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Clean Technology for the Treatment and Modelling of Acid Mine Drainage Effluent

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Abstract

Acid Mine Drainage (AMD) exists as a phenomenon that involves the release of acidic water and metal conjugates, in and around mines, degrading the surrounding water environment. A real-time mining effluent is treated using low-cost adsorption technology using Combined Vegetable Waste Carbon (CVWC) as sorbent. Batch sorption was reviewed to know the effect of process factors on the removal of Cadmium (Cd), Zinc (Zn), and Iron (Fe). A two-level CCD (Central Composite Design) with three factors was adopted in the optimization of process factors. Also, the same factors were considered to review the ANNs (Artificial Neural Networks), model. A comparative statistical analysis was performed for the experimental data based on RMSE and R^2 values in both RSM (Response Surface Methodology) and ANNs models. This study revealed that the ANNs model was well fit compared to RSM and this would probably reduce the experimental trials thereby reducing cumbersome calculations.

Introduction

The economic development of any country mainly depends significantly on the mining industry.[1] Majorly, the mining operations generate vast quantities of wastewater as the result of AMD.[2, 3]

The significant effect of the mining is the degradation of natural resources.[4] The amount of water used in the mining industry is huge and generally higher than what is predicted due to the mining processes involved. Furthermore, the effluent from slag washing has high acidity (pH<4) and is polluted with elevated levels of heavy metals.[5-7]

The long-term effects due to metal-ions (Cd, Ni, Cu, Hg, Cr, Zn etc.) even in mild concentrations are bio-accumulation and heavy metal poisoning.[8]

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The conventional Physico-chemical processes were employed in the treatment of AMD like coagulation-flocculation, sedimentation, and filtration. Researchers have been researching for easy, clean, and low-cost viable treatment options since the last decade.[9] In this context, adsorption technology would be a competent solution in the treatment of AMD effluent.[10-12]

The tedious batch experiments conducted for adsorption study can be optimized using statistical tool Response Surface Methodology (RSM)[13, 14] Recently, a study based on the tool optimized the following: -

- Adsorption of Fluoride wastewater using modified soil as adsorbent using central composite design RSM.[15]
- Adsorption of cationic metals Copper and Zinc on silica and optimized batch tests using RSM.[16]
- Dye sorption from aqueous solutions[17] by using Nanocomposites as adsorbents.

On the other hand, artificial Neural Networks (ANNs), tools based on Artificial intelligence that are used by many researchers to simplify the mathematical calculations. ANNs were used for:-

- Optimization and modeling the sorption of Copper and Lead using rice straw as adsorbent.[18]

- Biosorption process using various agricultural wastes in treating the metal-polluted waters.[19]

A combination of RSM and ANNs was used by many researchers for process optimization, statistical modeling in the adsorption process.[20]

The current study illustrates the batch adsorption onto composite vegetable waste carbon (CVWC) as a low-cost treatment option for AMD effluent.[21, 22] There is a two-fold advantage, one is the reduction of vegetable wastes which end up in the open dumps and economic development by the utilization of the wastes for treating wastes. The process optimization was carried out using RSM and modeling was done by Feed Forward Back Propagation Neural network. The regression models in both RSM and ANN were compared.

Materials and Methods
Adsorbate and Adsorbent Preparation
The real time AMD effluent was gathered from Iron ore mines located at Bayyaram, Telangana, India. According to USEPA, Cadmium, Copper, Nickel, Arsenic, Chromium, Lead, Zinc, and Mercury are the most toxic heavy metals discharged into the water environment.[23] The Characteristics of AMD effluent and US EPA effluent standards are shown in Table. 1. Three heavy metals Cadmium, Zinc, and iron (highlighted in Table. 1) are deviating from the US EPA standards, and hence those are considered for the study.

Table 1: AMD Effluent Characteristics and corresponding USEPA effluent disposal standards

Parameter	Concentration (mg/L)	US EPA standards (mg/L)
Cd	12.34	2.0
Cu	1.54	3.0
Zn	96.5	5.0
Cr	0.05	0.1
Co	0.023	0.05
Ni	0.13	3.0
Fe	146.75	5.0
Pb	0.013	0.1
Hg	0.0003	0.01

A 100% dilution ratio was considered for the laboratory scale batch study. The Composite Vegetable Waste (CVW) was used as adsorbent collected from local vegetable markets. The CVW was then dried sufficiently under sunlight, washed with plenty of water to remove any grit or sand. Again, the mass was air-dried, followed by oven drying at 110°C overnight. The recovered mass was roughly ground after cooling and was carbonized at 450°C for 2 hours. The so obtained product was Composite Vegetable Waste Carbon (CVWC).

