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Adsorptive removal of thiazine dyes from aqueous solutions by oil shale and its oil processing residues: Characterization, equilibrium, kinetics and modeling studies

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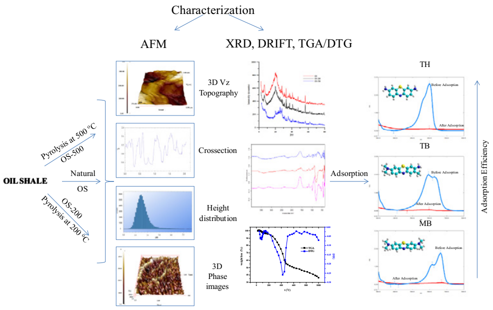
HIGHLIGHTS

- The oil shale and its pyrolysis residues at 200 and 500 °C were used for dye removal.
- The oil shale adsorbents were characterized using TGA/DTG, DRIFT, XRD and AFM.
- Sorption kinetics and equilibria of thiazine dyes TH, TB and MB were investigated.
- Adsorption rate decreased with increasing molecular size of the dyes.
- The byproduct at 500 °C has a great potential for remediation of water quality.

GRAPHICAL ABSTRACT



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ABSTRACT

Adsorption characteristics of oil shale (OS) and its pyrolysis byproducts for cationic thiazine dyes were investigated using thionine (TH), toluidine blue (TB) and methylene blue (MB).

The time dependent data for the OS adsorption were analyzed using the linear driving force (LDF) model by combining with the Langmuir isotherm. The external mass transfer (k_f) and surface diffusion (D_s) coefficients were analytically calculated based on McKay equation. They decreased with increasing molecular sizes of the dyes in the following order TH > TB > MB. In contrary, desorption efficiency in 0.1 M NaCl solution increased in the same order.

The thermogravimetric analysis (TGA/DTG), atomic force microscopy (AFM), diffuse reflectance infrared Fourier transforms (DRIFT) and X-ray diffraction (XRD) spectroscopy techniques were used in conjunction to characterize the OS samples. A comparison of (DRIFT) spectra of the dye loaded and unloaded adsorbents showed that the larger dye molecules are primarily adsorbed on the negatively charged surface hydroxyl groups and/or on organic functional groups with electrostatic interactions while the smaller molecules replace with structural cations in the interlayer space of the mineral matrices.

Adsorption capacity of the pyrolysis residue obtained in nitrogen atmosphere at 200 °C (OS-200) for the dyes decreased with respect to the OS whereas the byproduct at 500 °C (OS-500) had considerably higher adsorption ability. All of the dyes were completely removed by the OS and OS-500 from dilute solutions (<0.5 mmol L^{-1}). The OS-500 was also a good candidate for water remediation due to its high dye removal capacity in concentrated dye solutions.

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1. Introduction

Oil shale (OS) is a compact rock of sedimentary origin containing organic matter. The organic part of the OS consists of mostly kerogen, which is a polymeric matter of high molecular weight and a small amount of bitumen soluble in organic solvents. The inorganic part consists of mainly quartz, clay minerals, different types of carbonates and pyrite [1]. The estimated OS reserves in the world are 10^{15} t. The rocks containing sufficiently high content of organic matter are utilized for oil production by pyrolysis [2–4]. Currently, researches are directed toward development of alternate uses for oil shale such as the preparation of clean solid fuel [5], carbo-aluminosilicate materials [6] and admixtures in building industry [7]. Both raw oil shale [8] and its combusted wastes [9]; and ashes [10–14] have been developed as low cost sorbents for contaminant removal from aqueous solutions. Turkish oil shales have also been successfully used for the adsorptive removal of some herbicides [15–17], azo dye Basic Blue 41 (BB 41) [18] and uranium (VI) [19].

The discharge of color from waste effluents of textile, paper, leather, tannery, plastics and cosmetics has become an important environmental problem because of the potential health hazards associated with the entry of toxic components into the food chains of humans and animals.

In the present work, the OS and its pyrolysis residues at 200 and 500 °C were characterized using the DRIFT spectra and the AFM images and were used as the adsorbents for an experimental and modeling study on the removal of thiazine dyes from aqueous solutions.

2. Materials and methods

2.1. Adsorbate specifications

Thionine (TH), toluidine blue (TB) and methylene blue (MB) dyes used in this study were supplied from Aldrich Chem. Co., Carlo Erba and British Drug Houses Ltd., respectively. All dyes were analytical grade and used without further purification.

Molecular properties of the dyes were created using the semi-empirical PM 3 method in the Hyper Chem 8.0 package program and presented in Table 1.

