An eco-friendly bio-sorbent derived from fish (Carp) scale: A study of commercial dye removal.

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Abstract— An eco-friendly, cost effective bio-sorbent has been derived from the fish (Carp) scale after chemical processing. Commercial dye, methyl orange (MO), was deployed as a model adsorbate under different pH condition in the aqueous solutions. In neutral solution (ph~7) and in moderately acidic solution (pH 3.1-4.4), the removal pattern of the dye from colored solution shows an excellent behavior rather than two extreme conditions i.e. highly acidic or alkaline. Study also focuses the equilibrium time of almost 50% removal of the dye by the bio-sorbent which was within five minutes and afterwards it shows a monotonous pattern. The comparative study of dye adsorption at different pH shows that the equilibrium time was reached earlier in case of neutral pH solution than the acidic one. The desorption behavior of the dye from the fish scale was also monitored under varying percent (%) salinity. The fish scale fibers were resistant against release of adsorbed dyes at lower pH condition than the neutral one for MO. The fish scale fibers showed different nature of releasing the adsorbed dye (MO) under varying concentration of SDS, a popularly known surfactant. Almost all the dyes were desorbed under neutral pH before CMC1 value of SDS. A relatively monotonic dye releasing nature was observed in case of moderately acidic condition even after crossing the CMC values of SDS and it finally stops at nearly 50%. On the other side, some anomalous behavior of dye releasing was observed initially in case of highly acidic condition and the normal trend was followed even after higher CMC value of SDS. These data reflects that the surfactant action was prominent at higher CMC of SDS at lower pH condition.

Index Terms— Bio-sorbent, fish scale, dye, removal, waste-water, salinity, eco-friendly.

1 INTRODUCTION

DYE removal from the industrial waste water has become a burgeoning topic in the current decades. Synthetic dyes, particularly the azo dyes are frequently used in the effluents of textiles, leather, paper and food processing industries [Sun et al., 2003]. Some of these azo dyes are carcinogenic in nature and non-biodegradable in aerobic condition. Therefore, contamination of these dyes into surface water as well as ground water possibility due to long distance migration through surface run is a great environmental concern.

Various attempts has been taken from different corners of the world to meet up the supply and demand of usable water from non-usable condition through physio-chemical or biochemical methods, which are hardly cost effective. Now it became necessary to find out some naturally abundant low cost biomaterials which can easily remove such kind of carcinogenic dyes with simple contact process. A wide range of adsorbents like charcoal(active), zeolite, fly ash, clay, mud, coal etc are effectively utilized due to their easy availability [Begum et al., 2013]. Different type of biosorbents like chitin [Longhinotti et al., 1998], chitosan [Smith et al., 1993], sawdust [Grag et al., 2003], bagase [Raghuvanshi et al., 2004], banana pitch [Nasivayam et al., 1992], roots of water hyacinth [Low et al., 1995] etc, have also been tried as environment friendly materials. Other aquatic or marine bio materials are also been utilized in this regard.

In this work, fish scale of carp was used as a low cost biosorbent for removal of organic synthetic dyes. Fish scales are mainly composed of collagen fibre. The sorption sites of the fish scale collagen moiety are phosphates, carboxylates, amine and carbonyl. Heavy metal ions like copper, lead, cobalt, nickel, arsenic and chromium have been effectively adsorbed on preheated decalcinated fish scale Oreachronius nilotietus (Talapia fish) [Villanueva-Espinosa et al., 2001], Atlantic cod (Gadus morhua), Lethrinus nebulosus (Sprangled emperor) [Basu et al., 2006], Labeo rohita [Srividya et al., 2009] and catla catla [Nadeem et al., 2008] etc. has reported earlier by other group of authors. Methyl orange (MO), being a pH sensitive synthetic dye in aqueous solution, was used as a model adsorbate to the processed fish scale to monitor the efficiency of removal of the MO at a varying sorbent dose, time, pH, ionic strength (% salinity) of water. The desorption pattern was also monitored with varying concentration of SDS, a popularly known surfactant, in water.

