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Research paper

The removal of Cu^{2+}, Ni^{2+} and Methylene Blue (MB) from aqueous solution using Luffa Actangula Carbon: Kinetics, thermodynamic and isotherm and response methodology

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ABSTRACT

The removal of Cu^{2+}, Ni^{2+} and Methylene blue onto agricultural waste Luffa Actangula Carbon (LAC) was carried out. The surface morphology and functional group study for LAC was done by FTIR, SEM and EDAX technique. The data was best fitted by Pseudo 2nd order kinetic model. The equilibrium was attained in 120 min at pH 6 for Cu^{2+} with maximum adsorption capacity of 12.47 mg g^{-1} and pH 6 for Ni^{2+} with maximum adsorption capacity of 6.2 mg g^{-1} at 30 °C. The equilibrium for MB was attained in 120 min at 30 °C at pH 7 with maximum adsorption capacity of 10.32 mg g^{-1}. The methodology of Response Surface was used to study the process variables like contact time and pH and their interaction with removal efficiency as response. The data was nonlinearly fitted by Freundlich isotherm model for Cu^{2+} and Ni^{2+} ion with Regression coefficient of Cu^{2+} (0.965) and Ni^{2+} (0.950) whereas in case of MB it was best fitted nonlinearly by Langmuir Isotherm with higher regression coefficient(0.954) and smaller χ^2 value. The LAC shows higher adsorption capacity in the order of Cu^{2+} (12.47 mg g^{-1}) > MB (10.32 mg g^{-1}) > Ni^{2+} (6.2 mg g^{-1}). The Langmuir monolayer adsorption capacity is in the order of Cu^{2+} (33.16 mg g^{-1}) > MB (24.84 mg g^{-1}) > Ni^{2+} (23.84 mg g^{-1}). The data was also predicted by statistical error analysis tool like HYBRID, ARE. The Thermodynamic parameters ΔG°, ΔH°, ΔS° have been decided and it was found that the process was feasible, spontaneous and exothermic in nature.

1. Introduction

The heavy metals and dissolved organic compound are the pollutants that are highly toxic to the living system. Cu (II), Ni (II) ions are the toxic pollutants effecting the flora and fauna of the system. The most used heavy metal ion by industries and municipal wastewater is Copper that causes health hazard problems such as affecting the brain, heart, kidney and Liver. The permissible limit of copper given by EPA is 2.0 mg L^{-1}. Excessive level of nickel in water causes adverse effect on health such as causing cancer, skin allergy and lung fibrosis. One of the most important health problem caused by nickel and its compounds are allergic dermatitis (nickel itch) and increases incidence of cancers. The permissible limit for nickel given by EPA is 0.015 mg L^{-1} in drinking water (Hannachi et al., 2010). Methylene Blue (MB) as one of the dye effluents is considered to be highly toxic affecting the aquatic species through symbiotic process by disturbing natural equilibrium by reducing photosynthetic activity and production due to colorization of water (Rajendaran et al., 2016). The removal of heavy metal and dyes can be carried out by various physiochemical methods like: ion exchange process, metal extraction, chemical precipitation and membrane separation (Barakat, 2011). These methods have several disadvantages like high operation cost, imperfect removal of heavy metals ions, and lack of selectivity and production of waste during their production. The metal ion removal methods can remove as low as 50 mg L^{-1}. Development of efficient and low-cost separation processes is therefore the most importance (Gupta et al., 2012b) Alternatively related technique used for the removal of heavy metals and dyes are Adsorption process.

The most efficient and economic technique adsorption, is used worldwide for removal of heavy metals and dyes. Adsorption is found to be operative at all temperature,pH and recovery of metal and minimum generation of sludge (Saleh and Gupta, 2014). The scientist are trying to evaluate the adsorption capacities of heavy metals and dyes by low cost adsorbents which maybe conventional or non-conventional (Gupta et al., 2009; Gupta et al., 2011a, 2011b).

