (pH 11.7) to 1622 mg/L (pH 12.4) (Strontium, Sr). At pH 6.6, 8.1, and 9.5, Sr and Ba were not detected [31].

Xiang et al. reported on leached heavy metals upon modified leaching test (column leaching test at four different pH values, leaching time: 7 days) and detection via ICP-MS. The concentrations of leached heavy metals were high. They were 89.56 to 222.2 mg/L (Li), 2.17 to 5.46 (Be), 5415 to 6919 mg/L (Ti), 85 to 105.30 mg/L (Cr), 176.6 to 447.5 mg/L (Mn), 25.21 to 38.70 mg/L (Ni), 44.49 to 67.68 mg/L (Cu), 37.09 to 107.10 mg/L (Zn), 0.07 to 0.66 mg/L (Cd), 19.37 to 68.29 mg/L (Pb), 291.7 to 309.5 mg/L (As), and 7.6 to 8.6 mg/L (Hg) [35].

Chen et al. did speciation studies of heavy metals in horizontal flue ash with direct measurement using ICP-OES after digestion with nitric acid similar to US EPA method 3501A. The heavy metals ranged from 31.09 to 90.20 mg/L (As), 34.12 to 250.32 mg/L (Cd), 138.09 to 548.42 mg/L (Cr), 1004.68 to 1530.25 mg/L (Cu), 32.80 to 375.62 mg/L (Ni), 446.69 to 2341.17 mg/L (Pb), and 4336.82 to 7322.16 mg/L (Zn) [35].

Regardless of standard procedures of leaching test, acid or microwave digestion methods, or liquid extraction method of heavy metals, most studies do not present ecological

risk assessment in their findings [31–37]. However, Chen et al. reported ecological risk assessment of heavy metals from municipal waste, FA [38]. The extraction of heavy metals was based on nitric acid digestion method (method 3501A) and quantification by ICP-OES. As a result, the study obtained a huge concentration of heavy metals (i.e., cadmium (Cd), chromium (Cr), nickel (Ni), Pb, Cu, Zn and 'As') ranging from 116 to 6470 mg/kg with high ecological risk index (9937 to 75,678). The purpose of ecological risk assessment is to assess the impact of the leached material into aquatic environment. However, different perspectives can be seen as they reflect the ecological risk assessment of the total heavy metal contents from the raw material itself.

In statistical modelling, regression is a method used to estimate the strength and character of a relationship between dependent and one or more independent variables. In the current research, the Box-Behnken model was used to simulate ecological risk assessment and model risk indicators (ERI) based on four heavy metals that are commonly found in CA, namely lead (Pb), zinc (Zn), copper (Cu) and arsenic (As) collected from a Malaysian power plant. The regression equation will be useful for aquatic environment monitoring purpose specifically focusing on heavy metals of coal ash. These models will benefit civil engineers, the scientific community, and local authorities in the future, particularly for the integration of coal ash as cement replacement in concrete for construction industries.

2. Methodology

2.1. Ecological Risk Assessment

The description of the CA samples, sampling location, standard method of leaching test and the quantification of leached heavy metals were described in Beddu et al. [4] and Abd Manan et al. [41]. The ecological risk assessment was conducted following the Håkanson method [42] for risk estimation of heavy metals pollution in sediments to aquatic organisms. The same method was applied by Effendi et al. [43] and Yi et al. [44]. The contamination factor (C_f^i) (Equation (1)), the monomial potential ecological factor (Equation (2)) and potential ecological risk index (Equation (3)) are shown below:

$$C_f^i = \frac{C_o^i}{C_n^i} \quad (1)$$

C_o^i = Concentration of heavy metal in mg/Kg

C_n^i = Reference value for metals

$$E_r^i = T_r^i \times C_f^i \quad (2)$$

E_r^i = Monomial potential ecological factor (i.e., one heavy metal only)

T_r^i = Toxic response factor for a given substance

$$R_I = \sum E_r^i \quad (3)$$

R_I = Risk Index

The reference for ecological risk assessment of heavy metals is shown in Table 1. It has reference value for metals and toxic response factors for Pb, Zn, Cu and As [45] and interpretation of risk index values for heavy metals contamination in sediments.

