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PHOTOCATALYTIC PROPERTIES OF ALMALYK MINING COMPANY ZnS CONCENTRATE

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Mineralogical and chemical compositions of the Almalyk Mining zinc concentrate were studied. Experimental results indicated that sphalerite zinc concentrate can be used as a photocatalyst for decomposition of different reactive textile dyes in water treatment. The photodegradation rate constant increased in following order: Blue SPD>Red SPD>Black B150>Yellow 4GL. The adsorption properties decreased in order Red SPD>Blue SPD> Black B150>Yellow 4GL. Decolorization of dye is not corresponded to COD values of treated dyes solution except Black B150 dye, confirming it's complete mineralization in aqueous solution.

Keywords: sorption, photodegradation, reactive dye, water treatment.

ФОТОКАТАЛИТИЧЕСКИЕ СВОЙСТВА КОНЦЕНТРАТА ZnS АЛМАЛЫКСКОЙ ГОРНОЙ КОМПАНИИ

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Изучены минералогический и химический составы цинкового концентрата Алмалыкского горно-металлургического комбината. Экспериментальные результаты показали, что сфалеритовый цинковый концентрат может быть использован в качестве фотокатализатора для разложения различных реактивных текстильных красителей при очистке воды. Константа скорости фотодеградации увеличивается в следующем порядке: синий SPD> красный SPD> черный B150> желтый 4GL. Адсорбционные свойства понижаются в следующем порядке: красный SPD> синий SPD> черный B150> желтый 4GL. Обесцвечивание красителя не соответствует значениям ХПК для обработанных растворов красителей, за исключением черного красителя B150, что подтверждает его полную минерализацию в водном растворе.

Ключевые слова: сорбция, фотодеградация, реактивный краситель, водоочистка.

QUYOSH ENERGIYADAN OLINGAN BI/PB XONA-TEMPERATURASI O'TA O'TKAZUVCHAN FAZALAR T_C=291 K, 295 K

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Olmaliq kon-metallurgiya kombinati rux konsentratining mineralogik va kimyoviy tarkibi o'rganildi.Tajriba natijalari shuni ko'rsatdiki, sfaleritli rux kontsentrati suvni tozalash jarayonida turli xil reaktiv to'qimachilik bo'yoqlarining parchalanishi uchun fotokatalizator sifatida ishlatilishi mumkin. Fotodegradatsiya tezligi konstantasi doimiy ravishda quyidagi tartibda ortadi: ko'k SPD> qizil SPD> qora B150> sariq 4GL. Adsorbtsiya xususiyatlari quyidagi tartibda pasayadi: qizil SPD> ko'k SPD> qora B150> sariq 4GL. Bo'yoqni rangsizlantirish, suvli eritmada uning to'liq minerallashganligini tasdiqlovchi B150 qora bo'yoqdan tashqari, ishlov berilgan bo'yoq eritmalari uchun XPK qiymatlariga mos kelmaydi.

Kalit so'zlar: sorbsiya, fotodegradatsiya, reaktiv bo'yoq, suv bilan ishlov berish.

Introduction

Reactive dyes are major environmental contaminants produced from textile industry due to the toxicity and potential carcinogenicity [1]. Physical methods (e.g., adsorption), chemical methods (e.g., oxidation and reduction), biological methods; and electrochemical processes have been applied to dye contaminants during the past decades. However, these methods can generate of secondary contaminants and required specific, costly procedures. Advanced oxidation techniques such as photocatalysis for water treatment used as a pre-treatment for biological treatment of dye-containing wastewater. [2].

Among synthetic semiconductor photocatalysts special attention has been paid to ZnS because its large negative conduction band potential (−1.4V vs. SCE) [3] is thermodynamically suitable for photodecomposition of dyes. By photo-reduction, the azo-compounds showed decolorization of the dye-containing wastewater.

Development of environment friendly, cost-effective and visible light responsive photocatalyst is highly demanded. Sensitivity to solar light, low cost of naturally occurring sphalerite can be advantages for photocatalysis. Natural sphalerite consists of various impurity elements and complicated crystal lattice defects, which are required study for evaluation practical applications in wastewaters treatment [3, 4].