2.2. Adsorbent preparation and specifications

The chemical and mineralogical compositions of the OS provided from Göynük region (Bolu, Turkey) are as follows [15–17]: moisture, 5.7%; ash 24.4%, volatile matter 56.3% and fixed carbon, 13.6%; C, 49.92%; H, 6.42; S, 3.32%, N, 1.07% and O, 9.4%. The raw shale contained 8.1% bitumen and its ash consisted of 52.5% (calcium–magnesium carbonate and sulfate), 23.1% alumina silicate (including feldspar and Ca-montmorillonite), 1.1% pyrite, 1.1% bitumen and 21.4% kerogen which is a bitumen-like solid composed of a mixture of aliphatic and aromatic compounds.

Table 1
Molecular properties of thiazine dyes.

Molecular properties	TH	TB	MB
Surface area ($Å^2$)	291	420	482
Volume ($Å^3$)	656	808	869
Refractivity ($Å^3$)	76.8	89.8	88.1
Dipole moment (D)	0.71	1.43	1.50
Polarizability ($Å^3$)	26.05	28.56	34.48
Hydration energy (kJ mol^{-1})	−62.4	−28.3	−4.8
Mass (g mol^{-1})	228.3	270.4	284.4

The reported values of surface ionization constants (pK_{a1} and pK_{a2}) and point of zero charge (pH_{pzc}) of the OS are 2.64, 9.24 and 5.5. Surface site concentration of the OS arising from hydroxyl and carboxyl groups is 3.3 mmol g^{-1}. Its BET surface area and particle density are 11.0 $m^2\,g^{-1}$ and 1.44 g/cm^3, respectively [19].

TG analysis (TGA) was performed on a Linesis STA PT 1750 thermogravimetric analyzer. During the experiment, about 14.3 mg oil shale sample was placed in a ceramic crucible and heated from 25 to 1000 °C under N_2 atmosphere with a heating rate of 10 °C/min.

The OS was pyrolysed in a furnace for 30 min under nitrogen atmosphere at 200 and 500 °C. The residues were abbreviated OS-200 and OS-500, respectively.

The OS samples used as adsorbents were characterized by atomic force microscopy (AFM), X-ray diffraction (XRD) and diffuse reflectance infrared Fourier-transforms (DRIFT) spectroscopy techniques.

Surface roughness and morphology of the OS samples were examined by an atomic force microscopy (AFM) instrument (Nanomagnetics). The AFM images were recorded in non-contact mode. The statistical parameters were calculated from the AFM images using the built-in NMI Viewer 2.0.7. Image Analyser Software.

The DRIFT spectra were recorded using a Bruker-Alpha T model spectrophotometer. Mass ratio of sorbent to KBr was kept constant at 1/150.

The XRD analyses of the OS samples were made using Rigaku D/Max-2200/PC XRD diffractometer equipped with a Cu tube (Cu Kα radiation).

The cation exchange capacity (CEC) of the OS samples was determined by eluting the exchangeable ions with a cesium chloride solution spiked with radioactive Cs-137 [20]. The gamma activity of the samples was measured with a well type scintillation counter (Mol-Image).

2.3. Adsorption experiments

Time dependent studies were performed for the determination of equilibration time in the adsorption process. The samples were sieved below a size of 0.2 mm before used in adsorption experiments. 5 ml of the dye solutions of 0.2 mmol L^{-1} was contacted with 0.1 g of the OS for various time intervals in a thermostatic shaker at 200 rpm. Solid and liquid phases were separated by centrifuging at 7000 rpm for 15 min. Remaining concentration of the dyes in solutions were determined from the calibration curves constructed by measuring absorbance at λ_{max} of UV–vis spectra recorded using Shimadzu 1800 UV-spectrophotometer in the wavelength range of 400–700 nm. Extinction coefficients of the peaks located at around a λ_{max} of 600, 630 and 670 nm for TH, TB and MB were 4.6×10^4, 2.1×10^4 and 3.2×10^4 L mol^{-1} cm^{-1}, respectively ($r^2 > 0.999$).

The amount of adsorbed solute (q_t in mmol g^{-1}) at any time was determined by the following equation:

$$q_t = (C_0 - C_t)\frac{V}{m} \qquad (1)$$

where C_0 and C_t are dye concentration at initial and time t (in mmol L^{-1}), respectively. V/m is the ratio of the solution volume to the mass of adsorbent (in L g^{-1}).

Desorption tests were also performed by using NaCl solution of 0.1 mol L^{-1} at the same V/m ratio to study recovery of the dye from the loaded adsorbents (∼0.025 mmol g^{-1}).

Equilibrium experiments for the OS, OS-200 and OS-500 were performed by changing initial concentrations in 0.1–7.0 mmol L^{-1} range at the same solution/adsorbent ratio.