Table 1. Reference for ecological risk assessment of heavy metals.

Reference Value for Metals and Toxic Response Factors (Pb, Zn, Cu and As)				
Heavy Metals	Pb	Zn	Cu	As
C_n^i	25	80	30	15
T_r^i	5	1	5	10
Interpretation of Risk Index Values [45]				
E_r^i	Ecological risk of single regulator	R_I	Total ecological risk	
$E_r^i < 40$	Low potential ecological risk	$R_I < 95$	Low ecological risk for the lake/basin	
$40 \leq E_r^i < 80$	Moderate potential ecological risk	$95 \leq R_I < 190$	Moderate ecological risk for the lake/basin	
$80 \leq E_r^i < 160$	Considerable potential ecological risk	$190 \leq R_I < 380$	Considerable ecological risk for the lake/basin	
$160 \leq E_r^i < 320$	High potential ecological risk	$R_I \geq 380$	Very high ecological risk for the lake/basin	
$E_r^i \geq 320$	Very high ecological risk at hand for the substance in question			

2.2. Model Equation for Ecological Risk Indicators

Box-Behnken design with second order polynomial equation (Equation (4)) was employed using the Design Expert[®] software (Version 12) to establish the relationship between process variables namely heavy metals concentrations (i.e., Pb, Zn, Cu and As) that leached from coal ash and the response variable, ERI.

$$Y = \beta_0 + \sum_{i=1}^k \beta_i \cdot x_i + \sum_{i=1}^k \beta_{ii} \cdot x_i^2 + \dots + \sum_{i \leq j}^k \sum_j^k \beta_{ij} \cdot x_i \cdot x_{ij} + \dots + e \quad (4)$$

Y = Predicted response variable (Ecological Risk Index)

β = Regression coefficient

x_i = Linear term for variable 1 (Pb)

x_{ii} = Linear term for variable 2 (Zn)

x_{iii} = Linear term for variable 3 (Cu)

x_{iv} = Linear term for variable 4 (As)

x_i^2 = Nonlinear squared term for variable 1 (Pb)

x_{ii}^2 = Nonlinear squared term for variable 2 (Zn)

x_{iii}^2 = Nonlinear squared term for variable 3 (Cu)

x_{iv}^2 = Nonlinear squared term for variable 4 (As)

$x_i \cdot x_{ii}$ = Interaction term for variable 1 (Pb) and variable 2 (Zn)

$x_i \cdot x_{iii}$ = Interaction term for variable 1 (Pb) and variable 3 (Cu)

$x_i \cdot x_{iv}$ = Interaction term for variable 1 (Pb) and variable 4 (As)

$x_{ii} \cdot x_{iii}$ = Interaction term for variable 2 (Zn) and variable 3 (Cu)

$x_{ii} \cdot x_{iv}$ = Interaction term for variable 2 (Zn) and variable 4 (As)

$x_{iii} \cdot x_{iv}$ = Interaction term for variable 3 (Cu) and variable 4 (As)

k = Number of factors or process variables in the experiment

e = Random error

The ranges of process variables and code factors are shown in Table S1. The values of the coded factors (i.e., low (−1) and high (+1) coded factors) in Table 2 were calculated based on Equation (5). The range is the difference between highest and lowest values

(Equation (6)). The error percentage between experimental and predicted values was evaluated using Equation (7).

$$Coded = \frac{2 \times (Actual\ setting - Average\ actual\ setting)}{(Range\ between\ low\ and\ high\ actual\ settings)} \quad (5)$$

$$Range = Highest\ value - Lowest\ value \quad (6)$$

$$Error\ (\%) = \left| \frac{Experimental\ Model - Predicted\ Model}{Experimental\ Model} \times 100\% \right| \quad (7)$$

Table 2. Ecological risk index (ERI) of coal ash from Malaysian coal power plant.