The most widely used adsorbent for the removal of pollutants has been activated carbon. But due to its high cost and less regeneration, its applications are restricted. Whereas, the use of agricultural waste in comparison to activated carbonas a low-cost alternative adsorbent has received considerable attention (Malkoc and Nahoglu, 2005). Various agricultural waste like Cashew nut shell (Kumar et al., 2011) [9], tea

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factory waste (Malkoc and Nahoglu, 2005), dye groundnut shell (Shukla and Pai, 2005), tobacco dust (Qi and Aldrich, 2008), Banana Peels (Hossain et al., 2012), almond shells (Duran et al., 2011), CNT/Magnesium oxide composite (Saleh and Gupta, 2014), Aluminium Coated Carbon Nanotubes (Gupta et al., 2011a, 2011b), Multiwalled carbon nanotubes and Titanium Oxide (Gupta et al., 2015),waste rubber tyre derived carbon (Saleh and Gupta, 2014), Carbon Nano tubes (Gupta et al., 2013), orange peel and Fe_2O_3 nanoparticles (Gupta and Nayak, 2012), bottom ash (Mittal et al., 2010a, 2010b), Rice Husk (Ahmaruzzaman and Gupta, 2011), ZnO/CdO nanocomposite (Saravanan et al., 2015), Alumina/polyamide nanoparticle (Saleh and Gupta, 2012b), ZnO/Ag nanocomposite (Saravanan et al., 2013b), CeO_2/V_2O_5 composite (Saravanan et al., 2013b), PANI/ZnO (Saravanan et al., 2016), nanorod (Saravanan et al., 2015a), Porous Carbon and Fullerene (Gupta and Saleh, 2013), ZnO/ϒ-Mn_2O_3 (Saravanan et al., 2014), Groundnut-Guar Gum Composite (Ahmad and Haseeb, 2015) etc., are the adsorbents used for the removal of Cu(II), Ni(II) and MB.

The adsorbent used i.e. Luffa Actangula or commonly known as ridged gourd or Turai is a cheap vegetable easily available in abundance in northern India. This vegetable is rich in carbohydrate, potassium, fat. The peels of Luffa Actangula contain oleanoic acids, cartenoids and phenolic compounds (Kao et al., 2012) and functional groups like –OH and –COOH. The –OH and –COOH groups act as potential site for the adsorption of pollutants. These groups act as potential site for the adsorption of pollutants. The Luffa Actangula in its carbon form is used for the removal of Cu (II), Ni (II) and Methylene blue. The Response Surface Methodology was used to study the optimum variables like contact time and pH with removal efficiency as response. In order to study the adsorption mechanism and to judge the effectiveness of adsorbent, kinetics and isotherm parameters are discussed in details. The characterization was done to study the elemental, morphological and functional groups present in the adsorbent.

2. Material and methods

2.1. Chemicals and instruments

The stock solution of 1000 mg L^{-1} of Cu (II) and Ni (II) were prepared in double distilled water using the salts of copper nitrate, nickel nitrate. A stock solution of Methylene blue dye solution was prepared (500 mg L^{-1}) by dissolving 0.5 g of dye powder in double distilled water to obtain dye concentration. The chemicals purchased were of analytical grade (Gupta et al., 2012a).

The adsorbent surface was characterized by scanning electron microscopy (JSM −6510LV). The presence of functional groups in the adsorbent was characterized by FTIR spectroscopy model (Perkin Elmer, USA, model spectrum-BX, range 4000–400 cm^{-1}). The presence of element in the group can be characterized by the EDX model (JSM-6510LV). The resultant concentration was determined by atomic adsorption spectroscopy (AAS) model (GBC-902, Australia) for heavy metals. The Methylene blue solution concentration unloaded and loaded before was determined by using a double beam UV–Visible spectrophotometer (PG Instruments, UK). The pH was measured by using pH meter (Elico L1120, India).

