Aqueous wastewater treatment with aluminum oxide, silica, and alginite

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Abstract The adsorption of different types of dyes and stains over inorganic adsorbent materials such as silica, and aluminum oxide (basic and acidic) as well as over a mineral with an organic component, alginite, has been studied, with the idea of treatment of remnant dye solutions and solution wastes from small and educational laboratories. To recycle the adsorbents, they were heated to 600 °C where the adsorbates are combusted. The inorganic sorbents were compared to activated carbon derived from coffee grounds (ACCG) in their adsorption behavior. Acidic alumina was found to be an effective adsorbent material for azo dyes and anionic dyes/stains, but also for textile dyes, with very high adsorption capacity. The adsorption capacity of alginate and silica was found to be almost the same for cationic dyes, while the adsorption capacity of ACCG is the least.

Keywords: Adsorption, Adsorbent, Alginite, Dyes, Decolorization

1. Introduction

In many parts of the world, disposing of wastewater containing colored compounds such as organic dyes that are persistent in the environment is a serious issue. While not all dyes are harmful per se, some of them can be converted into potentially carcinogenic amines in the environment. Dyes and their contaminants in effluents discharged into water bodies have a negative environmental impact, especially on marine ecosystems. Dyes absorb light and prevent oxygen circulation making it for photosynthetic aquatic plants and algae more difficult to grow (Berradi et al., 2019; Elshaarawy et al., 2017; Khalid et al., 2010; Sinha & Jindal, 2019). Wastewaters can lead a variety of harmful issues, including changes in the water quality (color and odor). Some dyes can cause allergies, dermatitis, skin irritations, tumors, and mutations in humans. Azo dyes are the most popular and widely used synthetic dyes in the clothing, pharmaceutical, food, and cosmetics industries. Some azo dyes have been related to human bladder cancer, splenic sarcoma, hepatocarcinoma, and nuclear defects in animal studies, as well as chromosomal aberrations in mammalian cells. Cationic dyes are widely used in various dyeing processes for wool, cotton, silk, and other materials. Exposure to these dyes can cause harm to the skin (Akhtar et al., 2018). Therefore, there is a need to provide a cost-effective treatment methodology for the removal of organic pollutants in water and wastewater. For the removal of dyes from wastewater, a variety of treatment methods have been used, including filtration, reverse osmosis, and oxidation methods (Derouich et al., 2019). However, these approaches necessitate large amounts of reagent and very high consumption of energy, in addition to producing a large amount of waste (Titchou et al., 2020). Adsorption of dyes on inexpensive and reliable solid supports has been proposed as an easy and cost-effective approach for their removal from wastewater. Many adsorbents, including carbon-containing adsorbents such as biowaste-derived materials (Anastopoulos et al., 2017), have been used in practice. Following waste adsorption, either the carbon-based adsorbents must be considered chemically polluted wastes and disposed of in a landfill or the adsorbed chemical content must be desorbed in a separate process. This, in turn, results in waste. Inorganic-based adsorbents have the advantage that they can be recycled thermally, theoretically. Inorganic materials that offer themselves as adsorbents include silicon and aluminum-based materials such as silica and alumina. Silica gel with a large surface area and a large pore volume is known to be a good adsorbent. Aluminum oxide is another adsorbent with low cost and high decontamination efficiency. Lastly, alginate, a natural mineral, has been reported to be a useful agent for removing soil contaminants as well as serving as a good adsorbent of heavy metals in wastewater. Recently, alginite has been found to be an effective de-emulsifier of oil-water emulsions (Hippmann et al., 2018). Most of these adsorbent materials are cost-effective. Therefore, in this study, we will be investigating different inorganic adsorbents for the removal of organic dyes/stains used normally in experimental and educational laboratories, in addition to two reactive textile dyes.