2 MATERIALS AND METHODS

2.1 Materials

The fish scales of carp were collected from local fish market. Sodium hydroxide pellets, Sodium dodecyl sulfate (SDS) were purchased from sd fine-chem limited, India. Methyl Orange Dye (MO), Hydrochloric acid, Sodium chloride was obtained from Merck, India. Ethylene diamine tetra acetic acid disodium salt was procured from Loba chemie Pvt. Ltd., India. All the chemicals were of purity grade.

2.2 Preparation of Fish Scale

The raw fish scales of carp were washed thoroughly with fresh water followed by distilled water to remove the impurities attached with the fish scales. Then the scales were decalcified with the help of EDTA solution and repeatedly washed

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with distilled water. Absence of Ca2+ ion was confirmed after testing with eriochrome black-T (EBT) indicator after each wash. Fish scales were allowed to dry in sunlight for two days. The scales were then grounded carefully and kept in an air-tight plastic container for further use. The chemically treated fish scale collagen were scanned with the high-resolution field emission scanning electron microscope (FESEM, model no. JEOL JSM-6700 F) with 10.00 kV with the magnification of 1500 times as well as 6000 times a lateral resolution in the range 20-50 μm on the glass substrate. Aliquots were spayed over the glass slides and left for air drying at room temperature. These spray-dryed slides were finally gold coated before scanning under electron microscope.

2.3 Study of absorbance Through Spectral Analysis

The absorption spectra of the sample solutions were recorded from 300 to 800 nm at a final dye concentration of 30μM in each case at room temperature using a spectrophotometer, UV-1700 (Shimadzu, Japan). The concentrations of stock solutions were close to 1 mg/ml. The data points recorded at 500nm were made an average of triplicate measurements.

2.4 Dye Removal Capacity at Varying pH and Adsorbent Dose

The stock solutions of different pH were prepared and the pH of the experimental solutions was maintained 2, 3.5, 7 and 10 respectively. 100 μL of the dye solution was added into the final volume of 10 ml test solutions so as to maintain the final concentration of the dye 30μM. Innitially 0.1 gm of fish scales was added into the experimental dye solutions. The solutions of the three tubes were stirred well for half an hour for homogeneous mixing. The tubes were allowed to stand for another 15 minutes without any disturbance so that the solutions reach the equilibrium. Then the supernatants from three sample tubes were collected and centrifuged (5000-8000 rpm, REMI) to obtain clear solution. The absorbance of the three solutions was then measured at 500 nm wavelength as well as in absence of fish scale for reference. Adsorbent dose was extended upto 0.3 gm for the same dye solutions.Each data point was an average of the three repeats.

2.5 Study of Adsorbtion with Time

Time dependent adsorption behavior was monitored by measuring the absorbance of the aliquots taken out from the homogeneous mixture at 1 min. time interval. 50 ml of the prepared acidic solution (pH~2) was taken in a beaker. 500 μL of the supplied dye solution was added to maintain the identical dye concentration as earlier followed by the addition of 0.5 gm of fish scale in mixing condition. 2 ml of the solution mixture was taken out and absorbance was measured at λ_{max} = 500 nm. This same experiment was performed for other two cases of different pHs. No significant change was observed at higher pH. Therefore we deliberately avoided to carry forward the set of experiment at pH 10 (data not shown). Each data point was an average of three repeats.