Experimental
A laboratory-scale batch study was carried out for the elimination of Metal-ions from real-time AMD effluent after subsequent dilution (sample volume (v) 100 mL).[24, 25] The effect of process parameters for instance pH, adsorbent dose(M), the contact time was reviewed. The ranges selected for the parameters are pH (2 to 9), adsorbent dose (1-10 mg), and contact time (0.5 to 3 hours). The pre concentration (C_o) and post concentration(C_e) of the metals were obtained by spectrophotometry, and their % removal (%R) and adsorption capacity q_e(mg/g) was analysed as given in Equation (1) ad (2).

$$\%R = \frac{C_o - C_e}{C_o} * 100 \qquad ...(1)$$

$$q_e = \frac{C_o - C_e}{M} * v \qquad ...(2)$$

RSM Optimization
The 2-factorial 3-level central composite design in RSM used to optimize process factors. The effect of each factor, as well as the interaction, was studied. The optimum values of all the process variables coded values (-1, 0, +1) were obtained by replicating the experiments six times at center points. A quadratic expression is used in the optimization process as shown in Equation (3)

$$y_p = \beta_0 + \sum_{a=1}^{4} \beta_a x_a + \sum_{a=1}^{4} \beta_{aa} x_a^2 + \sum_{a=1}^{4} \sum_{b=a+1}^{4} \beta_{ab} x_a x_b$$
$$...(3)$$

Where, y_p is the response, i.e. the % removal and adsorption capacity, β_0 (constant), β_a (linear),β_{aa}

(quadratic) and β_{ab} (interaction) are coefficients, respectively.x_a (a= to 4) is the independent factor affecting the response. The coefficient of determination (R^2) was obtained from the ANOVA method in RSM using Design Expert® software.

ANNs Modelling
Matlab® environment was employed for modeling the experimental feed results using Feed Forward back propagation neural network. Of many forms of algorithms, the Levenberg-Marquardt (LM) was employed as it was more appropriate and considered for modeling. A total of 20 samples were considered 14 for training, three each for validation and testing. The performance of batch tests was analyzed using the ANNs model, and regression analysis compared to RSM.

Results and discussion
Experimental
The experimental details given in Table 2 highlights the effect of pH, adsorbent dose, contact time on multi-metal removal. The Optimum pH for Cd, Zn, and Fe was 5.5. The adsorbent dose was 5.5 for Fe and 9 for Cd and 10 for Zn. The optimum contact time was at 1.75 Hrs for all the metals. Fig. 1 (a), (b), (c) explains the effect of selected factors on the removal (%R).

CCD Design
Tests were performed on factors and their effect on the sorption onto CVWC. A 3-level full factorial central composite face-centered design and 25 runs with 3 (-1, 0, +1) center points was used to realize the effects of many process parameters upon sorption of the three metals Cadmium, Zinc and Iron.[27,28] Tests (20) were conducted randomly as per the selection by factorial design, as shown in Table 2. The effect of test factors like pH, Adsorbent dose, and contact time were studied upon the % removal using Origin® Pro Software.