2. Experimental

2.1. Materials

Silica gel (60-120 mesh, BDH), alumina (aluminum oxide active, acidic, Brockmann grade 1, BDH and alumina oxide active, basic, Brockmann grade 1, BDH), and alginite (Terra Natural Resources GmbH, Germany) were used as purchased. Silica gel (230-400 mesh,

Sigma-Aldrich) had been used for chromatography to separate organic reaction mixtures, especially from Wittig-olefination reactions and Appel-type reactions, and recycled thermally before utilizing it as an adsorbent material (Wahshi et al., 2020). Furthermore, coffee grounds were activated with phosphoric acid and used as an organic sorbent for comparison. Table 1 lists the different organic dyes/stains selected for the adsorption studies. Many of them are commonly used in research and educational laboratories. In addition, there are two Novacron® reactive textile dyes. All the compounds were used without further purification.

Table 1: Properties of the selected dyes/stains

Organic compound	λ_{max}(nm)	Type
Nitrazine yellow	*460*	*Azo dye*
Malachitgrin oxalate	*620*	*Cationic triphenylmethane*
Fast green	*625*	*Cationic*
Methylene blue	*665*	*Cationic*
Novacron yellow	*415*	*Reactive textile*
Novacron cherry red	*530*	*Reactive textile*
Phenol red	*430*	*Anionic*
Neutral red	*520*	*Cationic*
Rose bengal	*550*	*Anionic*
Crystal violet	*590*	*Cationic*
Methyl green	*635*	*Cationic triphenylmethane*
Alizarin red	*510*	*Anionic*
Toluidine blue O	*635*	*Basic cationic*
Chromotrope FB	*510*	*Azo dye*
Bromophenol blue	*590*	*Triphenylmethane*
Methylsulphonazo iii	*580*	*Azo dye*
Methyl violet	*585*	*Triphenylmethane*

2.2 Methods

2.1.1. Activation of the coffee grounds. - The coffee ground was initially dried for 7 h to remove moisture and a certain amount of the dried coffee ground was mixed in a ratio of 1 to 3 with a 10M aq. solution of phosphoric acid. The mixture was then stirred for 24h at rt and was subsequently filtered through a glass filter, washed the filter cake with an adequate amount of distilled water to remove the acid content. The leftover activated carbon was dried at room temperature in an oven at 37°C for 48h.

2.1.2. Stock solutions. - Aq. stock solutions (50 ppm) of each dye was prepared Various concentrations such as 45 ppm, 40 ppm, 30 ppm, 20 ppm, 10 ppm, 8 ppm, 6 ppm, 5 ppm, 4 ppm, 3 ppm,2 ppm, and 1 ppm were made by appropriate dilution of the stock solution.

2.2. Adsorption experiments

Optimum adsorption conditions for each dye on the different adsorbent materials were investigated through a series of batch adsorption experiments, where the effect of the initial dye concentration, contact time, solution pH, and temperature was investigated. 0.5 g of adsorbent was used in all adsorption experiments. The mixture was stirred for a maximum time of 30 minutes with a Labnet magnetic stirrer. At regular time intervals of 5 min., a sample was collected and centrifuged (Beckman model TJ-6, at 2000 rpm, for 5 min). The supernatant was filtered. UV-VIS spectroscopy (Cary 50 spectrophotometer) was used to determine the residual dye concentration at a wavelength range of λ = 200-800 nm, specifically at λ_{max} of the individual dye as listed in Table 1. The dye adsorption capacity (q_e) of all the sorbent materials and the percentage removal of the dyes were determined using the following equations, respectively:

$$Qe = \left(\frac{Co-Ce}{W}\right)V \quad (1)$$

$$\% \text{ Removal} = \frac{Co-Ce}{Co} x\ 100 \quad (2)$$

where Qe is the amount of dye adsorbed at equilibrium (mg/g), c_o and c_e are the initial and final dye concentrations (mg/L), V (L) is the sample volume, and w (g) is the adsorbent mass.