2.6 Study of Desorbtion behavior with (%) Salinity

In order to obtain the effect of ionic strength upon the adsorption profile, absorbance of the aliquots obtained from the dye solution with different concentration of NaCl was measured. 10 ml of the acidic solution was taken in a test tube, where 100μL of the dye was added followed by the addition of 0.3 gm of fish scale. The solution was allowed to stir for 20 minutes for homogeneous mixing and absorbance was measured. Then 0.1 gm of NaCl was added. After addition it was allowed to stir for 1 hour and the supernatant was centrifuged repeatedly to obtain a clear solution for measuring absorbance. This procedure was repeated for measuring absorbance at different concentration of NaCl (1%, 2%, 3%, 4%, 5%, 10% and 20% respectively. This same experiment was performed for neutral solution (pH~7) also. A blank experiment without the dye was performed accordingly for necessary corrections of the data points.

2.7 Dye Study of Desorbtion behavior at varying Surfactant Concentration

The dye desorption behavior in presence of various concentration of SDS was performed at different pH (~2, 3.1-4.4 and at ~7). Initially the dye was allowed to be adsorbed on the fish scale and then the SDS concentration was gradually increased from 0.1% to 1.8%. The test solutions were thoroughly homogenized followed by the centrifugation for 5 minutes at 5000 rpm, and finally the optical density of the supernatant was recorded.

3 Results And Discussions

3.1 Characterisation of Fish Collagen through Electron Microscopre

It was clearly viewed from the SEM images that there is a heterogeneous population of filamentous and ribbon like clusters primarily with diameter of ~20-25 μm (Figure 1). Dehydrated samples with different magnification were also been presented (Inset, Figure1). Some shrunken filamentous pattern was also noticeable in the plates which were probably the elongated fibers with a varying length of ~100–500 μm range and even larger.

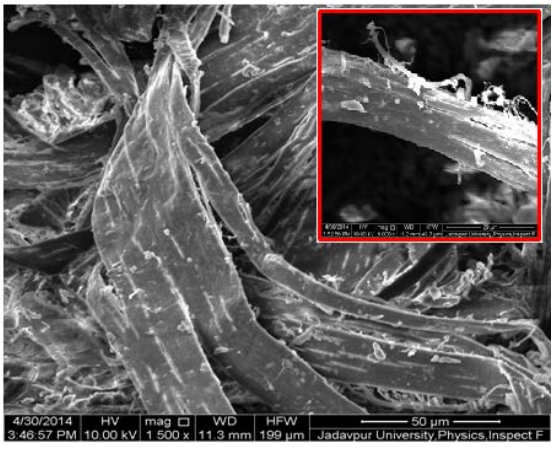

Fig. 1. Scanning electron microscopic view of chemically treated fish scale collagen. High-resolution field emission (FESEM) was done with 10.00 kV after the magnification of 1500 times as well as 6000 times (inset) along with lateral resolution in the range 20-50 μm on the glass substrate.

3.2 pH Dependant Adsorbtion Behavior

Methyl orange, being a pH sensitive dye, shows a bathochromic peak shift in its UV-Visible spectral pattern and the peak maxima shifts from ~465 nm to ~505 nm (i.e. almost ~40 nm red shift) in the visible region along with the increase in intensity when the pH of the solution was shifted from neutral to more acidic. Hence, a fixed wavelength was deliberately selected during spectral studies and it was fixed at 500 nm, where good quality of signals was obtained and correspondingly all the data points were normalized (Fig. 2a).

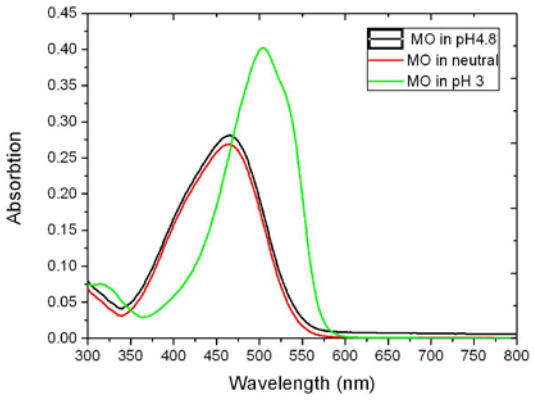

Fig. 2a. Absorption spectra of methyl orange (MO) dye solution at pH 3 (red), pH 4.8-5 (black) and pH 7 (green). Concentration of MO was maintained 1 mg/ml in all the cases. Each data point was an average of triplicate measurement.

