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Application of central composite design for simultaneous removal of methylene blue and Pb^{2+} ions by walnut wood activated carbon

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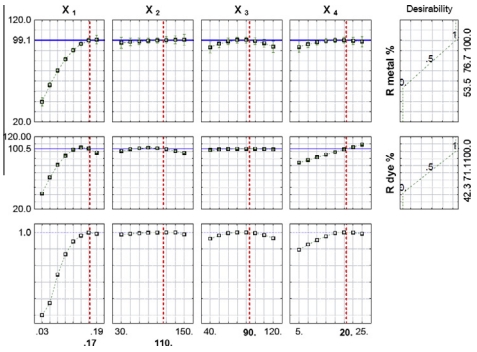
HIGHLIGHTS

- Activated carbon was prepared from walnut wood.
- The significant variables were optimized by using a CCD combined with DF.
- The equilibrium and kinetic studies were investigated for the adsorption process.

GRAPHICAL ABSTRACT



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ABSTRACT

Activated carbon was prepared from walnut wood which was locally available, non-toxic, abundant and cheap. This new adsorbent was characterized using BET, FTIR and SEM. Point of zero charge (pH_{pzc}) and oxygen containing functional groups were also determined. The prepared adsorbent was applied for simultaneous removal of Pb^{2+} ions and methylene blue (MB) dye from aqueous solution. The prominent effect and interaction of variables such as amount of adsorbent, contact time, concentration of MB and Pb^{2+} ions were optimized by central composite design. The equilibrium data obtained at optimum condition were fitted to conventional isotherm models and found that Langmuir model was the best fitted isotherm. Kinetic data were fitted using various models. It was revealed that the adsorption rate follows pseudo-second order kinetic model and intraparticle diffusion model.

Introduction

Heavy metal ions enter to various aqueous ecosystems. They may be toxic or poisonous for human health and animals even at low concentrations. On the other hand, their content strongly can be affected by the presence of other compounds, especially dyes. Another category of hazardous compounds and materials are dyes that may generate serious problems and hazards for human and other organism that attributed to their high biotoxicity, mutagenic and carcinogenic effects [1–4]. These associated hazards and problems make it necessity to design and develop new waste water treatment approach to reduce their level below threshold limit. One of the most well known and famous method for dye removal is adsorption that is superior to other conventional technique including biological treatment, adsorption, coagulation/flocculation,

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chemical oxidation, membrane separation and ion exchange [5,6]. Diverse materials such as activated carbon, zeolite, clay, polymer, and nanomaterials have been extensively applied for pollutants removal [7–9].

Methylene blue (MB) commonly applied as coloring dye, while it is also used for dying cotton and silk [10]. The harmful impacts of such dye on water make an urgent task to remove them from waste streams before discharge to water resources. Lead and its compound, especially as Pb^{2+} ions are known as important pollutants even at low concentrations by affecting central nervous system, kidneys, gastrointestinal system [11]. Therefore, the removal of these pollutants as sole component or their combination from waste water is a challenging requirement and needs more attention.

Previous studies have focused on single component removal, while limited reports for simultaneous adsorption of metal ions and dyes on natural zeolite [12–16] and activated carbon [17,18] are available. In this paper, the simultaneous adsorption of MB and Pb^{2+} ions was studied. Kinetics and equilibrium data were also studied and compared.

Activated carbons (amorphous solids with large internal surface areas and pore volumes) simply can be prepared from natural resources such as coal [19], wood [20], coconut shell [21], tea waste [22] and rice husk [23]. This approach is green and environmental friendly due to the conversion of unwanted, worthless agricultural waste to useful, low cost, cheep and high surface area adsorbent which are able to remove organic chemicals and metals of environmental and/or economic concern from various resources following their carbonization and activation [24,25].

Walnut tree (agricultural tree) grows rapidly in different regions, while its wood can be applied in carpentry work and fuel. Storm, natural and/or agricultural activities such as pruning lead to cutting and separation of the branches and trunks of many walnut trees. The high abundance of waste wood (walnut tree) makes an economic task to burn and put this tree waste into a sealed container that causes its simple conversion to carbon source. This behavior reveals that the present homemade walnut carbon (HWC) is very cost effective and non-toxic material with least energy consumption. In this work, the production was activated by concentrated nitric acid was.

In addition to significant decrease in the number of experimental runs by central composite design under response surface methodology (RSM), the main and interaction effects of variables including contact time, adsorbent dosage, initial MB and Pb^{2+} ions concentration simply were investigated and optimum value of each variable was specified.