Kinetic and thermodynamic adsorption studies were carried out with a variety of initial dye concentrations, at various temperatures, while keeping all other operating parameters constant, such as pH and sorbent dose.

3. Result and discussion

3.1 Adsorption Studies

Adsorption studies on different adsorbent materials were conducted with the organic water-soluble dyes listed in Table 1 above. The dyes' adsorption behavior was further investigated to determine the adsorption isotherm and kinetic model. The adsorption capacity of dyes on alumina acidic was large for azo dyes and reactive textile dyes and anionic dyes. The adsorption capacity of used silica gel was also large for cationic, anionic, and triphenylmethane dyes, while that of ACCG was smaller, e.g., when compared with that of used silica gel on cationic dyes. The charge on the dye is assumed to be the influencing factor for the adsorption capacity. The adsorption behavior of the individual dye can be related to the type of substituent attached to the chromophore which modifies the adsorption properties. We can relate the good adsorption of sulphonate substituted dyes on acidic alumina by the interaction of the alumina –OH groups with the suphonate group. On the other hand, silica gel, alginite and ACCG adsorbed dyes with an amino group through electrostatic attraction. The % percentage removal of each dye on different adsorbent materials is shown in Table 2 [(-) means: did not adsorb well or not at all].

Table 2: Adsorption capacity of different sorbent material on dyes

% removal of dyes	Alumina basic	Alumina acidic	Used silica gel	Silica gel	Alginite	Activated coffee

			230-400	60-120		
Alizarine red S	81.7 %	99.99 %	(-)	(-)	55.5 %	94.94 %
Bromocresol purple	(-)	100%	(-)	(-)	(-)	(-)
Bromophenol blue	(-)	97.1 %	(-)	(-)	(-)	(-)
Chromotrope TB	(-)	99.97 %	(-)	(-)	(-)	
Crystal violet	(-)	(-)	99.9 4%	(--+)	99.89 %	90.1%
Fast green	(-)	99.18 %	91.2 %	(-)	(-)	(-)
Malachite green oxalate	(-)	(-)	98.9 9%	88.3 6%	98.81 %	66.88 %
Methylene blue	(-)	(-)	99.7 5%	99.0 4%	99.75 %	92.06 %
Methyl green	(-)	(-)	98.9 8%	95.8 2%	98.72 %	73.34 %
Methyl violet	(+--)	(-)	100 %	96.9 2%	100%	99.1%
Methylsulphonazo III	(-)	99.82 %	(-)	(-)	(-)	(-)
Neutral red	(-)	(-)	96.2 %	86%	94.6 %	88.6%
Nitrazene yellow	(-)	98.08 %		(-)	(-)	(-)
Novacron cherry red	(-)	99.72 %	(-)	(-)	(-)	(-)
Novacron yellow	(-)	97.48 %	(-)	(-)	(-)	(-)
Phenol red	(-)	94%	36.2 4%	(-)	(-)	(-)
Rose bengal	(-)	97.98 %	98.2 4%	(-)	(-)	(-)
Toluidine blue	(-)	(-)	100 %	99.5 7%		(-)

Adsorption increases with an increase in adsorption time as shown in Fig 1, 2, and 3.

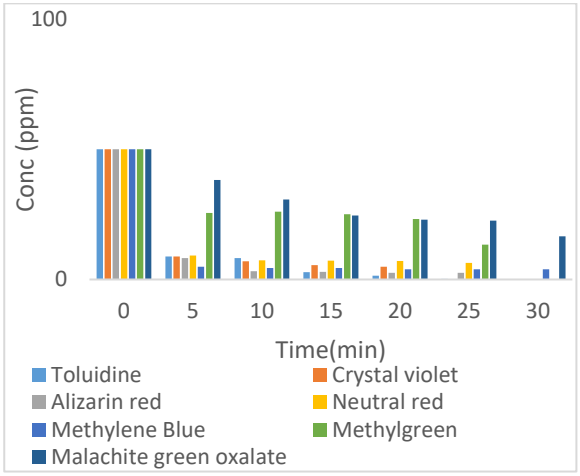

Fig 1: Effect of time on adsorption of different aq. dye solutions (50 mL, 50 ppm) on ACCG (0.5 g).