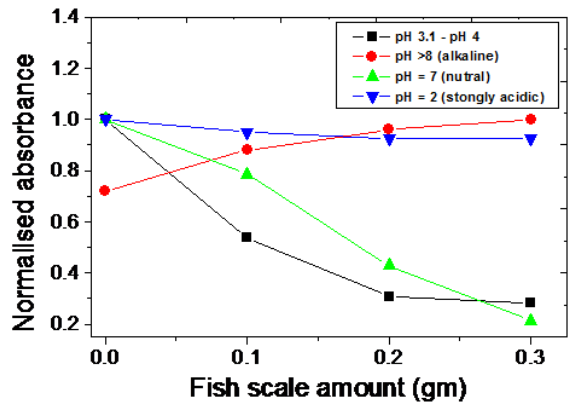

Fig. 2b. Effect of bio-sorbent doses on dye removal: Normalized absorption isotherm of MO dye in varying fish scale doses at pH 3.1 - 4 (black), pH >8 (red), pH 7 (green) and pH ~2 (blue). The initial concentration of the dye was 30µM in all the cases. Each data point was an average of triplicate measurement.

The pH dependent adsorption behavior of fish scale was almost same for the moderately acidic and neutral solutions (Fig. 2b). There was a decrease in absorbance with the increasing amount of fish scale. In moderately acidic solution, a sudden fall in optical density value was observed with the increase in adsorbent dose and finally reaches a saturation level within the range of 0.2-0.3 gm, where as in neutral solution a gradual decrease in optical density value is obtained with increase in adsorbent dose. In case of highly acidic or highly alkaline solution no remarkable adsorption behavior was noticed at this range of adsorbent dose. Mild alteration in the pattern of isotherms is probably due to the variation in surface charges of the collagen fibers and consequent protonation and deprotonation phenomena of electrostatic binding sites. On the other hand, in case of alkaline solution, no such significant change was observed with the increase in adsorbent dose. Mild alteration or increase in optical density value was probably due to the increase in colour intensity due to deprotonation at highly alkaline medium for which were within the error limit i.e. ±(0.1-0.2).

3.3 Determination of Equillibrium Time

The equilibrium time for adsorption was determined for acidic and neutral solutions. It was observed that within 1-2 minutes of mixing almost 35% adsorption occurred for both the cases and the solutions reached the saturation level within five minutes. The kinetic plot of the dye removed from the solution shows a difference in optical density value for different pH, where in acidic case the value is higher than neutral one. Therefore, for better understanding, a normalized absorbance plot was drawn (Fig. 3). Same kinetic adsorption behavior is obtained within first 1-2 minutes duration but with the propagation of time the removal pattern differs slightly. In the neutral medium a fluctuation in absorption data signifies that there exist a mutual attraction and electronic repulsive nature in between the two interacting molecules which ultimately attains an equilibrium after nearly 70% removal where as in mild acidic medium, where the side chain residues are protonated, keep on adhering the dye in a relatively slower rate and stops at nearly 50% of removal. Further, both of them follow a monotonic unchanged behavior after a certain period of time (7-8 mins) indicating the achievement of the saturation zone.

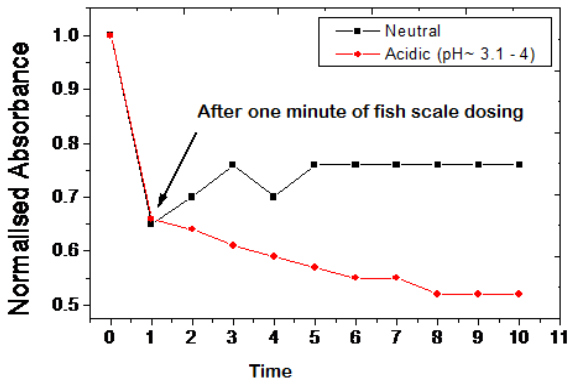

Fig. 3. Equilibrium time of MO dye removal in presence of bio-sorbent: Kinetic plot of dye removal at neutral pH (black) and at pH 3 - 4 (red). The initial concentration of the dye was 30µM in all the cases. Each data point was an average of triplicate measurement.

