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Full Length Research Paper

Decolorization of molasses spent using a novel adsorbent

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Removal of melanoidins pigments from molasses spent wash was investigated using a new adsorbent. Solid adsorbents were fabricated from charcoal fly ash and clay with the proportion of 60 and 40 weight percent. The fabricated adsorbents were packed in a column and the molasses solution was pumped through the column. The impact of various contact times of the pigments and the adsorbents in the column on color removal efficiency was investigated. The experiments were conducted with various contact times of 30, 60, 90 and 240 min. Also, the effect of influent molasses concentration on the performance of the adsorbents was evaluated. The effluent samples were taken from the column at a time interval of 30 min. The obtained results revealed that maximum color removal efficiency of 72% was achieved with molasses concentration of 6 g/l and contact time of 240 min. The obtained results from the fresh and regenerated adsorbents were compared. The achieved data showed that 90% of the capacity of the fresh adsorbent was recovered after the regeneration process. It was also concluded that the regenerated adsorbents were able to remove 65% of the color from the molasses solution. Langmuir and Freundlich isotherm adsorption models were investigated to interpret the experimental data. The obtained data were well represented by Langmuir adsorption model. The constants of the isotherms and the maximum adsorption capacity of the adsorbents were calculated.

Key words: Molasses, adsorption, clay, fly ash, semi batch system.

INTRODUCTION

Nowadays, mankind has two major concerns: depletion of fossil energy resources and deterioration of the environment. These issues remind the need to find alternative fuel resources. The new resources of energy should be renewable, sustainable and count for environmental-friendly fuels. Therefore, in developed countries, there is a growing trend towards the use of biomass based energies. These technologies which use waste or plant residues to produce energy emit less greenhouse gasses than fossil fuels and are cost competitive with conventional energy resources (Escobar et al., 2009; Saxena et al., 2009). Liquid biofuels, especially bioethanol is one of the alternatives with the potential to be replaced with fossil fuels (Demirbas, 2007). Among all these resources, sugar-based residues contain fermentable sugar and are appropriate raw material for ethanol production; while, the other resources require additional pretreatment processes to become fermentable sugar (Hatano et al., 2009). Molasses is one of the byproducts of sugar industries and is the final residue from the obtained sugar crystallization unit. It is used as a carbon source for animal feed and biofertilizer. Besides, molasses is the most common feedstock for fermentation industries such as ethanol and backer's yeast production. It has high content of sugar and locally available in low cost (Adikane et al., 2006; Sirianuntapiboon et al., 2004). The major problem associated with molasses industries is the production of large quantities of brown-colored effluents known as spent wash. It has been reported that molasses spent wash in alcohol fermentation is nearly 15 times of the total amount of alcohol produced (Raghukumar et al., 2004). Disposal of such huge quantity of waste stream without further treatment can cause serious environmental damages. The effluent streams of these industries are extremely colored and have high organic load. The spent wash is characterized as a waste effluent having very high chemical oxygen demand (COD)

(65,000–130,000 mg/L) and biochemical oxygen demand (BOD5) (30,000–96,000 mg/L), acidic pH (4-5), bad smell and dark brown color (Zeng et al., 2009).

The main colored compounds that are developed during sugar processing can be categorized into three major groups of melanins, melanoidins and caramels (Mudoga et al., 2008). Melanoidins are widely dominated as color agent in molasses which may disturb distilleries and fermentation industries. Formation of melanoidins involves in a set of chemical reactions between amino compounds and carbohydrates during Maillard reaction (Chandra et al., 2008). The melanoidins has the empirical formula of $C_{17–18}H_{26–27}O_{10}N$ with a molecular weight in the range of 5000 to 40,000 (Prasad and Srivastava, 2009b). Melanoidins has commercial and nutritional significance as it serves color and flavor of the foods which are the key factors to attract consumers. But, investigations have revealed some harmful effects of melanoidins as mutagenic, carcinogenic and cytotoxic effects (Chandra et al., 2008). Therefore, discharge of the highly colored spent wash which is enriched in melanoidins is a great threat to environment. Disposal of such waste streams into the soil reduces its alkalinity and manganese content. It also inhibits seed evolution and destroys vegetation (Tondee and Sirianuntapiboon, 2008; Tondee et al., 2008). Decolorization of molasses spent wash by physical, chemical and biological methods have been investigated by a number of researchers (Nandy et al., 2002; Adikane et al., 2006; Sohsalam and Sirianuntapiboon, 2008; Prasad and Srivastava, 2009a, b). However, these processes may have their own disadvantages and limitations. Current biological treatment of molasses spent wash is involved in a combined aerobic and anaerobic digestion process. This system successfully reduces the BOD to an acceptable level, but does not deal effectively with the dark color which is associated with COD of the effluents (Ryan et al., 2008). Melanoidins have antioxidant properties which makes them toxic to many microorganisms and recalcitrant to biodegradation (Liang et al., 2009; Sirianuntapiboon et al., 2004). The chemical treatment processes used for decolorization are quite expensive and also the removal efficiency is unstable (Tondee et al., 2008). Adsorption as a physical treatment technique is proved to be effective for wastewater treatment. Although adsorption may be a costly method however, utilizing low cost materials as adsorbent makes the adsorption process to be cost effective (Prasad and Srivastava, 2009a, b). Fly ash and clay have been found as potential and low cost adsorbents to remove color from waste streams. Clay is a natural scavenger of water pollutants and fly ash is a waste material originated in significant amounts in combustion process. Currently, annual worldwide production of coal ash is estimated to be 700 million tons, coal combustion may leave significant amount of fly ash (Prasad and Srivastava, 2009b). Although, part of the fly ash is used in applications such as light concrete preparation, still large quantities are not used and disposed. The large amount of fly ash discarded in coal-fired power stations can be utilized as a potential adsorbent for color removal (Ozturk and Kavak, 2005; Prasad and Srivastava, 2009 a, b). The main aim of this research is to investigate the decolorization of molasses spent wash using a novel adsorbent. The adsorbent was fabricated from a mixture of ash and clay. The performance of the fabricated adsorbent was evaluated in a series of semibatch experiments. The optimum operation parameters to enhance the melanoidines removal efficiency from the molasses spent wash were determined. Various adsorption isotherm models were investigated to interpret the experimental data. The breakthrough curves for the absorption process were obtained.

