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Potential of Fish Scales in the Eco-friendly Treatment of Fish Processing Industry Effluent

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Abstract

The discharge of effluent from seafood processing units is loaded with several organic and inorganic contaminants. This results in the deterioration of water quality and leads to water pollution in water bodies where effluents are discharged. Huge quantities of fish scales are discarded as solid waste from fish markets. In the present study, fish scales were utilized as potential adsorbent and tested for their adsorption ability in the treatment of fish processing industry effluent. The prepared adsorbent caused a significant reduction ($p<0.05$) (>50 %) in the concentration of alkalinity and hardness in the treated effluent. The concentration of Total solids (TS), Total Dissolved Solids (TDS), and Total Suspended Solids (TSS) showed significant ($p<0.05$) reduction (30-60 %) after treatment. Based on the results, the best adsorbent dosage and contact time for the most effective treatment of all parameters was observed to be 1g/100 mL and 180 minutes. The porous surface and functional groups of adsorbent were characterized before and after treatment. The results of the present study revealed that fish scale adsorbent can be effectively used for the treatment of excess alkalinity and hardness in the effluent.

Keywords: Effluent, fish scale adsorbent, treatment, water quality parameters

Introduction

The seafood industry is one of the leading food production sector in the world. The demand for aquatic foods and the global seafood trade are increasing day by day. Effluent discharged from seafood processing industries can have a number of negative effects on nearby ecosystems. Eco-toxicity due to polluted water affects living organisms and has become a main concern for the last few decades (Darge & Mane, 2015). The water quality parameters such as alkalinity and hardness are more interrelated because these parameters usually occur in the form of calcium/magnesium carbonates, bicarbonates, hydroxides, sulphates of divalent ions (calcium, magnesium, and sodium), and acid ligands (Amosa, 2016). A variety of methods such as adsorption, chemical precipitation, reverse osmosis, membrane filtration, ion exchange, and coagulation have been used for the removal of toxic organic and inorganic constituents from water and wastewater (Kannan & Mani, 2014). Apart from these methods, the use of the adsorption technique in effluent treatment receives much attention nowadays, owing to its simplicity and economic feasibility. Adsorption is considered to be one of the most promising techniques for wastewater treatment over the last decades (Kyzas & Kostoglou, 2014). Adsorbents are mostly microporous in nature and have a high surface area, which can be effectively used in the wastewater treatment process (Gupta et al., 2009). Among various adsorbents, the application of fish scales in effluent treatment is a recent innovation. No studies were reported about the usage of fish scales as an adsorbent in the treatment of excess alkalinity and hardness in seafood processing industry effluent. Therefore, the present work aims to explore the ability of fish scales to remove alkalinity and hardness in seafood processing plant effluent. The study was carried out with different adsorbent dosages and contact times during effluent treatment. In addition to that, the TS, TDS, and TSS reduction capacity of scales were also examined in the treatment process.

Materials and Methods

The effluent was collected from a local seafood processing plant in pre-washed sample cans. The temperature of collected effluent was measured in

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the sampling site itself using a standard mercury thermometer with an accuracy of 0.1 ^{o}C. The filled sample cans were transported to the laboratory immediately for the estimation of physicochemical parameters. The initial concentration of alkalinity and hardness in the effluent was measured using the indicator method and EDTA-titrimetric method (APHA, 1926). The initial concentration of physical parameters such as TS, TDS, and TSS was measured using the gravimetric method (APHA, 1926). The pH was measured using an "ELICO" digital pH meter.

Fish scale adsorbent was prepared using waste fish scales of *Lethrinus* sp. The collected scales were washed repeatedly in running water to remove the adhering dust and impurities from the surface. The fish scales were soaked in 15 % nitric acid (commercial grade) for 24 h in a ratio of 2:1 (acid: scales). The scales were further soaked in distilled water for 24 h to remove excess acid and then dried in an oven at 60 °C until they became crispy. The dried scales were ground with a mortar grinder and the pulverized scales were sieved through a 100-mesh test sieve to achieve 150 μm particle size. The prepared adsorbent (Fig. 1) was stored in an airtight plastic container for further experimental use.

The experiments were carried out with varying adsorbent dosage levels and contact times in the laboratory at room temperature. A volume of 100 mL of wastewater samples was taken in 150 mL conical flasks. The samples were mixed with 5 different adsorbent dosages viz., 0.0625 g, 0.125 g, 0.25 g, 0.5 g, and 1 g. They were shaken in an orbital shaker at 250 rpm for three different contact times (45, 90 and 180 minutes). Then the separation of adsorbent and effluent samples was carried out by filtration with Whatman filter paper No. 42 (Grade 1, 125 mm) and the filtrate was stored in sample cans. The final concentrations of water quality parameters were estimated in the treated effluent samples and recorded for comparison with the initial concentrations. All experiments were conducted in triplicate and the average was used for analysis.