3.4 Dye Removal Behaviour with Varying Salinity

Salinity changed MO desorption behavior by the fish scales in

different way for neutral and acidic solutions. Alteration in absorbance value was more prominent in case of neutral solutions immediately after reaching 1% salinity. The gradual increase in percent salinity showed no significant change in acidic solution rather the solutions reached equilibrium (Fig. 4). A mild increase in absorbance in the plot was observed in the acidic case which reflects a partial release of the adsorbed dye from the collagen matrix. For acidic solution, equilibrium was reached rapidly with the increase in NaCl concentration. In neutral solution, the equilibrium was reached after addition of 4-5% NaCl and almost the complete release of the adsorbed MO dye was achieved. The functional groups like carboxyl (-COOH), phosphate (PO_4^{3-}), attached to the collagen fiber are the primary source of electrostatic binding and also other polar groups of amino acid moiety within the fish scale matrix are responsible for dye binding which can be removed by sodium ions by electrostatic replacement or simple ion-exchange method. In this ion exchange process, the adsorption-desorption did not occur in equimolar ratio. Initially the dyes bound to fish scales were almost instantly while desorption of dyes were merely observed with increasing ionic strength which proves that fish scales were resistant to higher salinity in removal process of the bounded dyes at lower pH. Nonetheless, at lower pH, the active binding sites being protonated, the hydrophobic environment is also prevailed within the collagen matrix. Hence dye releasing occurs slowly and partially.

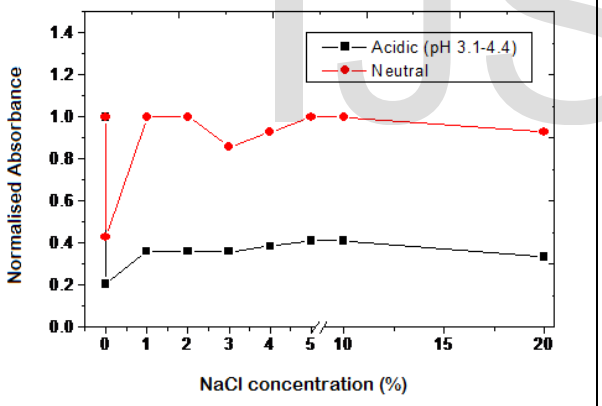

Fig. 4. Desorption profile of MO dye in presence of percent salinity: isotherm represents the effect of percent salinity (0% - 20%) on removal of adsorbed dye on fish scale at pH 3.1-4 (black) and pH 7 (red). The initial concentration of the dye was 30µM in all the cases. Each data point was an average of triplicate measurement.

