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Low-cost sorbent for the removal of aniline and methyl orange from liquid-phase: Aloe Vera leaves wastes

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ABSTRACT

In this study, Aloe Vera leaves wastes-based sulfuric acid modified activated carbon (AV-SAC) was applied for the sorption of aniline as a health-toxic substance and methyl orange (MO) as a anionic dye from aqueous phase. The batch sorption system was used to assess the effect of different parameters including contact time, pH, adsorbent dosage, and adsorbate contents on the adsorption. The equilibrium was obtained at contact time of 60 min for both the adsorbates. The pH of 3 had a significant influence on the uptake capacities of aniline and MO from aqueous media. Fitting the experimental data to different kinetics and isotherms models indicated that the experimental data were well fitted by the pseudo-second-order kinetic and Freundlich isotherm models, respectively. The maximum monolayer adsorption capacities were acquired 185.18 and 196.07 mg/g for aniline and MO, respectively. Due to its low-cost and high uptake capacity, AV-SAC can be considered as one of the effective sorbents for wastewater treatment contains of aniline and MO.

1. Introduction

Water pollution due to irregular discharge of many organic and inorganic pollutants by various industries wastewater is one of the most important envitonmental concerns in the current century, especially in the developing countries [1,2]. Aniline is one of the most important of these contaminants that widely found in wastewater from the pesticides, dyestuffs, paints, rubbers, pharmaceutical, and plastics industries [3–5]. It is very toxic and resistant to biodegradation compounds and also is harmful for human health [5–7]. U.S. Environmental Protection Agency (USEPA) has listed aniline as one of the priority contaminant [5]. Methyl orange (MO) or acid orange 52 is a water-soluble anionic dye that is widely used in textile, paper manufacturing, printing, food, and pharmaceutical industries [8]. It is regarded as an allergy-substance after contacting by skin, which causes shin eczema. Therefore, because of its toxic structure, its removal from aqueous media is very important [9]. Many treatment techniques including photodecomposition, ion-exchange, electrolysis, membrane processes, photocatalyst, oxidation, biodegradation, and adsorption have been performed for the treatment of these compounds from polluted waters. Among these approaches, adsorption is an effective method due to its high efficiency, simplicity, and flexibility [10–12]. In general, adsorption is known as one of the best techniques for the separation and remove of various organic and inorganic impurities from wastewater [13,14]. This method do not generate harmful by-products and it is possible to regeneration of both the adsorbent and adsorbate [15,16]. One challenge faced by sorption technologies is the finding new adsorbents that effectively remove the organo-pollutants [3,17]. Due to high sorption capacity and high surface area, adsorption on the surface of activated carbon is generally used for the removal of toxic contaminants, but it is high-cost and difficult to regeneration [18,19]. Thus, several researches have been conducted for the production an activated carbon from available local agricultural wastes which are cheaper and have eco-friendly properties [20]. In addition to activated carbon, application of some non-conventional sorbents like lignin [3], graphitic carbon nitride [10], pine sawdust [21], Cr-bentonite [22], grafted acrylic acid [23], spherical carbon [24], organo-clay [25], Fe_3O_4-activated carbon [26], Moroccan clays [27], LDHs [28], tree

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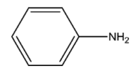
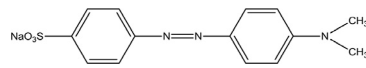
Table 1
General characteristics and chemical structures of aniline and methyl orange.

Generic name	Scientific name	Chemical formula	Chemical structure	M_W (g/mol)	λ_{max} (nm)
Aniline	Aminobenzene	$C_6H_5NH_2$		93.13	260
Methyl orange	Acid orange 52	$C_{14}H_{14}N_3NaO_3S$		327.23	415

bark powder [29], metal-organic frameworks [9], chitosan [12], bottom ash [30], surfactant modified montmorillonite [31], *etc.* have been evaluated for the removal of aniline and MO from aqueous solutions. Aloe Vera is a tropical plant that widely grows in the warm areas such as United State, India, Australia, Africa, Mexico, South America, and Iran. The Aloe Vera leaves wastes are by-products of the agricultural and pharmaceutical industries that are applied to produce latex and drug substances [2]. In this work, activated carbon prepared from the Aloe Vera leaves wastes was modified by sulfuric acid and then used as a low-cost adsorbent for the sorption of aniline and MO from synthesized wastewater. The influences of various factors including contact time, pH, sorbent dosage and initial concentration of pollutants were evaluated and optimized on the adsorption.