Final Equation in Terms of Coded Factors

%R (Cd) = 84.70 + 8.16 A + 0.9210 B + 7.39 C + 6.45 AB + 5.44 AC + 11.93 BC - 18.78 A^2 + 0.2155 B2 - 11.96 C^2

%R (Zn) = 84.97-2.40 A + 6.91 B + 2.37 C + 0.0775 AB + 4.59 AC + 8.82 BC - 12.89 A^2 + 0.2000 B2 - 1.08 C^2

%R (Fe) = 85.78 + 3.13 A + 14.15 B + 0.2950 C - 3.14 AB + 0.1825 AC + 11.43 BC -22.62 A^2 - 2.67 B2 + 6.93 C^2
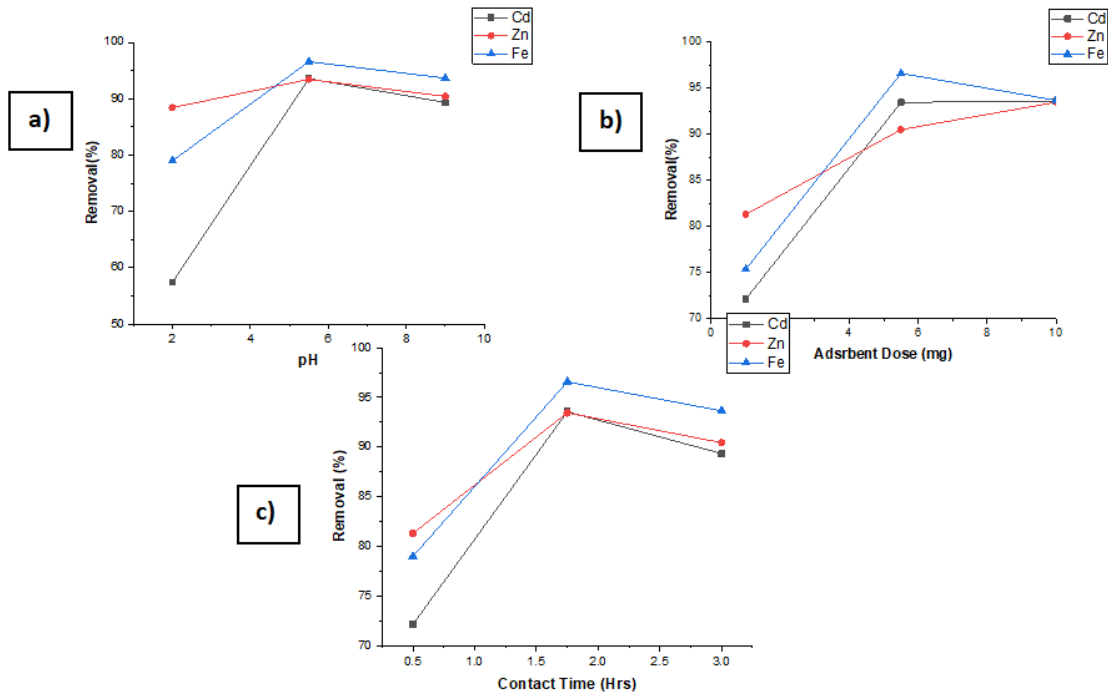

Fig.1: Effect of a) pH, b) Adsorbent Dose and c) Contact time on %R (Experimental)

Table 2: Effect of factors on % R (Experimental, RSM and ANNs) for Cd, Zn and Fe

Run	pH (A)	Ads. Dose (mg) (B)	Contact Time (Hrs) (C)	%R (Cd)			%R (Zn)			%R (Fe)		
				Exp	RSM	ANNs	Exp	RSM	ANNs	Exp	RSM	ANNs
1	9	5.5	1.75	86.45	85.89	85.77	78.45	79.21	78.76	67.45	66.89	67.21
2	5.5	1	1.75	54.33	54.76	53.89	67.33	67.45	67.19	55.45	55.22	55.33
3	5.5	10	1.75	93.56	92.80	93.06	93.45	93.90	92.32	90.35	90.56	90.76
4	5.5	5.5	1.75	91.76	90.99	90.96	85.43	85.11	85.41	91.56	91.89	91.77
5	5.5	5.5	1.75	92.33	92.78	92.58	86.43	86.04	86.07	91.41	91.33	91.34
6	2	1	0.5	72.16	72.57	72.79	81.32	80.80	82.10	63.22	63.15	63.25
7	9	1	0.5	68.34	68.65	69.05	64.66	64.34	64.32	75.38	74.45	75.87
8	9	10	0.5	34.56	32.98	34.06	53.65	53.21	53.90	67.23	67.78	67.16
9	2	10	0.5	43.22	43.64	43.48	78.54	78.09	78.21	78.99	79.49	78.54
10	5.5	5.5	3	89.32	90.02	89.37	79.56	80.05	79.56	88.9	88.54	89.43
11	5.5	5.5	1.75	92.67	92.21	91.59	86.77	86.22	86.12	94.89	95.12	93.78
12	9	1	3	44.74	43.90	43.99	57.63	57.32	57.36	44.76	44.24	44.23
13	5.5	5.5	1.75	90.56	90.78	91.21	89.51	90.03	88.98	91.31	91.53	91.81
14	2	10	3	45.56	45.34	45.44	88.41	88.77	88.11	53.34	53.61	53.62

15	5.5	5.5	1.75	91.34	91.86	91.41	90.48	90.66	90.32	89.77	89.05	89.09
16	5.5	5.5	0.5	34.22	33.81	34.06	78.65	77.79	78.16	76.09	77.31	75.74
17	9	10	3	89.33	89.01	88.21	90.44	90.67	90.17	93.65	93.67	93.96
18	5.5	5.5	1.75	93.43	93.87	93.53	90.3	90.21	90.87	96.57	96.34	96.32
19	2	1	3	57.45	57.71	56.18	64.45	64.87	64.34	43.21	43.45	43.34
20	9	1	1.75	23.45	24.78	22.63	56.15	56.64	56.35	38.45	39.17	39.17

The predictions about each factor and their response arrived from the equation in relation to the coded factors. The coded levels +1 and -1 denotes high to low with reference to coded factors.

ANNs Modelling

Back propagation Neural Network was used for modeling of experimental data onto CVWC.[25, 26] The network has 3 input and output neurons, the hidden and output layer has 10 and 3 neurons, respectively.