3.4 Dye Removal Behaviour with Varying SDS Concentration

The study of dye removal efficiency in presence of a popularly used surfactant, SDS, shows very good reversibility in case of neutral solutions even at lower concentrations (Fig. 5). While the removal pattern at moderately acidic conditions and highly acidic conditions were quite distinctly different with concomitant addition of the SDS. It is necessary to mention that SDS, at higher concentrations forms molecular aggregates, *vizly* 'micelles'. The CMC values of SDS in pure water at room temperature are approximately 8.2 mM (~0.23 - 0.25%, CMC1) [Mukerjee et al. 1971] and 40 mM (~1 - 1.5%, CMC2) respectively where the shapes of the micelles differ from spherical to lamellar and /or cylindrical. Now, interestingly, it is observed that the dye removal efficiency was reached up to the highest level i.e. complete removal was achieved in case of neutral solution immediately after reaching the CMC value and higher. On the other hand, the trend of dye removal in case of moderately acidic condition was achieved only approximately 50% even after reaching its first CMC value and follows a constant path even in higher concentration of SDS. In case of highly acidic condition, the removal pattern shows a characteristic nature of decrement at the beginning, and in between the first CMC value (CMC1) and second CMC value (CMC2) it was observed to be almost constant and finally the removal dye was increased with the gradual increment of the SDS concentration. The complete surfactant behavior was observed at a very higher concentration of SDS. These results could be explained on the basis of the availability of proton in the solution and the binding with the negatively charged sulfonate group which results in competitive binding / adsorption on the fish scale collagen moiety through hydrophobic and electrostatic interactions. Nonetheless, the surfactant (SDS) self assembly may also play an important role in association and dissociation of the dye with the collagen fiber.

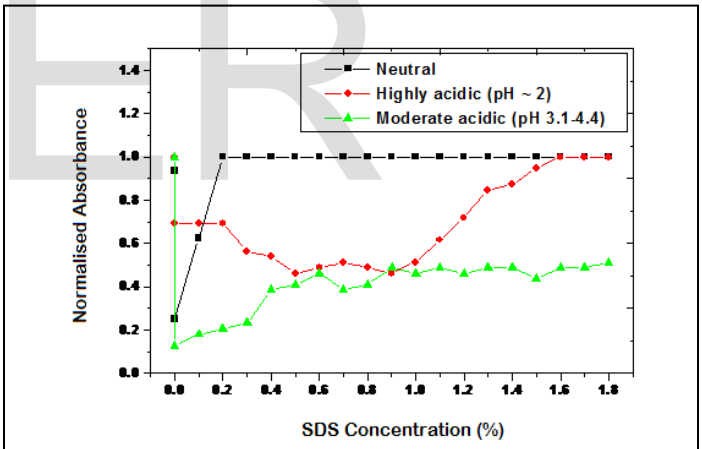

Fig. 1. Abroption- desorotion profile of MO dye in presence of SDS surfactant (0% – 1.8%) at pH ~7 (black), pH ~2 (red) and pH 3.1 – 4 (green). The initial concentration of the dye was 30µM in all the cases. Each data point was an average of triplicate measurement.

4 Conclusion

The study shows that, the low cost fish scales of carp are good quality adsorbent in the removal of dye from water. The adsorption is very effective in the lower pH range as well as in neutral medium rather than in case of higher pH range. The equilibrium time for this adsorption process is 1-2 minutes at neutral pH and the same is obtained for neutral solutions within 4-5 minutes. The addition of NaCl indicates that at 1% salinity, the loosely bounded dyes to the collagen fiber were

easily replaced by Na^+ ion and gained equilibrium without any further removal of dyes with increasing salinity at moderately acidic condition. On the other hand, almost complete reversibility in dye binding and release was observed in case of neutral solutions and the equilibrium is achieved at ~5% salinity. The release of bounded dyes through hydrophobic interactions with the deployment of surfactant, SDS, shows that nature of dye release is dependent on the pH of the solution and also on the CMC value of the SDS. Both the hydrophobic and the electrostatic interactions are responsible for dye binding on fish scale collagen matrix and partial or fractional release of the dye is also regulated by the CMC value and also on the efficacy of the surfactant molecules in aqueous solutions. Hence it is proposed that the biosorbent processed in our laboratory is a cost effective, eco-friendly biodegradable bio-derived material and suitably applicable for the removal of synthetic industrial dyes from water with the specificity of the environmental condition and optimization.

ACKNOWLEDGMENT

Technical support of scanning electron microscopic facilities provided by the Department of Physics, Jadavpur University, Kolkata is gratefully acknowledged. Authors also like to acknowledge Camellia Institute of Engineering & Technology, Budbud, Burdwan, WB, India, for providing academic and administrative help.

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