Ecological Risk Assessment of Heavy Metals		E_r^i				R_I (Observed)
		Pb	Zn	Cu	As	
TCLP	FA	1.80×10^{-1}	2.70×10^{-3}	4.70×10^{-3}	10.08×10^0	10.27×10^0
	BA	1.35×10^{-1}	1.90×10^{-3}	4.50×10^{-3}	9.77×10^0	9.91×10^0
	FA + BA	2.05×10^{-1}	2.50×10^{-3}	5.50×10^{-3}	12.36×10^0	12.58×10^0
SPLP	FA	1.81×10^{-1}	2.70×10^{-3}	5.00×10^{-3}	10.15×10^0	10.34×10^0
	BA	1.36×10^{-1}	1.90×10^{-3}	4.70×10^{-3}	9.76×10^0	9.90×10^0
	FA + BA	2.02×10^{-1}	2.40×10^{-3}	5.50×10^{-3}	12.40×10^0	12.61×10^0

3. Results and Discussion

3.1. Ecological Risk Assessment

The ecological risk assessment of coal ash from a coal power plant in Malaysia is shown in Table 2. The R_I values for TCLP were 10.27×10^0 (FA), 9.91×10^0 (BA) and 12.58×10^0 (FA + BA); whereas R_I for SPLP were 10.34×10^0 (FA), 9.90×10^0 (BA) and 12.61×10^0 (FA + BA). As shown in Table 3 [45], all values of E_r^i and R_I obtained in this study were less than 40 and 95 respectively, suggesting low risk to aquatic organisms.

Our ecological risk assessment aimed to evaluate and characterize risk posed by an actuator of environmental stressors (e.g., physical, biological, and chemical pollutants, introduction or infestation of invasive alien species, effects from forestry and land use, waterborne diseases, and global climate change) towards aquatic organisms [27,46].

Heavy metals are hazardous upon continuous exposure and highly toxic even at low concentrations [9,47–49]. The natural concentration of heavy metals in fresh water (mg/L) has been reported to be 0.4 mg/L (As), 0.2 mg/L (Cd), 0.2 mg/L (Cr), 10 mg/L (Cu), 0.08 mg/L (Hg), 5 mg/L (Pb), and 10 mg/L (Zn) [42] (Table 3). The current research presents the ecological risk assessment of leached heavy metals (Pb, Cu, Zn, and As) from coal ash (i.e., FA, BA, and FA + BA) via standard procedure of leaching tests (method TCLP-1311 and SPLP-1312) that has shown the potential for the application in concrete technology due to its pozzolanic property [4,41]. The Pb, Cu, Zn and 'As' are major trace elements commonly found in coal ash. The concentrations of leached heavy metals ranged from 0.673 to 1.026 mg/L (Pb), 0.027 to 0.033 mg/L (Cu), 0.149 to 0.219 (Zn), and 14.636 to 18.605 mg/L (As) [4,41] (Table 3). As is a water-soluble heavy metal [50] and was observed to leach the most. Nevertheless, the 'As' concentrations were still below the permissible limit of hazardous waste criteria. The concentrations of Pb, Cu, Zn and As were below the permissible limits by US EPA (Pb and As) [51] and obeys the limits for industrial effluent (Standard A and Standard B) [52] and national drinking water quality standards (Zn and Cu) [53]. Most of all, the concentrations were comparable to the natural concentrations of traces of heavy metals in freshwater [42]. The ranges of ecological risk assessment obtained and presented in the current study were from 9.91×10^0 to 12.58×10^0 (TCLP) and from 9.90×10^0 to 12.61×10^0 (SPLP). The ecological risk assessment was equal to low ecological risk for the lake/basin.

Table 3. Comparison of concentrations of heavy metals in natural freshwater and current research.

