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Withdrawal of Mn(II) from aqueous solution using low cost adsorbents: isothermal, kinetic and ANN modeling studies

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Residual solid material left after complete extraction of oil from groundnut, sesame seed and coconut were used in their raw form as adsorbents in the withdrawl of Mn(II). A temperature of 40°C, contact time of 60 min, 1.0 g of adsorbent dosage, initial metal concentration of 60 mg/L and a pH of 4 was found to be effective for the withdrawl (99.7%) of Mn(II). Langmuir adsorption isotherm fits apt for the withdrawl of Mn(II) by the three adsorbents with R^2 values of 0.9785, 0.985 and 0.984. Adsorption of Mn(II) on the three adsorbents followed pseudo-second order kinetics. Back propagation L-M algorithm was adapted for predicting withdrawl of Mn(II) using ANN tool in MATLAB. A strong positive correlation with R^2 value of 0.9825 was observed between the ANN predicted and experimental values. The maximum withdrawl capacity was found to be 4.99 mg/g with all the three adsorbents.

Keywords: Artificial neural networks, manganese, adsorption, isotherms, kinetics.

Introduction

Water scarcity and availability of safe drinking water are the biggest challenges in 21st century. Industrialization, urbanization, natural and manmade activities, and many other phenomena are responsible for the degradation of water quality. In light of these facts the authors have carried out investigations on the suitable methods for the adsorption of pollutants like heavy metals and dyes from water. In continuation to the previous investigations[1–4], the authors have studied the withdrawl of Mn(II) using three inexpensive bio adsorbents. Manganese is one among the heavy metals that are known for their toxic and carcinogenic activities, other harmful activities. Among the various methods available for the water treatment bio adsorption has proven to be the best methodology as it is economic, green, effective and efficient. In literature, many inexpensive bio adsorbents were cited by researchers for the withdrawl of heavy metals from aqueous as well as industrial effluents. Solid residual waste from edible oil industry like coconut cake, groundnut seed cake and sesame seed cake has not been used in bio-sorption studies so far. Foremost, the authors have used these materials for the first time. For large scale/industrial applications, proceeding directly without a pilot study is always cumbersome. In view of this modeling or simulations studies have been adopted in recent years. ANN modeling has been used by the authors to ascertain the suitability of the chosen adsorbents.

Materials and methods

Only analytical grade chemicals and double distilled water were used for experimentation. A stock solution of Mn(II) was prepared by dissolving adequate amount of manganese sulphate in double distilled water and standardized further. Samples of adsorbents were collected from local markets. These samples were dried under sunlight for twenty four hours.The dried samples were subjected to size reduction, only the homogenous particles are used further. The sample structure and the presence of carbonyl and OH groups were established by using FTIR analysis and XRD analysis[1] (Fig. S1-S6). Batch adsorption experimentation was used for the present study. In detecting the concentration of the metal Atomic absorption spectrophotometer was used.

Results and discussion

The details of adsorption characteristics or optimization conditions of the adsorption process are presented in Table 1.

Table 1. Adsorption optimization parameters

Parameter	Name of the adsorbent		
	GNCSP	SSCP	CCP
pH	4	4	4
Temperature (°C)	40	40	40
Adsorbent dosage (g)	1.0	1.0	1.0
Initial metal concentration (mg/L)	60	60	60
Contact time (min)	60	60	60
Q_{max} (mg/g)	4.995	4.98	4.99

Graphical representations were presented in Figs. S1-S7. Correlation between ANN predicted and experimental values were presented in Fig. 1.

