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Determination of Concentration of Various Phases in Activated and Dye Treated Sewage Sludge Samples using Synchrotron X-Ray Diffraction

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Sludge sample collected from sewage treatment plant was used to develop an effective adsorbent for the removal of various dyes from wastewater. A quantitative estimation of major compounds in without activated (as collected), activated and various dyes treated sludge samples using synchrotron XRD technique is reported. Sewage sludge sample activated at 900 ºC for 30 min was found to have maximum adsorption efficiency (~ 95%) for the removal of different dyes (*e.g.* brilliant green, crystal violet and malachite green) from aqueous solution. The result shows that the adsorption using activated sewage sludge is the simplest and effective method for the removal of dyes from wastewater. As expected, the major compound in all the samples is SiO_2 (~ 50 mol%). However, SiO_2 was found in three different space groups. On activation at 900 ºC, a part of monoclinic SiO_2 phase changes to the hexagonal phase. On the other hand, on various dyes adsorption such as brilliant green, crystal violet and malachite green, the monoclinic phase changes to the tetragonal phase.

Keywords: Adsorbent, Analysis, Sludge, Synchrotron radiation, X-ray diffraction.

INTRODUCTION

Water pollution is a major issue throughout the world. During the dyeing process, approximately 10-15% of the dyes used are released into the wastewater. It is recognized as one of the root causes of environmental pollution [1]. Many industries like food, textile, rubber, paper, plastics, pharmaceuticals and cosmetics generate coloured effluents containing various dyes and pigments and discharge them into natural waterbodies [2]. Most of the coloured dyes are toxic, carcinogenic and mutagenic, which have very harmful effects on human beings as well as aquatic life [3]. Dyes are resistant to aerobic digestion and characterize one of the tough group to be eliminated from the industrial wastewater. Disposal of untreated, coloured industrial wastewater is one of the major concerns worldwide [4,5].

There are number of methods for the treatment of textile effluent containing dyes which include adsorption [6], froth flotation [7], coagulation-flocculation [8], electrocoagulation [9], decolorization and biodegradation [10], degradation and detoxification [11] and biological methods [12]. Out of these techniques, adsorption has an advantage over other techniques because of its cost-effectiveness and performance [13].

Several waste products were used as a low-cost adsorbents *e.g.* mango leaf powder [14], spent mushroom waste [15], banana peel [16], prunus dulcis [17], rambutan seed [18], litchi pericarps [19], coconut shell [20], cupuassu shell [21], jackfruit [22] and coconut coir [23]. Sludge generated from sewage treatment plants normally is in the form of semi-solid waste or slurry. It has to go through further treatment before being suitable for disposal. Currently, China & India contributes maximum of undigested sewage sludge [24], hence the safe disposal of sewage sludge is important for the protection of human health and environment [25-28]. Presently sludge is being used in the cement industry as an alternative fuel source and frequently disposed off on agricultural lands for manure purposes [29]. It has been reported that the activation of sewage sample is an important step for the removal of water contaminants [30-32].

Therefore, activated sewage sludge prepared at different temperatures and time intervals and used to evaluate its efficiency as an adsorbent for the removal of dyes from wastewater. In this study, synchrotron XRD technique is used to estimate compounds present in sewage sludge samples in as-obtained, activated and dye-treated samples quantitatively.

EXPERIMENTAL

Sludge sample was collected from the sewage treatment plant (STP) in New Delhi, India. Three dyes *viz.* malachite green, crystal violet and bright green dyes were procured from Merck, India and the physico-chemical characteristics of dyes are listed in Table-1. All the reagents used were of analytical grade and used as such. Gallium was used as a binder for the pellet preparation.