Experimental

Instruments and reagents

Chemicals including NaOH, HCl, $NaNO_3$, $Pb(NO_3)\cdot 2H_2O$, Na_2CO_3 and $NaHCO_3$ with the highest purity available were purchased from Merck (Darmstadt, Germany). MB dye (Sigma–Aldrich) has following information (a) color index number: 52.015, (b) molecular weight: 319.86 g/mol, (c) empirical formula: $C_{16}H_{18}N_3SCl$ and (d) λ_{max}: 664 nm. Analyte solutions were prepared by dissolving their appropriate amount in double distilled water, while the pH was adjusted using pH/Ion meter model-686. The absorbance spectra for MB was recorded in the range of 300–750 nm using Jasco UV–Visible spectrophotometer model V-530 with a fixed slit width of 2 nm and scan speed of 1000 nm/min. Pb^{2+} ions was determined by atomic absorption spectrophotometer Varian model AA 220 at λ = 217 nm. Fourier transform infrared spectroscopy (FTIR in the range of 400–4000 cm^{-1}) of the adsorbent was recorded using FT-IR spectrophotometer (Model: FT-IR JASCO 460 Plus). Spectra obtained were analyzed.

The STATISTICA, a statistical package software version 7.0 (Stat Soft Inc., Tulsa, USA) was used for experimental design analysis and their subsequent regression analysis. Statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA). The quality of the polynomial model equation was judged statistically by the coefficient of determination R^2 and its statistical significance was determined by *F*-test. *P*-values less than 0.05 were considered to be statistically significant.

Multi-component adsorption of Pb^{2+} ions and MB on natural activated carbon

Binary system of MB–Pb^{2+} ions was used in the adsorption experiments. All experiments were carried out using different amounts of adsorbent in 50 mL beakers on a magnetic stirrer at 400 rpm to obtain the optimum conditions (pH, contact time and initial dye and Pb^{2+} ions concentration), while all experiments conducted at room temperature. The effect of pH on the simultaneous removal of adsorbates was investigated by conducting similar experiments as follow: 50 mL of solution of 50 mg L^{-1} of Pb^{2+} ion and 15 mg L^{-1} of MB was thoroughly mixed with 0.05 and 0.10 g of adsorbent at pH values of 2–6 until the achievement of equilibrium. After the optimization of pH, a central composite design (CCD) was applied for the investigation of the influence of variables on the adsorption and their interaction. Adsorption capacities for Pb^{2+} ions and dye (q_i, mg g^{-1}) on adsorbent were calculated by a mass balance:

$$q_i = \frac{(C_{0,i} - C_{f,i})V}{m} \quad (1)$$

where $C_{0,i}$ and $C_{f,i}$ are respectively the initial and final concentration (mg L^{-1}) of pollutant *i* (i.e., dye or Pb^{2+} ions) in the binary solution, *V* is the solution volume (L) and *m* indicates the adsorbent amount (g).

Preparation of activated carbon

Dry branches of walnut tree were grinded and cut into small pieces (lower than one centimeter). They were washed with distilled water and triton X-100 to remove impurities and subsequently were dried in outdoors for 72 h. Then, 500 g of dried sample was placed into a container with a small hole (about 5 mm) and was directly heated in flame for about 2 h. The obtained coal was washed again with distilled water and held at 105 °C for 24 h for drying it that lead to the conversion of raw material to carbon.

This carbon was milled and sieved in the mesh range of 50–60 and activated thoroughly by the addition of nitric acid solution as follows: 10 g of carbon was mixed with 150 mL of 5 mol L^{-1} nitric acid and the mixture was refluxed for 6 h at 105 °C [26–28]. This HNO_3-activated carbon was filtered and washed with deionized water at 50 °C until approaching neutral pH and finally was dried at 105 °C for 24 h. This adsorbent was used for the simultaneous adsorption of MB and Pb^{2+} ions. The pH corresponding to the point of zero charge of the adsorbent was determined by the pH drift method reported elsewhere [29]. Determination of oxygen containing functional groups was performed by the Boehm titration method [30]. In this method, 1.0 g of the activated carbon (AC) were kept in contact with 15 mL solution of $NaHCO_3$ (0.1 M), Na_2CO_3 (0.05 M) and NaOH (0.1 M) to identify its acidic groups and 0.1 M HCl for basic groups/sites (in separate experiments) respectively, at room temperature for more than 2 days. Subsequently, the aqueous solutions were back titrated with HCl (0.1 M) for