2. Materials and methods

2.1. Materials

Aloe Vera leaves wastes were collected from suburban farms of Dezful and Ahvaz (cities of Khuzestan Province, Iran). The chemical substances including aniline (with purity greater than 99.5%), methyl orange, sulfuric acid and sodium hydroxide were purchased from Merck Co (Germany). Table 1 shows the characteristics and chemical structures of aniline and MO. The pH of solutions was adjusted with diluted and concentrated sulfuric acid and sodium hydroxide solutions using a digital pH-meter (50-pp-sartorious model). The stock solutions of aniline and MO (1000 mg/l) were prepared in distilled water and the working concentrations were also obtained with dilution of the stock solutions. The suspensions containing adsorbent and adsorbate were mixed using an orbital shaker (Behdad-Rotomix model, Iran) at 200 rpm.

2.2. Preparation of adsorbent

After separation the gel of Aloe Vera leaves, the remaining waste was carefully washed with deionized water to remove impurities and dried in an electrical oven at 150 °C for 24 h. Then, the dried leaves waste was crushed by a laboratory mill to obtain the particle size in the range of 300–600 µm. After that, particles were carbonized in a furnace at 550 °C for 20 min. The carbonized sample was transferred into 500 ml sulfuric acid solution (0.1 N) for 12 h. The suspension was filtered and the modified samples were washed several times with deionized water. Finally, the modified activated carbon was dried in an electrical oven at 105 °C for 12 h. The modified activated carbon-based Aloe Vera leaves waste (AV-SAC) was crushed and then sieved to have a uniform particle size of 40-mesh for the adsorption experiments.

2.3. Characterizations and analysis

The surface morphology of original and modified activated carbon, before and after the sorption process, was performed and characterized under a vacuum running by a scanning electron microscope (SEM, Jeol Model Jsm-T330) equipped through energy dispersive X-ray Spectroscopy (EDX) system. Elemental analysis of Aloe Vera leaves wastes-based modified activated carbon (AV-SAC) was performed using a Heraeus Elemental Analyzer (Jobin-Yvon Ultima ICP-AES). FTIR spectra study of the original and modified activated carbon were also recorded by a FTIR spectrophotometer (JASCO, FT/IR-6300 Japan) with Diffuse Reflectance Technique (DRIFT) at resolution of 1 cm^{-1} in the region of 400–4000 cm^{-1}. The concentrations of aniline and MO in the solution phases were determined by an UV–vis spectrophotometer (PG Instrument Limited Model, UK) at maximum wavelengths of 260 nm and 415 nm, respectively.

2.4. Determination of pHzpc

The pH at the zero point charge (pHzpc) for the Aloe Vera leaves waste-based activated carbon (AV-AC) and the sulfuric acid-modified activated carbon (AV-SAC) was determined by preparation 50 ml of 0.01 M NaCl solution into a series of 100 ml Erlenmeyer flasks. The initial pH values of NaCl solution were adjusted, as initial pH (pH_i), between 2 and 12 by adding H_2SO_4 (0.1 M) and NaOH (0.1 M) solutions. Then, sufficient amounts of adsorbent were poured into each flask and the suspensions were mixed by a mechanical shaker for 24 h at 200 rpm. After this period, the solutions pH was measured as finally pH (pH_f). The pHzpc was determined by plotting difference between pH_f and pH_i values ($pHzpc = pH_f - pH_i$) versus pH_i. The resulting curve with abscissa gives the pHzpc, the point at where pH is equal to zero.

2.5. Batch adsorption study

The batch sorption system was used to identify the influence of different parameters including contact time (0–90 min), pH (3–11), adsorbent dosage (1–5 g/l), and initial content of pollutants (20–100 mg/l) on the sorption of aniline and MO from synthesized wastewater. All of the adsorption experiments were carried out at room temperature (25 °C) and agitated in 200 rpm with 100 ml pollutant solution in 250 ml Erlenmeyer flasks. After the process, the mixture of adsorbates and AV-SAC was filtered using fiberglass paper. The sorption experiments were conducted in duplicates and the average amounts were considered. The uptake capacities of the sorbent were computed by Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

Where, q_e (mg/g) is the equilibrium uptake capacity of the adsorbates per gram AV-SAC. The parameters of C_0 and C_e (mg/l) are the initial and equilibrium concentrations of the pollutants, respectively. Also, V (l) is the volume of the solution and m (g) is the adsorbent mass [2].

3. Results and discussion

3.1. Characterization

Fig. 1(a) and (b) show the surface morphology of the sorbent. As it is obvious from Fig. 1(a), the original activated carbon has