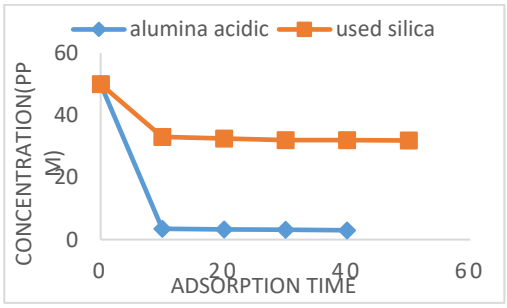

Fig 2: Effect of time on the adsorption of phenol red on acidic alumina and used silica gel (measured at λ = 430 nm).

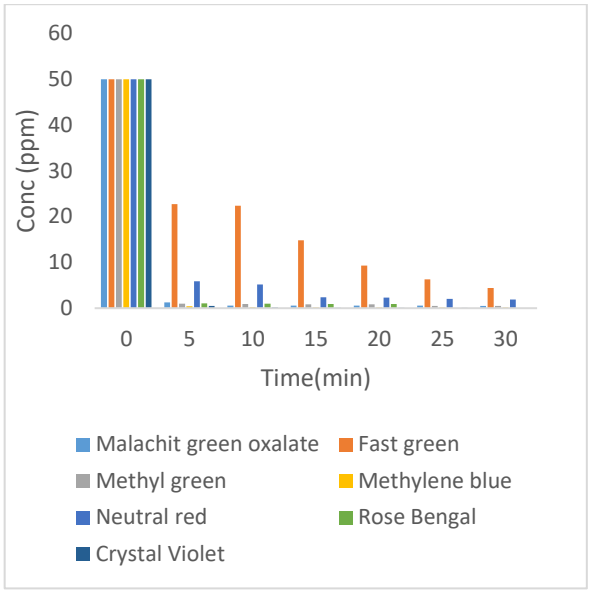

Fig 3: Effect of time on the adsorption of different aq. dye solutions (50 mL, 50 ppm) on used silica (230-400 mesh, 5 g)

3.2 Adsorption isotherm model

The experimental data obtained from the adsorption studies were fitted to Langmuir and Freundlich isotherms using the model equations shown below :

Langmuir model : $\frac{Ce}{Qe} = \frac{1}{bXm} + \frac{Ce}{Xm}$ (3)

Freundlich model: $logQe = logK + \frac{1}{n}\log Ce$ (4)

The correlation coefficient value is then used to validate the result in addition to the value of the equilibrium parameter R_L.

$$R_L = \frac{1}{1+K_L C_0} \quad (5)$$

C_0 is the value of initial adsorbate concentration (mg/L). K_L constant of Langmuir isotherm (mg/g) related to adsorption capacity (the larger the surface area and pore volume, the higher the adsorption capacity). R_L greater than 1 adsorption behavior is not favorable. For 1> R_L> 0, adsorption behavior is favorable, and lastly when $R_L \approx$ 1. the absorption behavior is linear. As an example, the adsorption isotherms of toluidine blue O and methyl violet are shown in Fig 4, with the fitting to different models in Fig. 5 and 6.