The aim of this work is characterizations of Almalyk Mining natural sphalerite as the photocatalyst, and study of adsorption and photo-degradation of a number of reactive dyes widely used in the textile industry [5, 6].

Experimental

Materials

The ZnS concentrate was obtained from Almalyk Mining and Metallurgical Complex, Uzbekistan. The concentrate sample used after gravitational separation and flotation, it has a grey

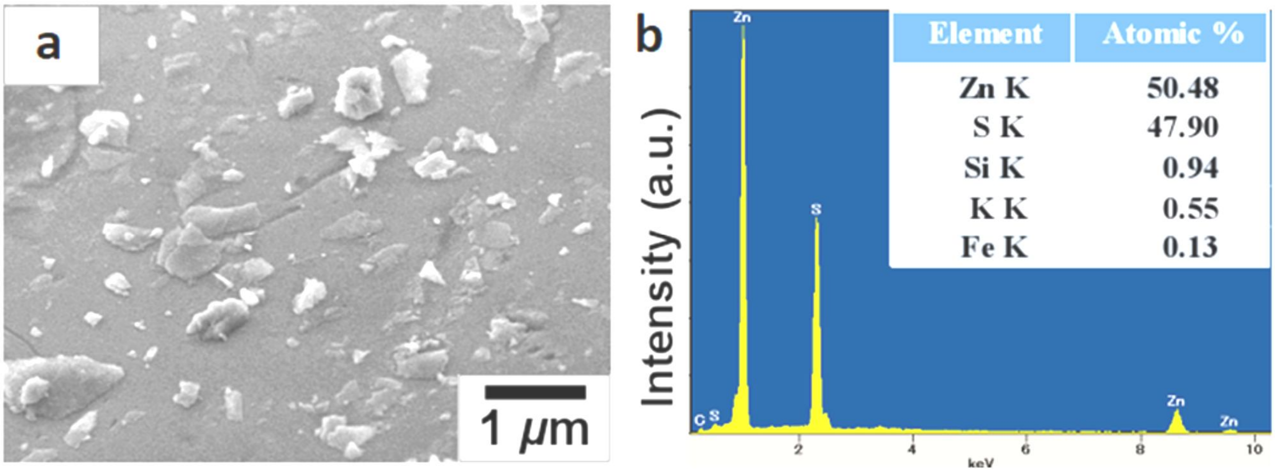

Figure 1. SEM images of sphalerite concentrate ZnS (a), element composition by EDX (b).

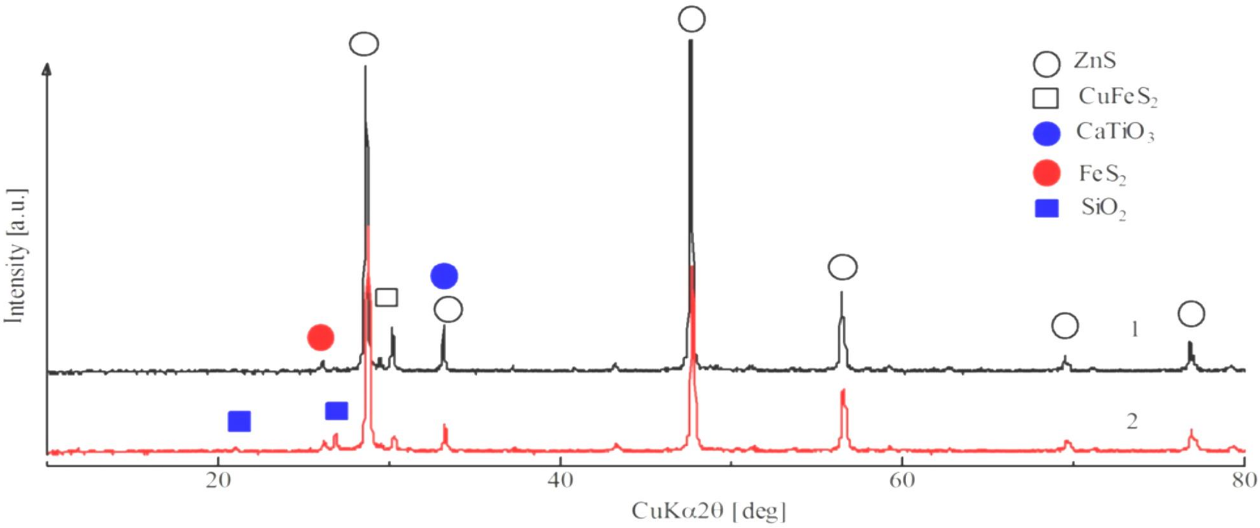

Figure 2. XRD of zinc concentrate after gravitational separation (1) and flotation (2).