Comparison of RSM and ANNs Models

The regression analysis for tedious problems can be analyzed using RSM and ANNs. These models were employed to investigate the adsorption of AMD wastes onto CVWC.[26-28] The statistical analysis based on RMSE and R^2 were calculated based on the following equations for RSM and ANNs presented in Table 3.

$$RMSE = \left(\frac{1}{n} \sum_{i=1}^{n} (y_i - y_{di})^2 \right)^{\frac{1}{2}}$$

$$R^2 = 1 - \frac{\sum_{i=1}^{n} (y_i - y_{di})^2}{\sum_{i=1}^{n} (y_{di} - y_m)^2}$$

Where n refers to the number of points, y_i being the predicted (RSM & ANNs) value, y_{di} is the actual (experimental) value, and y_m is the mean of the actual values.
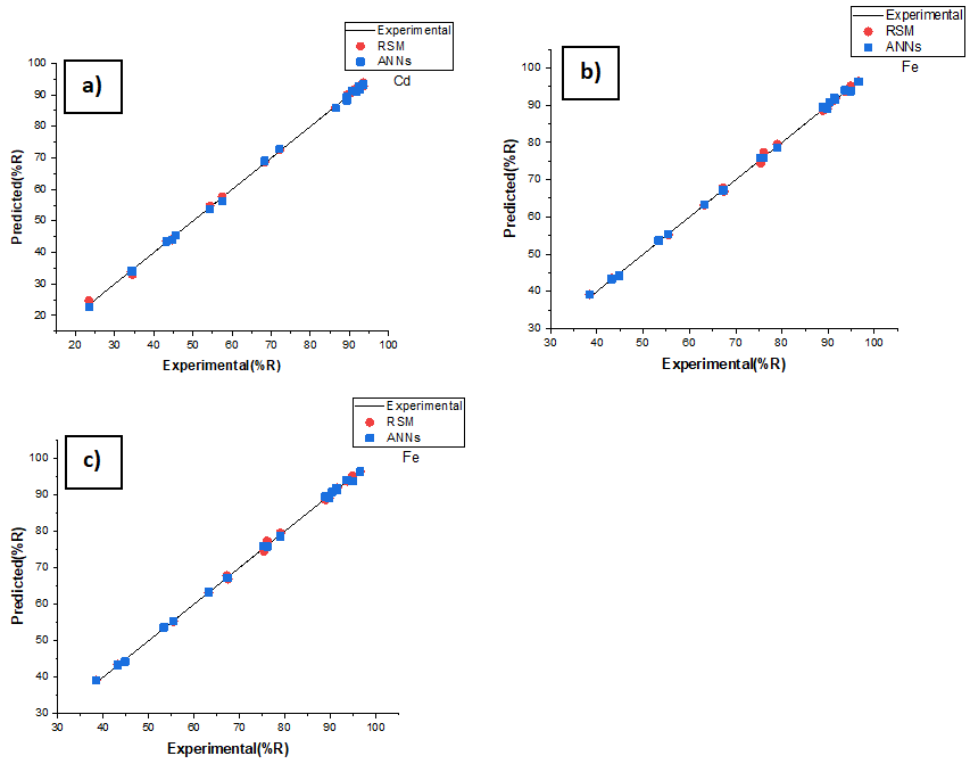

Fig.2: Experimental %R versus predicted (RSM & ANNs) for a) Cd b) Zn and c) Fe

The RMSE for RSM and ANNs were reported to be 0.346 and 1.258 respectively; this shows that the values of ANNs deviated compared to RSM. R^2 (coefficient of correlation) for RSM and ANNs were obtained to be 0.89 and 0.96, respectively. The regression analysis gives an idea about how well data fits the model. Fig. 2 (a), (b), (c) convey the comparison for removal (%R) for experimental, RSM, and ANNs predicted values. No significant deviation from the experimental data was found.

Though RSM and ANNs models fit well to experimental data, comparatively, the ANNs model was more dominant than RSM. However, RSM is advantageous over ANNs in depicting the relationships between various operational factors in terms of responses. However, the major drawback of RSM is that it presumes only a quadratic form of non-linear correlation. However, ANNs have an inbuilt system that can naturally encapsulate most of the non-linearity, in contrast to RSM.

Conclusion

The study supports that combined vegetable waste carbon (CVWC) is effective in the Treatment of AMD effluent in an eco-friendly manner. The laboratory-scale batch study was successful in the elimination of the three metals, i.e. Cadmium, Zinc, and Iron from AMD effluent. The experimental data revealed the highest removal was observed for Iron at an optimum pH and the adsorbent dose of 5.5 and at a contact time of 1.75 hours, respectively. RSM and ANNs models were employed to forecast the adsorption efficiency of the metals from wastewater onto CVWC. RMSE and R2 were used to predict the working of RSM and ANNs models. The plots with experimental versus predicted data revealed a good correlation with the experimental data.

Conflict of Interest

The authors do not have any conflict of interest.

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