TABLE-1
ELEMENTAL COMPOSITION OF SEWAGE SLUDGE SAMPLES

Elements	As collected sewage sludge (wt.%)	Activated sewage sludge (wt.%)
Fe	0.45	0.82
Ca	0.40	0.81
K	0.06	0.11
Sr	0.06	0.09
Zn	0.05	0.08
S	0.04	0.02
Zr	0.04	0.07
Ar	0.03	0.05
Ti	0.03	0.05
Cl	0.01	–
Rb	0.01	0.01
Mn	0.01	0.01
Cu	0.01	0.01

General procedure: Sewage sludge was activated in air at different temperatures (100-1100 ºC) and at different time interval (15-120 min). Conditions of activation had been carefully managed to get the product having batch to batch reproducibility. It was observed that at 900 ºC and 30 min time, the sludge sample shows maximum dye adsorption.

Synchrotron XRD measurements: The samples were grounded to fine powders for XRD measurements. The XRD measurements were performed using angle dispersive X-ray diffraction (ADXRD) beamline (BL-12) [33], at Indian synchrotron source, Indus-2. These measurements were done in transmission mode using a monochromatic X-ray beam of 0.3 mm × 0.3 mm dimension and mar 345 image plate area detector. The monochromatic photon energy and the sample to detector distance were accurately calibrated by taking the diffraction pattern of the NIST LaB_6 standard. Fit2D software [34] was used to integrate the image plate data to get the XRD pattern in the I (2θ) form, where I is the scattered intensity and 2θ is the scattering angle.

The elemental analysis of all the samples was performed to get an idea of various elements in the samples which helps in determining various compounds in the samples. JCPDS data provide information regarding various phases and their crystal structures [35-37]. It has not been possible to perform Rietveld analysis in these samples because of their multiphasic nature. The phases were identified by having prior knowledge of different elements in these samples, using XRF measurements. The XRF results of without activated and activated sludge samples are given in Table-1. Some trace elements also found to be present (< 0.01%) in sewage sludge sample which are Y, V, As, Kr, Cl, Cr, Br and Ni.

The first three most intense Bragg peaks were identified from the JCPDS data. All the compounds of possible elements were considered and the Bragg peaks were identified. For quantitative determination of the concentration of various phases in as collected, activated and various dye treated sludge samples, the area under the X-ray diffraction peaks of various phases were investigated. These areas were normalized for their scattering efficiencies.

The process is explained as a photon energy 15.686 keV (0.7904 Å) was used for the measurements of without activated and activated sludge samples, whereas, photon energy of 18 keV (0.71721 Å) was used for the measurement of various dyes treated activated sludge samples. The structural factor $|F|^2$ was calculated theoretically using the following equation for each phase, identified in the sample:

$$F_{hkl}(q) = \sum_{i=1}^{n} K_i \times K_i \times f_i \times e^{2\pi i(hx_i + ky_i + lz_i)} \quad (1)$$

where K_i is the occupancy factor, f_i the atomic scattering factor (as given in eqn. 1). x_i, y_i, z_i are the fractional atomic coordinates of the i^{th} atom. We have assumed that the Debye-Waller factor is the same for all the phases.

Eqn. 1 after summation for all the atoms can be written as real (eqn. 2) and imaginary components (eqn. 3).

$$F_{hkl} = F_{1(hkl)} + i\,F_{2(hkl)} \quad (2)$$

and $$|F_{hkl}|^2 = F_1^2 + F_2^2 \quad (3)$$

The area of 100 % XRD peaks of each phase were calculated by fitting the XRD peaks with Gaussian. We have normalized the area of XRD peak intensities with theoretically calculated $|F|^2$ values, to estimate the weight percentage of the compounds in the samples. Let W_i be the mass (in amu) of unit cell of a particular phase i in the sample and A_i is the area of the 100% Bragg peak, for the phase. Then $X_i = K \times [(W_i \times A_i)/|F|^2] \times 100$ is the relative wt. percentage of the i^{th} phase. Similarly, X_i for all the phases was calculated in the sample and $\Sigma X_i = 100$ gives K value and hence the wt.% of all the phases in the sample.