2.2. Preparation of adsorbent

The adsorbent was collected from the local market of Allahabad city. The Luffa Actangula peels were washed with double distilled water before use to remove dirt and then dried at 80 °C. The dried material was then placed in silica crucible in the muffle furnace at 750 °C. The resultant carbon was then cooled, grinded and sieved to 50–100 mesh size (Ahmad and Haseeb, 2017). The obtained carbon was then further washed with distilled water and then dried in an oven and used as such for further adsorption studies.

2.3. Point of zero charge

The solid addition method was used to determine the zero surface charge characteristics (pHzpc) of Luffa Actangula carbon (LAC) using 0.1 M KCl (Haseeb and Ahmed, 2017). The pH of the 25 mL solution of KCl in a conical flask was adjusted between 2 and 10 by using 0.5 M HCl and NaOH. After the measurement of pH_i (initial pH), 0.1 g of adsorbent was added to a series of solution of different pH_i and allowed to equilibrate for 24 h. The final pH of the solutions were then observed and noted. The difference between the initial pH (pH_i) and the final pH (pH_f) (ΔpH = pHi − pHf) values were then plotted against pH_i. The point of intersection of the resulting curve with the abscissa, at which ΔpH = 0, gave the pHzpc value.

2.4. Metal selection test

The absorptive nature of LAC was studied using Cu^{2+}, Ni^{2+}, Pb^{2+}, Methylene Blue (MB),2,4-D.dichorophenols. It follows in the order as $Cu^{2+} >> MB >> Ni^{2+} >> Pb^{2+} >>$ 2,4-D dichlorophenol.

2.4.1. Batch adsorption studies

The adsorption of Cu^{2+}, Ni^{2+} and MB was carried in batch mode with 25 mL solution of desired concentration (10–100 mg L^{-1}) and 0.1 g adsorbent in 100 mL conical flask for 24 h after equilibration pollutant samples were filtered and analyzed by AAS. The pH was studied in the range of pH 2–8 and adjusted by using 0.5 M HCl and NaOH. The experiment was performed at pH 7.0 for MB and pH 6.0 for Cu^{2+} and Ni^{2+} ion. All the experiments were reported in triplicates. MB concentration was determined by UUV–Visble spectrophotometer with maximum absorbance at 664 nm.

The removal percentage (%) and adsorption capacity (q_e, mg g^{-1}) of MB, Cu^{2+} and Ni^{2+} were calculated using the following relationship:

$$\% = \frac{(C_o - C_e)}{C_o}100 \tag{1}$$

$$q_e = \frac{(C_o - C_e)V}{W} \tag{2}$$

Where, C_e is the concentration of adsorbate at equilibrium (mg L^{-1}), V is the volume of the solution (L), q_e is the adsorption capacity at equilibrium, C_o is the initial concentration of the adsorbate (mg L^{-1}) and W is the mass of the adsorbent.

The desorption study for Cu^{2+}, Ni^{2+} and MB was carried out using 0.1 g LAC loaded with 0.1 M HCl, 0.1 M $H_2C_2O_4$ and 0.1 M HNO_3 for 2 h. The supernatant was filtered and then analyzed.

2.5. Error analysis

Various Error function are used to evaluate the models by using the EXCEL FUNCTION and Origin Pro8. They are RMSE (Residual Mean Square Error), χ^2 (Chi-sqr-test) and HYBRID test. There equations are as follows:

$$HYBRID = \frac{100}{N-P}\sum_{i=1}^{n}\left[\frac{q_{e\,\mathrm{mod}\,el} - q_{ecal}}{q_{ecal}}\right] \tag{3}$$

$$ARE = \frac{100}{P}\sum_{i=1}^{n}\left[\frac{(q_{emeas} - q_{ecal})}{q_{emeas}}\right] \tag{4}$$

3. Results and discussion

3.1. Characterization

The SEM image reveals the adsorbent is quite porous in nature. After adsorption, all the pores sites are occupied by metal ions are shown in Fig. 1(a,b). The Weight (%) element present in LAC was