color and presence of low amount of associated minerals. The reactive dyes used in this work were Blue SPD, Red SPD, Black B150, Yellow 4GL (Turkey), which are stable to visible and near UV light but can be potentially decomposed in the presence of semiconductor photocatalysts. All chemicals and reagents were analytical grade and purchased from Sigma Aldrich (USA). All solutions prepared by using deionized water.

Characterization

The X-ray diffraction (XRD) patterns were acquired with a MiniflexII (Rigaku, Japan) diffractometer using Cu Kα radiation (λ = 0.15418 nm) in the 2θ scan range of 10-80° and compared with entries from the ICDD-PDF-2 powder pattern database. The particle morphologies and sizes of the samples were examined using a JSM-7600F field-emission-type scanning electron microscope (SEM, JEOL, Japan). The chemical composition of the samples was determined by energy dispersive X-ray spectroscopy (EDX) attached to the SEM. The FTIR-spectra was studied by IRAffinity-1 spectrophotometer (Shimadzu, Japan). The elemental analysis in solution was carried out using ISP–MS (Thermo, USA)

Photocatalytic activity test

The photodegradation of reactive dyes was conducted at room temperature using a water circulating cooling system. 100 mg of powder sample was placed in a quartz test tube containing 100 mL of dye aqueous solution with the concentration of 10 mg/L. Prior to UV light irradiation (Toshiba FL10BLB black-light lamps with a wavelength range of 290–420 nm with a peak at 352 nm, 4.02 mW·cm^{-1}), the suspension was continuously stirred in the dark for 24 hours to ensure the adsorption-desorption equilibrium. During the photodegradation process, approximately 2 mL of the suspension was taken out from the reactor at a predetermined time interval for the subsequent analysis of dye concentration by using UV-2600 spectrophotometer (Shimadzu, Japan). The concentration of total organic carbon (COD) was measured by an automatic chemical oxidation demand analyzer DR 2500 (HACH, USA).

Table 1
Data of spectral elemental analysis of zinc concentrate

Element	Spectral analysis, %	ICP-MS, %
Si	2-8	Do not determined
Al	0.5-3	0.36-1.56
Ca	0.1-0.8	0.68-0.39
Na + K	0.2	0.14-0.72
Fe	2-1	6.31-3.71
Mg	3	0.49-0.53
Au	-	0.00005-0.00004
Ag	0.01	0.02-0.01
Cu	1-0.6	1.27-0.62
Pb	2-1.5	4.03-3.51
Zn	50-45	46.41-45.13
As	0.1-0.03	0.0021-0.0015
Sb	0.3-0.05	0.09-0.02
Cd	-	0.09-0.09
In	-	0.0003-0.0020

Results and discussion

Characterization of ZnS-containing industrial concentrate

The sphalerite concentrate of Almalyk Metallurgical Plant was selected as raw material as photocatalyst. Different composition and physical properties of the zinc sulphide concentrates samples can be explained by chemical and phase composition, porosity, microstructure, thermal properties.

Fig. 1 shows the microstructure of the sphalerite concentrate with the energy dispersive analysis data. It can be concluded that the major concentrate impurities are iron, silicon and potassium. XRD analysis was performed to clarify the composition of sphalerite concentrate and micro-impurities.

The XRD pattern of natural sphalerite is shown in Figure 2. The sharp peaks at 28,5°, 47,5° 56,4° are corresponded to (1 1 1), (2 2 0) and (3 11) planes, respectively (value (JCPDS 05-0566). The sample belongs to the cubic spheroidal phase and contains some impurities. Zinc sulfide is represented as the beta-form (blende, zinc blende) with small amount of quartz. X-ray diffraction data indicate that the sphalerite zinc concentrate is a mixture of natural minerals (ZnS, $CuFeS_2$, $CaTiO_3$, FeS_2 and etc.) (Figure 2).