RESULTS AND DISCUSSION

XRD studies: Sewage sludge was in the form of small spherical grayish-black powder. Fig. 1 represents the XRD pattern of as collected sewage sludge. Collected sewage sludge shows a high amount of monoclinic SiO_2 (47.3%) and hexagonal SiO_2 (26.6%). Small amounts (< 10%) of other oxides like $CaCO_3$, $ZnSO_4$, Fe_3O_4, SrO_2, ZrO_2 and FeO were also identified. The peaks were identified with the help of JCPDS data. The lattice parameters of monoclinic SiO_2, as obtained from the JCPDS datasheet were (a) 13.705º, (b) 21.771º, (c) 13.119º.

The concentration (wt.%) of each compound along with their space groups are summarized in Table-2, which shows as collected sewage sludge consists of high amount of SiO_2. These results are in agreement with literature [38-40].

Activated sewage sludge: The sewage sludge was then activated by heating the sample at 900 ºC in air for 30 min. The optimized temperature and time were chosen for better adsorption capacity. Fig. 2 shows the ADXRD pattern of the

TABLE-2
IDENTIFIED PHASE COMPOSITION OF SEWAGE SLUDGE SAMPLES

Chemical formula	(Plane corresponding to maximum Bragg peak) space group	JCPDS No.	As collected sewage sludge (wt.%) (± 0.2)	Activated sewage sludge (wt.%) (± 0.2)
SiO_2 (M)	(-111) P21/n	000511377	47.3	4.0
SiO_2 (H)	(101) P3221	000331161	26.6	64.1
$CaCO_3$ (R)	(104) R3C	000050586	6.3	5.1
$ZnSO_4$ (C)	(111) F23	010701254	6.9	9.7
Fe_3O_4 (C)	(311) Fd3m	010846700	8.6	10.2
SrO_2 (T)	(101) I4/mmm	040074074	2.3	–
ZrO_2 (M)	(-111) P21/a	000650728	1.0	5.6
FeO (C)	(200) Fm3m	010890687	1.0	1.2

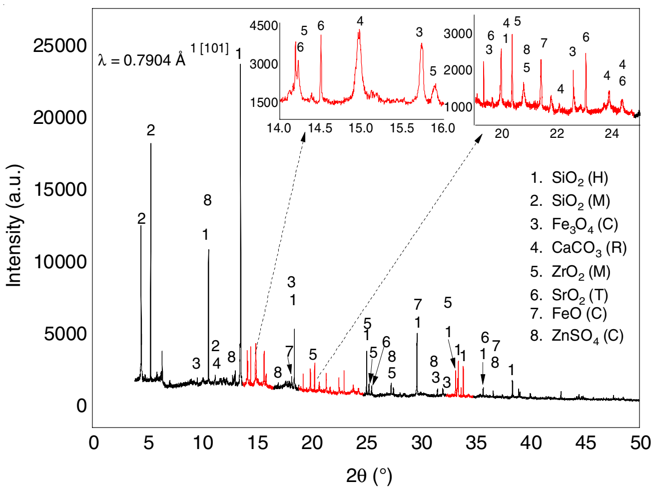

Fig. 1. ADXRD pattern of as collected sewage sludge samples (1-8)

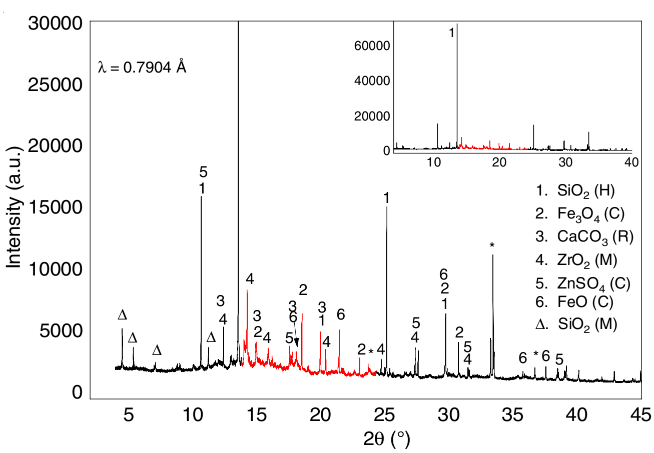

Fig. 2. ADXRD patternof activated sewage sludge sample. [Δ] represents SiO_2 (monoclinic), preferred orientation along (101) direction and *represents peak not identified