MATERIALS AND METHODS

Molasses was provided from a local sugar factory, Fariman, Iran. It was dark brown and dense liquor with total reduced sugar concentration of 350 g/L. DNS method was applied to determine the sugar concentration of the molasses before and after the decolorization process (Thomas and Chamberlin, 1980). Fly ash was locally obtained from Tonekabon, Iran. It was supplied from combustion of wood-wastes. Clay was provided from a ceramic industry, Sophal Tabarestan, Neka, Iran. A solid mixture of fly ash and clay with proportions of 60 and 40 weight percent was prepared. The mixture was blended thoroughly and uniformly. In preparation of the granulated adsorbents, 10 ml of distillated water and 10 ml of 8 weight percent polyvinyl alcohol solution (Merck, Germany) were added to 8 g of uniformly mixed solid adsorbent. The paste material was pelletized in a stainless steel cast and compacted in hydraulic press. The air dried pellets were placed in furnace (Nobertherm, Germany), heated to 600°C for 2 h. The porous and calcined solid pellets were used in semi-batch experiments.

Semi-batch experiments

To evaluate the performance of the adsorbents and to remove melanoidins from the molasses solution, the porous and calcined cylindrical shape pellets were packed in a Plexiglas column with internal diameter of 7 cm and height of 100 cm. Molasses solution was pumped through the column using a peristaltic pump (B series peristaltic pump, Italy) at the selected concentration with flow rate of 10 ml/min. To investigate the effect of contact time on color removal efficiency, various retention times of 30, 60, 90 and 240 min were selected. In order to create such contact times between the colored solution and the adsorbents, the effluent streams of the adsorption column was recycled. Also, to evaluate the performance of the adsorbents with various influent dye

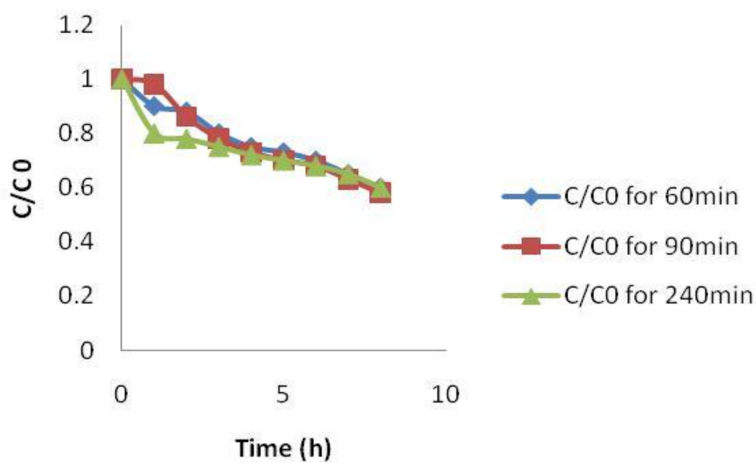

Figure 1. Effect of various contact times on breakthrough curve development for fresh adsorbent.

concentrations, molasses concentration was varied in the range of 6 to 12 $g.L^{-1}$ with an increment of 2 g/L. The effluent samples were collected with respect to time at a time interval of 30 min. Standard calibration curve was prepared with defined dye concentration as explained earlier. The experimental data were collected. Breakthrough curves were developed and the obtained data fitted with the adsorption models.

Regeneration of the adsorbents

In order to regenerate the saturated adsorbents, the used adsorbents were heat treated and baked in the furnace at 600°C for 1 h. Similar experiments for semi-batch experiments were conducted with the regenerated adsorbents. Breakthrough curves were obtained and the dye removal efficiency of the fresh and regenerated adsorbents was compared.