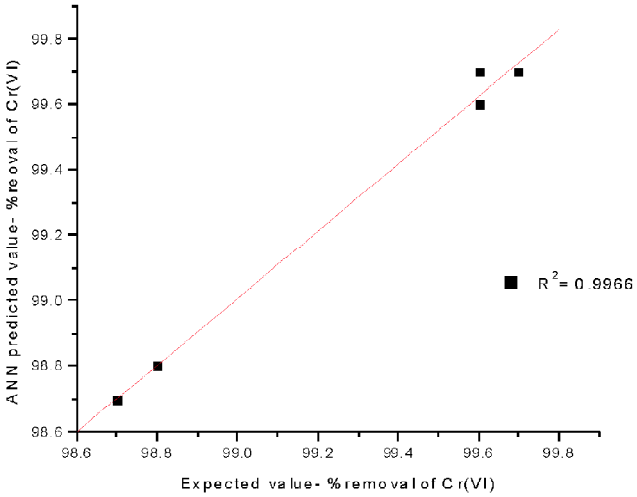

Fig. 1. Correlation plot between the experimental and ANN predicted results.

Optimization of various parameters:

As of the results, it was proved that the pH of 4 is best for the present study. As the pH of the solution rises, there is a significant increase in the equilibrium capacity of Mn(II) withdrawl by the adsorbents. At a higher initial pH (> 8) precipitation of manganese ions was found.

By fixing the adsorbent dosage, a series of batch experiments were carried out at varying time intervals. From the results obtained, 99.7% of withdrawl of manganese ions was found at time of 60 min using all the three adsorbents.

An analysis of series of experiments were carried out by taking 0.25, 0.5, 0.75, 1.0, 1.5 and 2.0 g of the adsorbents. From the results, it was found that withdrawl of manganese ions from aqueous solution was effective with 1.0 g of all the three adsorbents.

By fixing dosage and pH, a series of Mn(II) solutions of concentration 10, 20, 30, 40, 50, 60, 70, 80, 90 mg L^{-1} were thoroughly mixed with all the three adsorbents for 60 min. Due to the saturation of the active sites in the adsorbent, a decrease in the withdrawl efficiency with increase in concentration was found from 70 mg L^{-1}.

By fixing the adsorbent dosage, contact time, pH and initial metal concentration batch experiments were carried out at varying temperatures. From the results obtained 99.7% of withdrawl of manganese ions was found at a temperature of 40°C.

Adsorption isotherms:

Three adsorption isotherms were adopted for the withdrawl of Mn(II). From the isothermal results it was inferred that the adsorptive withdrawl Mn(II) fits with Langmuir type-I adsorption isotherm. This infers the monolayer and heterogeneous adsorption of the metal on the chosen adsorbents.

Kinetic models of the present study:

Investigations were carried out to study the kinetics of adsorption of Mn(II). Results showed that the adsorption of Mn(II) followed pseudo-second order kinetics. The plot drawn between t against t/q_t fitted a linear plot with R^2 value of 0.9994. This infers the reaction happening on surface and solution too.

Adsorption modeling using ANN:

The present study is limited to laboratory application only. To investigate the application of the selected adsorbents to large scale or industrial effluents, prediction techniques helps a lot. Hence to study the large scale applications, artificial neural networks (ANN) tool in MATLAB was used. Parameters like pH, contact time, adsorbent dosage, temperature and type of adsorbent were given as inputs to the network. Percent withdrawl of manganese ions was obtained as output. The values obtained were compared with the experimental values of same set of data. Results showed an error of 0.4% between the experimental and ANN predicted values. Hence it is inferred that the chosen adsorbents with the

specified optimized conditions can be useful for industrial applications without any difficulty.

Conclusions

Edible oil industry solid waste has proven to be the best bio adsorbent for the withdrawl of Mn(II) from aqueous solutions at a pH of 4, temperature of 40°C and with 1.0 g with a maximum adsorption capacity of (Q_{max}) as 4.99 mg/g. It was found that the withdrawl of Mn(II) using the three adsorbents followed pseudo-second order kinetics and adsorption of Mn(II) fit perfectly to Langmuir isotherm with correlation coefficient of 0.9785. The value of R_L was found in between 0 and 1 implicating that the process of adsorption is favorable. ANN modeling was adopted and found to have high correlation between the predicted and experimental values.

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