activated sewage sludge and it is observed that the wt.% of hexagonal SiO_2 increase at the cost of monoclinic phase. Also SiO_2 in monoclinic form appears in the sample. The organic materials were removed after activation. The monoclinic SiO_2 transforms into the hexagonal SiO_2 phase, which also decided to alter the phase concentrations. Activated sewage sludge has a higher concentration of hexagonal SiO_2 (64.09%). Sewage sludge activation caused a simultaneous decrease in monoclinic SiO_2 and $CaCO_3$ phases and increase in the other phases. The concentrations of all the phases are listed in Table-2.

Adsorption studies: The activated sewage sludge was further used for the removal of brilliant green, crystal violet and malachite green dyes from wastewater. Batch studies were conducted by adding definite amount of activated sewage sludge in these dye solutions to evaluate parameters like contact time, pH, amount, initial adsorbate concentration and temperature. After ADXRD analysis of dye treated activated sewage sludge samples was performed. It is found that after adsorption, some phases removed were monoclinic SiO_2, FeO, $CaCO_3$ and SrO_2. The introduction of two new phases such as tetragonal SiO_2 and FeOOH took place, while FeO changes to Fe_3O_4. The concentration of ZrO_2 increased and other phases were decreased simultaneously in all the dye treated samples.

Fig. 3 shows ADXRD pattern of sewage sludge after the adsorption of brilliant green dye. The main phase of this pattern is hexagonal SiO_2 (45.0%), which is similar to activated sludge sample, whereas the second large phase is tetragonal SiO_2 (23.5%). The concentrations of phases were estimated and are listed in Table-3.

Figs. 4 and 5 show the ADXRD pattern of the crystal violet and malachite green dye treated activated sewage sludge, which indicated that crystal violet and malachite green treated samples have a higher concentration of hexagonal SiO_2 (53.0%). The second largest compound in the crystal violet dye treated

TABLE-3
IDENTIFIED PHASE COMPOSITION OF VARIOUS DYES TREATED ACTIVATED SEWAGE SLUDGE SAMPLES

Chemical formula	(Plane corresponding to maximum Bragg peak) space group	JCPDS No.	BG treated activated sewage sludge (wt.%) (± 0.2)	CV treated activated sewage sludge (wt.%) (± 0.2)	MG treated activated sewage sludge (wt.%) (± 0.2)
SiO_2 (H)	(101) P3221	000331161	45.0	53.0	53.0
SiO_2 (T)	(101) P41212	000391425	23.5	8.3	10.1
FeOOH (O)	(110) Pbnm	040145919	18.1	10.8	11.4
ZrO_2 (M)	(-111) P21/a	000650728	6.8	12.9	11.0
$ZnSO_4$ (C)	(111) F23	010701254	3.6	7.7	8.1
Fe_3O_4 (C)	(311) Fd3m	010846700	3.0	7.3	6.4

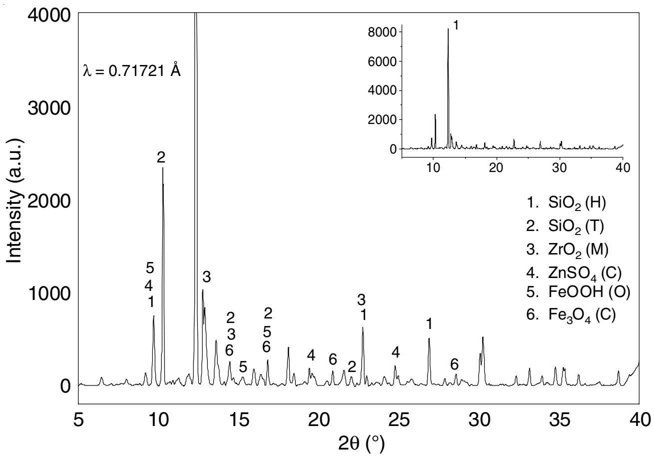

Fig. 3. ADXRD pattern of Brilliant green dye treated activated sewage sludge sample

