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Optimal isotherm parameters for phenol adsorption from aqueous solutions onto coconut shell based activated carbon: Error analysis of linear and non-linear methods

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ABSTRACT

Removal of phenolic pollutants from wastewaters has become mandatory due to stringent environmental regulations and adverse effects on aquatic marine environment. Adsorption process which is most effective process to remove pollutants, hinders its applications in diverse field due to high cost of adsorbents. In this study, a low cost and easily available agricultural waste of coconut shells based activated carbon were utilized as adsorbent to study its viability and efficiency for phenol removal from wastewater. The efficacy of the phenol removal by adsorption process in a batch reactor is evaluated with respect to contact time for effective adsorption and influence of initial phenol concentration on percentage phenol removal. The experimental adsorption data were examined with conventional isotherms models to describe the equilibrium characteristics of adsorption of phenol. The vigorousity and non-linearity inherent in the isotherm models were validated using various traditional linear and non-linear estimation methods namely gradient method, non-linear least square method and hybrid evolutionary optimization. A novel inverse modeling technique based on differential evolution (DE) optimization which is first of this kind for adsorption applications was implemented to estimate the isotherm parameters in their non-linear form. The model predictions from the DE based optimized parameters provided better predictions and closer to experimental values. The percentage removal of phenol from four different adsorbent dosages with constant initial feed concentrations of phenol found to be varying from 63% to 96% as increase in carbon loading at constant liquid flow rate. These experimental results also revealed that coconut shell based activated carbon is a viable cheaper adsorbent for phenols removal from effluent wastewater.

1. Introduction

Phenolic compounds are the major predominant forms of organic pollutants typically found in wastewater released from industries and small/medium scale manufacturing units [1]. The most important sources of phenol contamination in the water bodies are effluent wastewaters released from petrochemical, oil refineries, coke oven by-products, textile industries, leather processing units, pharmaceutical industries, insecticides production units, etc., [2–6]. Mostly these effluents have phenol and its derivatives in higher concentrations and they are very harmful to flora and fauna besides aquatic organisms. Phenol contamination can also come into contact with natural reservoirs and lakes through the domestic waste and agricultural runoff [7]. Phenolic compounds are highly mobile and easily water soluble, henceforth they can mix with sources of natural drinking water via downstream from discharges, thus pose severe risk and health hazards to human population. Chronic toxic effects and lethal impacts due to phenols in drinking water was reported to cause vomiting, sore throat, headache, trouble in gulping, fainting, damage to liver and kidney, and other mental disorders [8]. Phenol is very difficult to degrade biologically and hence led to stringent regulations on the presence of phenol and its derivatives in the aqueous environment. According to the regulations framed by world health organization, the permissible concentration of phenolic compounds in potable waters should be less than 1 μg/l [9].

The presence of phenols along with derivatives in effluent wastewaters that have hostile effects on aquatic environment

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and implementation of tough regulations draws the attention of the environmental researchers for its remediation. Hence, treatment of wastewater containing phenol is a critical issue to ensure general wellbeing of human beings. The most commonly used techniques for phenol removal from aqueous solutions are biological treatment, solvent extraction, electro coagulation, chemical oxidation, membrane filtration, ion exchange, precipitation, distillation, adsorption, reverse osmosis, etc., [10–16]. Chemical oxidation technique is widely used, where phenol concentration in effluent is very high. Biological treatment is well suited for treatment of effluent containing lower phenol concentration. Coagulation and flocculation process is also used for high concentrated phenol removal, but application of these processes are limited due to disposal of sludge that is generated in large quantity. Among the various physico-chemical processes, adsorption technique is commonly adapted for the phenol removal from effluent wastewater [5,7,10,17]. However, the greatest hindrance in adapting these techniques in the process industries was the highest cost of adsorbents, in spite of various adsorbent regeneration techniques [18–21].

The applications of adsorption methodology can be increased by reducing the cost of adsorption. Therefore, there is a huge demand from the market to explore low cost and easily available adsorbents. These adsorbents can be from biomass, fly-ash, various solid substances and agricultural waste products [22–26]. Many studies devoted on production of activated carbon from agricultural waste products were mostly focused on the either preparation of high quality activated carbon or applied in batch adsorption process [25–30]. The source of activated carbon also signifies the performance of the adsorption process. Since process industries generate huge amount of effluents regularly, therefore they tend to utilize large quantities of adsorbent. Regular usage of large amount of adsorbent will be very expensive, but they were made compulsory to use best treatment practices for effluent wastewater due to stringent environmental regulations. Hence, cheaper and effectives adsorbents are viable alternatives for process industries. Therefore, this requirement from the industries drive the researchers to explore more low cost adsorbents especially derived from natural and agricultural products.