Heavy Metals (Ref.)	Natural Concentration in Fresh Water (mg/L) [42]	Preindustrial Reference Value for Lake Sediments (mg/L) [42]	This Research				
			Concentration of Leached Heavy Metals from Coal Ash Via TCLP and SPLP (mg/L) [4,41]	Monomial Potential Ecological Factor (i.e., One Heavy Metal Only) (E_r^I)	Ecological Risk of Single Regulator	Ecological Risk Index (R_I)	Ecological Risk Assessment of Heavy Metals
As	0.4	15	14.636–18.605	9.76–12.40	Low potential ecological risk $E_r^I < 40$	9.90–12.61	Low ecological risk for the lake/basin $R_I < 95$
Cd	0.2	1.0	n.a.	n.a.			
Cr	0.2	90	n.a.	n.a.			
Cu	10	50	0.027–0.033	4.70–5.50			
Hg	0.08	0.25	n.a.	n.a.			
Pb	5	70	0.673–1.026	1.36–2.05			
Zn	10	175	0.149–0.219	1.90–2.70			

Nevertheless, the importance of following standard methods has been emphasized by Abd Manan et al. (2021) showing comparison studies with inconsistencies of datasets due to modification of normal standard methods (e.g., modification duration and pH of leaching test). Thus, the term chemical speciation is preferable. The term ‘leaching studies’ for any modified leaching test must be avoided to prevent confusion with the existing standards.

3.2. Model Equation for Ecological Risk Indicators

The 29 combinations of four independent variables, in accordance with Box-Behnken design (Table S2), were used to compute the corresponding values of the dependent variable. The independent variables were leached heavy metal concentrations. The ranges were from 0.5 mg/L to 2.0 mg/L (Pb), 0.05 mg/L to 0.30 mg/L (Zn), 0.01 mg/L to 0.04 mg/L (Cu) and 13.00 mg/L to 19.00 mg/L (As). The dependent variable was ERI.

The analysis of variance (ANOVA) from the quadratic model for ERI is shown in Table 4. Sum of squares (SS) is a sum of squared differences on the plots. It measures the difference between values of the dependent variables and their mean values. Therefore, the data dispersion can be identified and the adequacy of the data for the regression analysis can be determined [54]. The mean square (MS) is the SS divided by the degrees of freedom (DF). The lower SS and MS values imply better model. The SS and MS values obtained were low equivalent to less than 0.5 implying admissible model.

The F value, also called F -statistic (Fisher), evaluates the overall significance level of a regression model [55]. It is calculated by dividing the MS over residual mean [56]. The high F value shows large variability of group means as compared to the within group variability. As a result, the null hypothesis indicating group means are equal is rejected. The model F value of 682,375.55 implies that the model is significant. There was only a 0.01% chance that a model F value this large could occur due to noise. The $Prob > F$ value is the probability for null hypothesis of the full model is true whereby coefficient of determination (R^2) equals to zero. Values of $Prob > F$ less than 0.05 shows that the model terms are significant. Meanwhile, values of $Prob > F$ greater than 0.10 show that the model terms are not significant. Both values indicate 5 and 10 chances out of 100 accordingly for all of the regression parameters or R^2 in the model terms to be zero [55,57]. The indications of model terms based on $Prob > F$ value are shown below.

Table 4. ANOVA for quadratic model.

Scheme	SS	Coefficient Estimate	DF	MS	F Value	Prob > F	Indication
Quadratic Model	0.4160	2.39	14	0.0297	682,375.55	<0.0001	Significant
A-Pb	0.0023	0.0139	1	0.0023	53,186.95	<0.0001	Significant
B-Zn	2.513×10^{-7}	0.0001	1	2.513×10^{-7}	5.77	0.0307	Significant
C-Cu	6.433×10^{-7}	0.0002	1	6.433×10^{-7}	14.77	0.0018	Significant
D-As	0.4116	0.1852	1	0.4116	9,452,514.58	<0.0001	Significant
AB	1.544×10^{-11}	-1.965×10^{-6}	1	1.544×10^{-11}	0.0004	0.9852	Not significant
AC	3.953×10^{-11}	-3.144×10^{-6}	1	3.953×10^{-11}	0.0009	0.9764	Not significant
AD	0.0000	-0.0026	1	0.0000	622.03	<0.0001	Significant
BC	4.330×10^{-15}	-3.274×10^{-8}	1	4.330×10^{-15}	9.944×10^{-8}	0.9998	Not significant
BD	2.938×10^{-9}	-0.0000	1	2.938×10^{-9}	0.0675	0.7988	Not significant
CD	7.521×10^{-9}	-0.0000	1	7.521×10^{-9}	0.1727	0.6840	Not significant
A ²	6.185×10^{-8}	-0.0001	1	6.185×10^{-8}	1.42	0.2532	Not significant
B ²	1.795×10^{-11}	1.664×10^{-6}	1	1.795×10^{-11}	0.0004	0.9841	Not significant
C ²	1.759×10^{-11}	1.647×10^{-6}	1	1.759×10^{-11}	0.0004	0.9842	Not significant
D ²	0.0019	-0.0171	1	0.0019	43,323.12	<0.0001	Significant
Residual	6.096×10^{-7}		14	4.354×10^{-8}			
Lack of Fit	6.096×10^{-7}		10	6.096×10^{-8}			
Pure Error	0.0000		4	0.000			