RESULTS AND DISCUSSION

Breakthrough curve development

Effect of contact time on dye removal efficiency

To investigate the effect of contact time of the molasses solution with the adsorbent in the column on dye removal efficiency, various retention times of 30, 60, 90 and 240 min were selected. Figure 1 shows the effect of contact times on breakthrough curves development. It was observed that the dye removal efficiency increased as the contact time was gradually increased. The value of C/C0 decreased from 0.63 to 0.46, while the contact time was increased from 30 to 240 min. It was concluded that in a long contact time, decolonization process was enhanced. This is due to the fact that during the adsorption of pigments from the molasses solution, dye molecules reach to the surface of the adsorbents. Then, they penetrate into the porous structure of the adsorbent. Therefore, dye removal efficiency was enhanced as the contact time was prolonged.

Figure 2 depicts similar results for the regenerated adsorbent. When the dye molecules occupy and covered all the vacant spaces inside the adsorbent, the adsorbent capacity was saturated by the adsorbates. The saturated adsorbent is not able to remove any dye molecules from the colored streams and it should be regenerated or replaced with the fresh adsorbents. In the conducted experiments with the regenerated adsorbents, it was observed that they were able to remove more than 50% of the pigments in a contact time of 240 min. Considering that the applied regeneration process was a simple method, it was able to enhance the economical feasibility of the adsorption process. As the saturated adsorbents heated to 600°C, the melanoidins which occupied the surface and porous structure of the adsorbent, burn in the furnace. This process creates some vacancies inside the adsorbents and makes them to be suitable for further adsorptions of the pigments from molasses solutions.

Effect of influent molasses concentration on dye removal efficiency

To evaluate the effect of molasses concentration on dye removal efficiency, various concentrations of 6, 8, 10 and 12 g/L were examined. depict the obtained breakthrough curves for fresh and regenerated adsorbents. It was observed that after 7 h of operation, the value of C/Co for fresh adsorbent reaches 0.62 and 0.27 for influent molasses concentration of 12 and 6 g/L, respectively. A similar trend was observed when the regenerated adsorbents were used. The obtained values of C/Co for the regenerated adsorbents were slightly different from the fresh adsorbent; the effectiveness of the regeneration

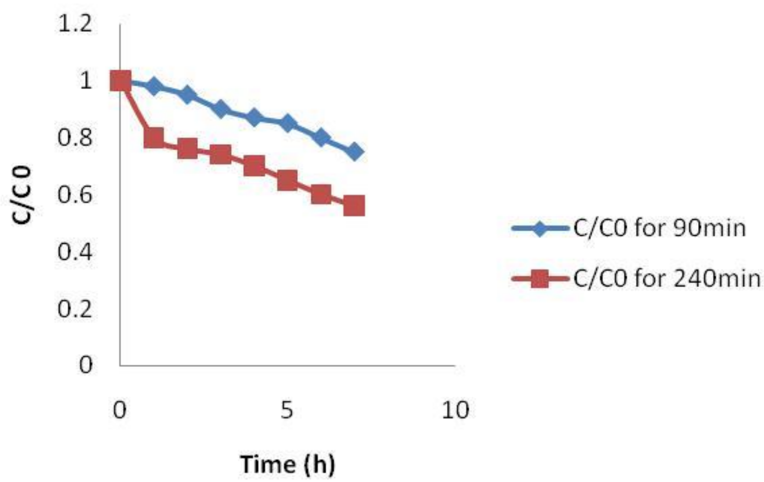

Figure 2. Effect of various contact times on breakthrough curve development for the regenerated adsorbent.

process was confirmed by the presented results. The obtained results demonstrated that the value of C/Co increased as the influent concentration gradually increased. High concentrations of molasses create great concentration gradients which affect the saturation rate.

Conclusion

Removal of melanoidins from molasses spent wash was investigated using a novel fabricated adsorbent. In order to evaluate the performance of the fly ash-clay adsorbent to remove dye from the molasses solution, several semi-batch experiments were performed. Experiments were conducted with various molasses concentration and also different contact times of the dyes and adsorbent. It was observed that more than 72% of the dye was removed for the duration of 7 h in semi-batch operation. Similar experiments were conducted using the regenerated adsorbent. The obtained results revealed that the regenerated adsorbents were able to remove 65% of the color at the same condition. The adsorption capacity of the regenerated adsorbents was retained (90% of the fresh adsorbent), which confirms the effectiveness of the regeneration process. Langmuir and Frundlich adsorption isotherms were implemented to interpret the experimental data. The achieved data were well represented by the Langmuir isotherm for both the fresh and regenerated adsorbents. Maximum adsorption capacity of 20 $mg.g^{-1}$ was obtained with the fresh adsorbent in a contact time of 240 min. It was also concluded that the decolorization process did not influence the sugar concentration of the molasses solution.

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