According stoichiometrical data, the cubic sphalerite lattice filled by sulfur atoms, and half of the tetrahedral positions of the sulfur atoms are occupied by zinc. However, crystal lattice always contains minor and trace elements embedded in the crystalline structure with variable stoichiometry. In order to identify the heterogeneity of natural sphalerite, the ISP-MS analysis in solution was performed. It was shown that the major impurity was Fe. Enriched by Fe sphalerite contained different Fe quantities due to the complex process of mineral formation in nature.

The Almalyk Mining zinc concentrate is an potential photocatalyst based on wastes and by products of metallurgical industry. Table 1 shows the spectral analysis data of the Almalyk Mining sphalerite samples with the Zn mass fraction is equal to 45-50%. According to spectral analysis in solid, zinc concentrates have a higher content of Ca, Na, K, with a low content of Fe and As. However, comparing the data obtained by spectral analysis in solid with ICP-MS data in solution, it was found the presence of gold, cadmium and indium in dissolved form. In general, zinc concentrate has a complex

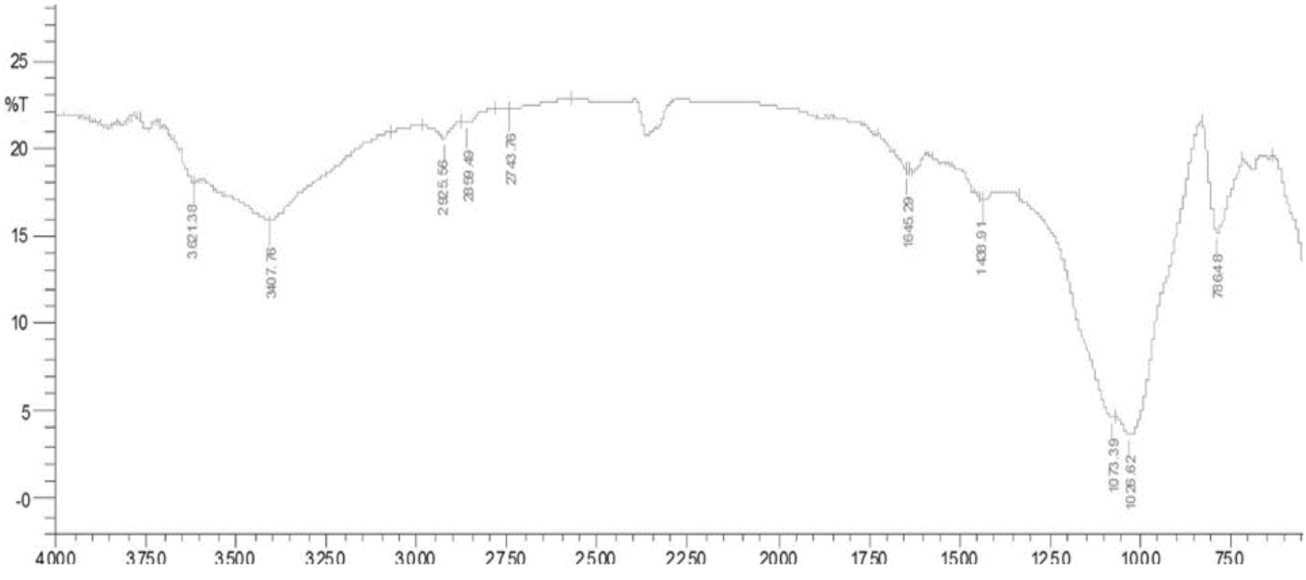

Figure 3. IR spectra of samples of zinc concentrate (Si - 8%).