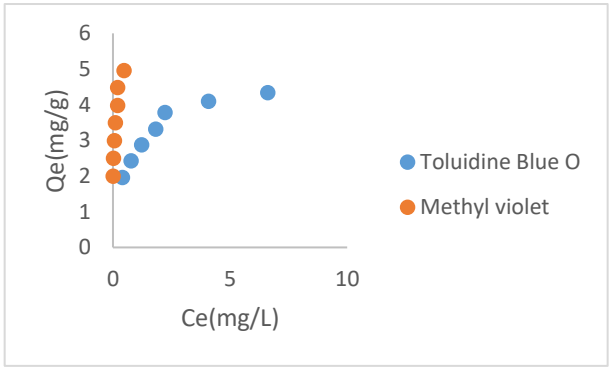

Fig 4: Adsorption Isotherm of toluidine blue O and methyl violet on ACCG

The values of 1/ Qe vs. $1/c_e$ are plotted for the Langmuir plot, while log Qe vs log c_e is plotted for the Freundlich plot, as shown in the figure below

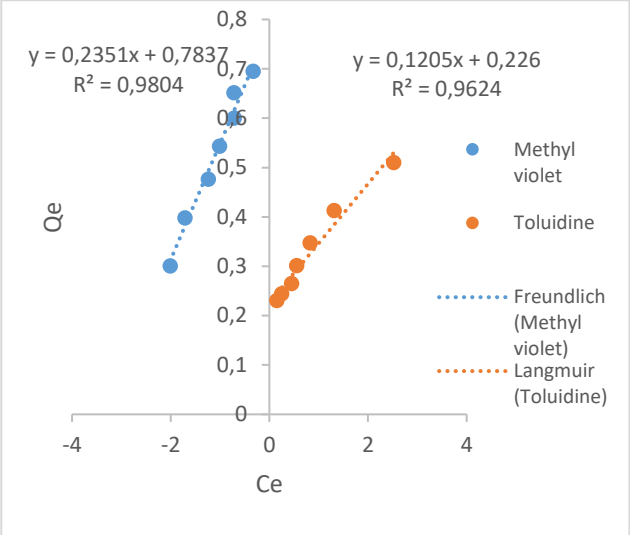

Fig 5: Linear fitting of the adsorption of toluidine blue O on ACCG to the Langmuir isotherm and methyl violet on ACCG to the Freundlich isotherm

The R_L value of toluidine blue is 0.01 and since $0<R_L<1$, the Langmuir isotherm fits well the data, and the adsorption behavior is favorable. Also, its n_F value is 3.37 which also falls within the range of favorable adsorption behavior of n_F within 1-10. The sorption capacity of methyl violet on ACCG is 4.95 mg/g which is larger than that of toluidine blue on ACCG with 4.33 mg/g. Both toluidine blue and methyl violet have the amine auto chrome group upon which the H_3PO_4 activated ACCG forms electrostatic interaction, however, the difference in the adsorption capacity can be attributed to the two of the carbon atom in the aromatic ring of toluidine replaced with sulfur and a nitrogen atom. Methyl violet is expected to easily access the ACCG inner pore while the nitrogen and sulfur in one of the aromatic rings of toluidine blue O will block the occupied active site and prevent contact interaction with other adsorbates with the active site. The adsorption capacity of chromotrope FB dye on acidic alumina is found to be 4.81 mg/g which is a little less than that of bromophenol blue on acidic alumina (4.99 mg/g).

3.3. *Recycling of the adsorbents*

It must be noted that silica gel and alumina can be recycled at 600°C where the recycled adsorbent shows qualitatively the same behavior as the unused sorbent material. ACCG cannot be recycled, and alginite can only be recycled within limits.

4. Conclusion

In this study, acidic alumina was discovered to be an excellent recyclable adsorbent for reactive textile dyes, azo dyes, and anionic dyes. ACCG has been shown to have a selective adsorption capacity towards cationic dye (basic and triphenylmethane) with that of basic dyes slightly higher than triphenylmethanes. Also, alginite and used silica were discovered to be excellent adsorbent materials for cationic dyes. In addition used silica is effective for anionic dyes an d can be recycled. Almost all of the adsorbent material used in this study adsorbed very fast with almost all dyes adsorbed within the first 5 minutes.

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