Owing to the limited studies on phenol adsorption process conducted in batch process and need of low cost absorbent, this study is mainly focused to meet these two requirements. Therefore, the core objective of this research study is to evaluate the efficiency of a low cost agricultural waste (coconut shell) based activated carbon through a laboratory scale batch process for phenol removal. In the present batch adsorption study, granular activated carbon produced from coconut shell, is selected as an adsorptive medium to evaluate the performance of phenol adsorption from aqueous systems. To understand the adsorption equilibrium mechanism and inherent characteristics associated within the system, various two parameter and three parameter isotherm models with different dimensions of non-linearity are examined. Presently, in most of the various adsorption/bio-sorption applications, researchers use the traditional linear transform techniques or reduced gradient techniques. To the best of author's knowledge, implementation of hybrid evolutionary optimization technique is not been reported so far for adsorption/bio-sorption applications, even though these techniques are extensively used for parameters estimation in other applications [31–34]. A novel approach in which estimation of equilibrium isotherms and kinetic models by inverse modeling approach using different evolution optimization is implemented to estimate the best optimal parameter set based on non-linear error functions in the framework of hybrid evolutionary optimization technique. This approach not only guarantee the global minima in the error distribution, but also retains the non-linearity of the system. Finally, a detailed analysis is presented to compare the methodology and efficacy of traditional linear transformation methods, versions of non-linear least square analysis, conventional usage of Microsoft excel based solver and hybrid evolutionary differential evolution optimization technique. The performance of all these various methods are examined and compared in terms of non-linear error functions which are statistically significant and measure the error distribution.

2. Materials and methodology

2.1. Experimental procedure

Initially activated carbon was produced from coconut shells and they are chemically activated by dissolving in pure acetic acid in a batch container. To improve the activation process, this mixture is continuously stirred for a duration of two hours at a temperature of 50 °C. After that, the acid adsorbed coconut shells slurry is placed in a vacuum dryer for about one day which is maintained at 100 °C to remove the moisture from the coconut shells. Later this dried acid impregnated coconut shells are washed with distilled water to remove any excessive activated agent. After the chemical activation was completed, the physical activation (carbonization) was applied to acid impregnated coconut shells. During this carbonization process, a batch samples of 200 g were heated in a stainless steel tubular furnace under a flow of carbon dioxide of 100 ml/min steadily with a raise of temperature 10 °C/min until the temperature of the furnace reaches 800 °C. Once the furnace temperature reaches 800 °C, furnace is maintained at this temperature for another two hours for attaining equilibrium state. These samples were taken out from the furnace and cooled for about an hour. These carbonized acid impregnated coconut shells were initially rinsed with 0.5 N HCl at 85 °C and later rinsed with distilled water to remove residual organic matter and maintain the mixture at pH at 6. Finally this mixture was subjected to drying at 110 °C and the activated carbon was produced for further experimental studies on adsorption of phenol removal from effluent water.

Batch adsorption experiments were carried out using the above produced activated carbon samples along with 100 ml of aqueous solution (effluent) at different phenol concentrations. These experiments were performed in a thermal shaker at room temperature over a period of two hours at 120 rpm using 250 ml Erlenmeyer flasks containing 100 ml samples at different phenol concentrations. Continuous stirring of these samples facilitates higher interfacial contact area thus improving the mass transfer rates. After an adsorption process, the concentration of phenol in each sample after regular time intervals was analyzed using spectrophotometer (Shimadsu TU-1901, UV–vis). The phenol concentration retained in the adsorbent phase is determined from the difference between the initial and equilibrium concentrations and it is mathematically expressed as

$$q_e = (C_i - C_e) * \dot{\nu} \quad (1)$$

where C_i and C_e are the initial and equilibrium concentrations (mg/l) of phenol solution respectively; $\dot{\nu}$ is the solution to adsorbent mass ratio (l/g). For fitting the adsorption data to various equilibrium isotherm models for statistical comparison to identify the best suitable isotherm model to describe the phenol adsorption onto coconut shell based activated carbon, the approach uses the initial concentration, C_i as the true independent variable which is generally referred as predictor variable. The phenol concentration retained in the adsorbent phase, q_e is treated as responsible variable. Each experiment was repeated for three times for repeatability and the average of these results are presented and analyzed.

2.2. Adsorption equilibrium isotherms

To evaluate and optimize the design of an adsorption equilibrium isotherm model to remove phenol from effluent waste