The β coefficient or standardized regression coefficient of determination (R^2) for quadratic model and model terms for coded factors are; 2.39 (y-intercept), 0.0139 (A), 0.0001 (B), 0.0002 (C), 0.1852 (D), -1.965×10^{-6} (AB), -3.144×10^{-6} (AC), -0.0026 (AD), -3.274×10^{-8} (BC), -0.0000 (BD), -0.0000 (CD), -0.0001 (A²), 1.664×10^{-6} (B²), 1.647×10^{-6} (C²), and -0.0171 (D²). The β coefficient for quadratic model and model terms for actual factors are; 0.870324 (y-intercept), 0.037472 (A), 0.002303 (B), 0.030839 (C), 0.12385 (D), -2.1×10^{-5} (AB), -2.79×10^{-4} (AC), -1.16×10^{-3} (AD), -1.7×10^{-5} (BC), -7.2×10^{-5} (BD), -9.64×10^{-4} (CD), -1.74×10^{-4} (A²), 1.06×10^{-4} (B²), 7.32×10^{-3} (C²), and -1.90×10^{-3} (D²). Quadratic model and model terms A, B, C, D, AD, and D² for both coded and actual factors are significant (p -value < 0.05) (Table 4). The significant regression parameters of predictive models in terms of coded and actual factors are shown in Equations (8) and (9) accordingly. The β coefficient for quadratic model and model terms of coded and actual factors are shown in Figure 1. The calculation of coded factors is shown in Table S3.

$$\ln(ERI) = 2.39 + 0.0139A + 0.0001B + 0.0002C + 0.1852D - 0.0026AD - 0.0171D^2 \quad (8)$$

$$\ln(ERI) = 0.870324 + 0.037472A + 0.002303B + 0.030839C + 0.123850D - 0.001157AD - 0.001895D^2 \quad (9)$$

(a) Coded Factors

(b) Actual Factors

Figure 1. The β coefficient for quadratic model and model terms of (a) coded and (b) actual factors.

Overall, the quadratic model is significant. The R^2 coefficient indicates the ratio of sum of squares due to regression (SSR) to total sum of squares (SST). It shows goodness of fit between one variable and another variable. Generally, a higher coefficient close to 1 indicates a good fit for the model (Table S4). The $Adj. R^2$ increases only if the new term improves the model more than would be expected by chance. The $Adj. R^2$ can be negative and will always be less than or equal to R^2 . R^2 values smaller than 0.75 usually indicate an insufficient description of the experimental data by the model [58].

The patterns of predicted versus actual values plot for ERI are shown in Figure S1. There was no outlier observed and scatterplots were in a straight line showing a linear relationship between predicted against actual values plot. Therefore, the proposed model terms were sufficient, and constant variance assumption was verified.