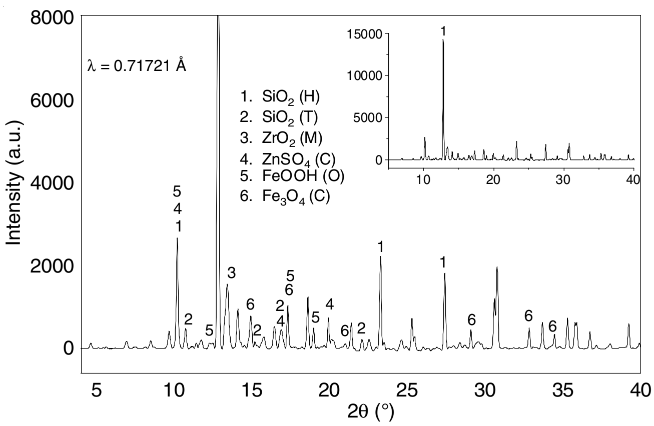

Fig. 4. ADXRD pattern of Crystal violet dye treated activated sewage sludge sample

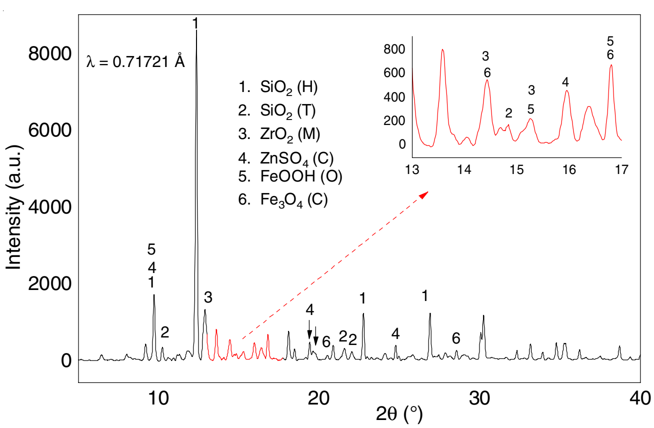

Fig. 5. ADXRD pattern of Malachite green dye treated activated sewage sludge sample

sample is ZrO_2 (12.9%), while in malachite green dye sample is FeOOH (11.4%). Although activated sewage sludge samples are found to be efficient dye adsorber, however, qualitative changes in the XRD patterns were not observed. Only weight percentage of some phases were found to have altered. One major change observed is formation of FeOOH phase at the cost of FeO and Fe_3O_4 phases, for all dye treated activated sewage sludge samples. Also tetragonal phase of SiO_2 has been formed. These may be due to the chemical reaction between iron oxide phase in sludge samples and dye. Despite this, no diffraction peaks were seen from the adsorbed dyes, which might be because of their low concentrations or because organic dyes are made up of low Z elements and are the weak scatterers of X-rays.

Conclusion

Sewage sludge principally contains quartz SiO_2 as the main phase in as collected sewage sludge. After activation of sewage sludge at 900 ºC, phase of SiO_2 changes from monoclinic to hexagonal. From XRD patterns, the presence of SiO_2, $CaCO_3$, $ZnSO_4$, Fe_3O_4, SrO_2, ZrO_2 and FeO were confirmed in as collected sewage sludge samples. Insertion of the tetragonal SiO_2 and FeOOH phases in dyes treated sewage sludge samples were observed, which were formed at the cost of monoclinic SiO_2 and iron oxide, respectively. Significant changes in concentrations of contents were traced after the activation of sewage sludge. The dye treated samples do not show any diffraction peak due to adsorbed dye component because of low concentration of the adsorbed dye component and low Z elements in the dye.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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