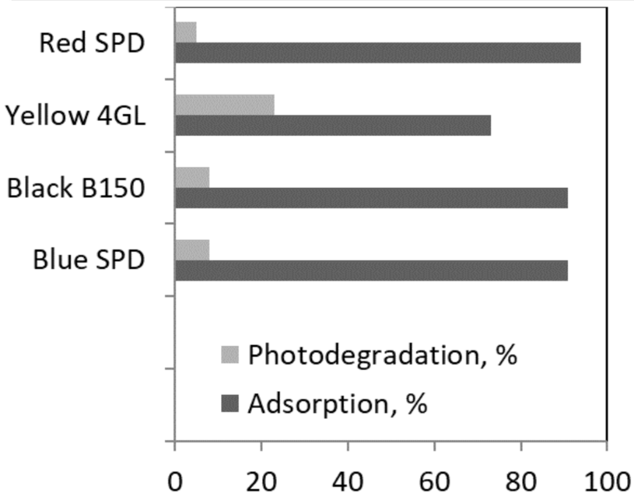

Figure 4. Photodegradation and adsorption properties of Almalik Mining zinc concentrate.

composition and contains more than 20 minor chemical elements.

Figure 3 shows the FTIR spectrum of the concentrate, which indicates the presence of absorption bands of the OH-vibrational groups in the region of 3600-3200 cm^{-1}, the bands corresponding to the vibrations of the Si – O – Al and Si – O bonds (1100-400 cm^{-1}). The bands have broad structures, due to intermolecular interactions in the crystal structure of the mineral object (Figure 3). After sorption of MO on sphalerite, the absorption bands of the dye are fixed.

Adsorption and photodegradation

The photodegradation of dyes was estimated using adsorption (%) in the dark, photodegradation under UV-light (%), and the apparent rate constant (k_{app}). The k_{app} was obtained from photodegradation with good linear relationship for the experimental data between $\ln(C/C_0)$ and time (t) in the first 15 min using the following equation:

$$\ln(C/C_0) = -k_{app}\, t \quad (1)$$

The k_{app}, dye adsorption and photodegradation data related to different dyes are listed in Table 2. The decolorization under UV irradiation is a very complex process and depends on the combined effects of heterogeneous photodecomposition on the surfaces of concentrate, direct photolysis of dye under UV light, and adsorption-desorption equilibrium, which can take place in solution. In particular, it was observed that the concentrate yield significant photodegradation of dye under UV irradiation for Yellow 4GL dye (Figure 4). The concentrate samples showed that decolorization is most likely the adsorption-desorption effects than the effect of heterogeneous photocatalysis on the surface of iron oxides and related materials.

As the reduction of chemical oxygen demand (COD) reflects the extent of degradation or

Table 2

Adsorption and photodegradation properties

Dye	k_{app}, min^{-1}	pH	Photodegradation, % (2 hours)	
			UV-Vis	COD
Blue SPD	-0.0035	3.26	19	8
Black B150	-0.0044	3.3	28	21
Yellow 4GL	-0.0085	3.7	71	5
Red SPD	-0.0038	3.4	52	18

mineralization of an organic species, the percentage change in COD was studied for dye samples (initial concentration 6 mg/l) under optimized conditions as a function of the UV light irradiation time. The optimum pH was about 3.5 and photodegradation treatment was carried out directly without pH regulation. The results are listed in Table 2. It can be seen that under UV light, the percentage of the COD reduction was around 20% in 2 h for BlackB150 and RedSPD, as well as, 5-8% in 3 h irradiation times for Yellow 4GL, Blue SPD. Whereas under UV- irradiation, the COD reduction is less than percentage of the optical density decolorization which may be due to the formation of small amounts of the uncolored products. Therefore, it seems that to achieve complete mineralization of dyes, longer irradiation time is required.

Similar performance in decolorization and TOC (total organic carbon) removal were reported after 120 min of treatment of dye solution [7-11]. UV- and solar radiation takes advantage of photoreduction and photodecarboxylation reactions to accelerate catalyst regeneration, formation of organic radicals, mineralization of the original compound, and formation of more biodegradable species.

Conclusions

Thus, the nature of dye was essential for adsorption and photodegradation of dyes on mineral photocatalyst. The enhancement in dye removal can be attributed to the photocatalytic activity of concentrate and adsorption effect.

Decolorization of dye is not corresponded to COD values for dyes confirming uncomplete mineralization in aqueous solution. The adsorption properties decreased in order Red SPD>Blue SPD> Black B150>Yellow 4GL.

The higher rate of photodegradation led to desorption of Black B150 dye into aqueous solution during UV irradiation, and rate constant increased in following order: Blue SPD<Red SPD<Black B150<Yellow 4GL.

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