Figure 2 shows the three-dimensional plots of Pb, As and ERI. ERI of below 9 was a combination of Pb and 'As' at 0.5 to 1.4 and 13 to 13.4 respectively. ERI of 9 up to 12 has a consistent range of Pb equal to 0.5 to 2. Apparently, As plays an important role as the main contributor to ERI. The ERI ranges from 9 to 10, 10 to 11 and 11 to 12 have As in the range of 13.4 to 14.8, 14.8 to 16.4 and 16.4 to 17.8 accordingly. The ERI values of 12 and above were for 17.8 to 19 of As. The relationship of As (13 to 19) is in direction perpendicular to ERI ranging from 9 to 12 for both plots. The Zn (0.05 to 0.3) and Cu (0.01 to 0.04) have uniform values for all ascending ERI ranges (12.2 to 12.4).

Figure 2. The interaction between ERI and heavy metals (Pb vs. As, Zn vs. As, Cu vs. As).

ERI of below 12.2 was from 0.5 to 0.8 for Pb. The ERI range from 12.2 to 12.3 was from 0.8 to 1.3 for Pb. The ERI range from 12.3 to 12.4 ranged from 1.3 to 1.8 for Pb. ERI value more than 12.4 was of 1.8 and more for Pb. Zn (0.05 to 0.3) and Cu (0.01 to 0.04) have uniform values for all ascending ERI ranges (12.2 to 12.4). A cross pattern was observed at each ascended ERI. ERI below 12.19 has $\text{Cu} < 0.022$ and $\text{Zn} < 0.2$. The ERI ranging from 12.19 to 12.129 has $0.022 > \text{Cu} > 0.034$ and $0.2 > \text{Zn} > 0.3$. The ERI ranging from 12.192 to 12.194 has $\text{Cu} > 0.04$ and $\text{Zn} > 0.3$. The calculation and validation of optimized model is shown in Table S5 and Table S6.

CA is a sustainable supply for numerous innovative applications [1,12,14–22,59]. The reuse of CA as cement replacement material has been practiced in the US construction industries for decades [23,24] due to its pozzolanic property [3,10,11,26]. Waste management need to be strategized at much lower risk posed to the environment (i.e., water, air, soil, plants, and animals) and human health [3].

This study is important for the prediction of ecological risk assessment of leached heavy metals from coal ash application in construction industries promoting sustainable supply for concrete technology [2,26,60]. The error percentages of coded and actual factors ranged from 0.14 to 0.32% and 0.01 to 0.15% accordingly. The optimized model risk indicators (ERI) (Equations (8) and (9)) are sufficient for this purpose and validated with error percentage of less than 5% [15,57].

4. Conclusions

This study focused on identifying the desired values of independent variables how the ecological risk of single regulators, namely Pb, Cu, Zn and As, can achieve the sustainable material goals. The responses known as ecological risk index of each heavy metal were regressed by the multiple independent variables using a polynomial quadratic equation. The ecological risk assessment values ($E_r^i < 40$ and $R_I < 95$) of coal ash (i.e., FA, BA and FA + BA) showed low risk to aquatic organisms showing potential application of FA and BA as cement replacement material. The established model risk indicator (ERI) (coded and actual factors) of Pb, Cu, Zn and As showed significant model terms perfectly fit to the corresponding ERI (sum of squares = 0.4160, F value = 682,375.55) with probability of 0.01% for an F-value could occur due to noise. The optimized ERI models were validated with error percentage of less than 5%. The established model risk indicators will be beneficial for ecological risk assessment of coal ash application in the construction industry.

Recommendation

Industrial areas of the coal mining [61,62], forestry [63], oil, and gas industries [61,62] are exposed to anthropogenic metal enrichment in soil, air, and snow. The ecological risk assessment of leached heavy metals from CA is specific to the aquatic environment. Nevertheless, risk assessment of human, topsoil and/or sediment, air, and snow as presented in [61–63] could be performed using the application of a similar approach. Other than heavy metals, polycyclic aromatic hydrocarbons [61] could be another indicator for risk assessment of CA.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/su131810222/s1>, Figure S1: Predicted vs. actual values plot for ERI, Table S1: Process variables and code factors, Table S2: Box-Behnken design and responses results, Table S3: The calculation of coded factors, Table S4: Fit summary results for response parameters, Table S5: Calculation for the validation of the models, Table S6: Validation of optimised model.

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