Fig. 1. Prepared fish scale adsorbent

The surface morphology of raw and effluent treated fish scale adsorbent was analyzed using Field Emission Scanning Electron microscopy (FESEM, MIRA 3. TESCAN make). The functional groups of the adsorbent before and after treatment was observed using Fourier Transform Infrared Spectroscopy (FT-IR, Thermo Fisher Scientific). The FTIR spectrum was measured in the range of 400-4000 cm^{-1} (32 scans) with a resolution of about 4 cm^{-1}. The percentage removal (%R) of parameters and adsorption capacity (q_t) of adsorbent were determined using equations (1), (2), and (3) as described by Nayl et al. (2017).

$$\%R = \frac{(C_0 - C_t) \times 100}{C_0} \quad (1)$$

$$qt = \frac{(C_0 - C_t)\, V}{m} \quad (2)$$

The removal rate (Kr) of pollutants was calculated using equation (3) as given by Huang (2007).

$$Kr = \frac{C_0 - C_t}{Contact\ time} \quad (3)$$

Where C_0 is the initial concentration (mg/L), C_t is the final concentration (mg/L) at time t, q_t is the adsorption capacity of fish scale adsorbent at time t, V is the volume of sample (L) and m is the mass of adsorbent (g). The recorded data was analyzed and statistically tested with the help of statistical software SPSS version 25. Two-way ANOVA was used to test the significant potential of fish scale adsorbent at 5 % significance level between two factors such as dosage and contact time during the treatment of wastewater samples. The correlation between increasing adsorbent dosage levels and the percentage removal of studied parameters in the treatment was determined.

Results and Discussion

The percentage removal (%R), maximum adsorption capacity (q_t) and removal rate (Kr) of parameters such as alkalinity, hardness, TS, TDS and TSS by adsorbent during effluent treatment are shown in Table 1. Adsorption dosage is important in adsorption study since it shows the percentage removal of parameters in the effluent. The best adsorbent dosage was studied at five different dosage levels (0.0625 %, 0.125 %, 0.25 %, 0.5 % and 1 %). The nitric acid-treated adsorbent significantly ($p<0.05$) reduced the pH value of effluent from 8.3 to 5.3 and this drop in pH coherently reduced the alkalinity and hardness values in the effluent during treatment. The values of alkalinity, hardness, TS, TDS and TSS in effluent decreased with increasing adsorbent dosage with maximum reduction observed at the dosage of 1 % as shown in Fig. 2. In this study, a high amount of adsorbates were removed from effluent with increasing adsorbent dosage levels during treatment. This was due to the availability of more surface area of fish scale adsorbent with increasing dosage levels and hence the maximum percentage of removal was observed at higher dosage levels. The fish scales used in this study were subjected to acid wash, which enhanced the porous nature of the adsorbent. These micropores play a major role in entrapping suspended and particulate solids from effluent and they also aid in the diffusion of divalent calcium and magnesium cations into adsorbent (Kannan & Mani, 2014).

The adsorbent efficiency was assessed at three different contact times (45, 90 and 180 minutes). The efficacy of fish scale adsorbent in reducing the concentration of water quality parameters with respect to different contact times during effluent treatment is shown in Fig. 2. The values of all water quality parameters decreased significantly ($p<0.05$) with increasing contact time. This is due to the fact that more time will be available for the suspended, particulate matter and ions to get adsorbed on the adsorbent surface. The maximum percentage removal (%R) of parameters such as alkalinity, hardness, TS, TDS and TSS were observed at 180

Table 1. Percentage removal (%R), maximum adsorption capacity (q_t) and removal rate (Kr) of parameters after treatment with fish scale adsorbent (1g/ 100 mL) in seafood processing effluent

Water quality parameters	%R (Mean ± SD)	q_t (Mean ± SD)	Kr (Mean ± SD)
Alkalinity (mg/l)	53.38 ± 0.13	32.42 ± 0.08	1.80 ± 0.004
Hardness (mg/l)	52.20 ± 1.28	48.33 ± 1.15	2.69 ± 0.06
TS (mg/l)	46.95 ± 0.64	0.22 ± 0.003	0.01 ± 0.001
TDS (mg/l)	33.79 ± 1.41	0.15 ± 0.006	0.01 ± 0.001
TSS (mg/l)	57.51 ± 1.92	0.02 ± 0.001	0.001 ± 0

Table 2. Functional groups identified in fish scale adsorbent

Before treatment Wave number (cm^{-1})	Functional groups	After treatment Wave number (cm^{-1})
3319.61	N-H stretching	3502.73
2926.10	C-H stretching vibrations of -CH3, –CH and -CH2	Not detected
1652.92	Carbonyl (C = O) stretching vibrations; N-H bending	1627.92
1540.45	Nitro compound (N=O) group; N–H bending vibrations	1543.05
1448.85	Amino substituted alkyl group; Carbonate group	1404.18
1234.09	Amines group (C-N) stretching	Not detected
1077.97	Phosphate stretching	1041.76
875.47	Sulphonate group	810.10
530.13	Alkane group	Not detected

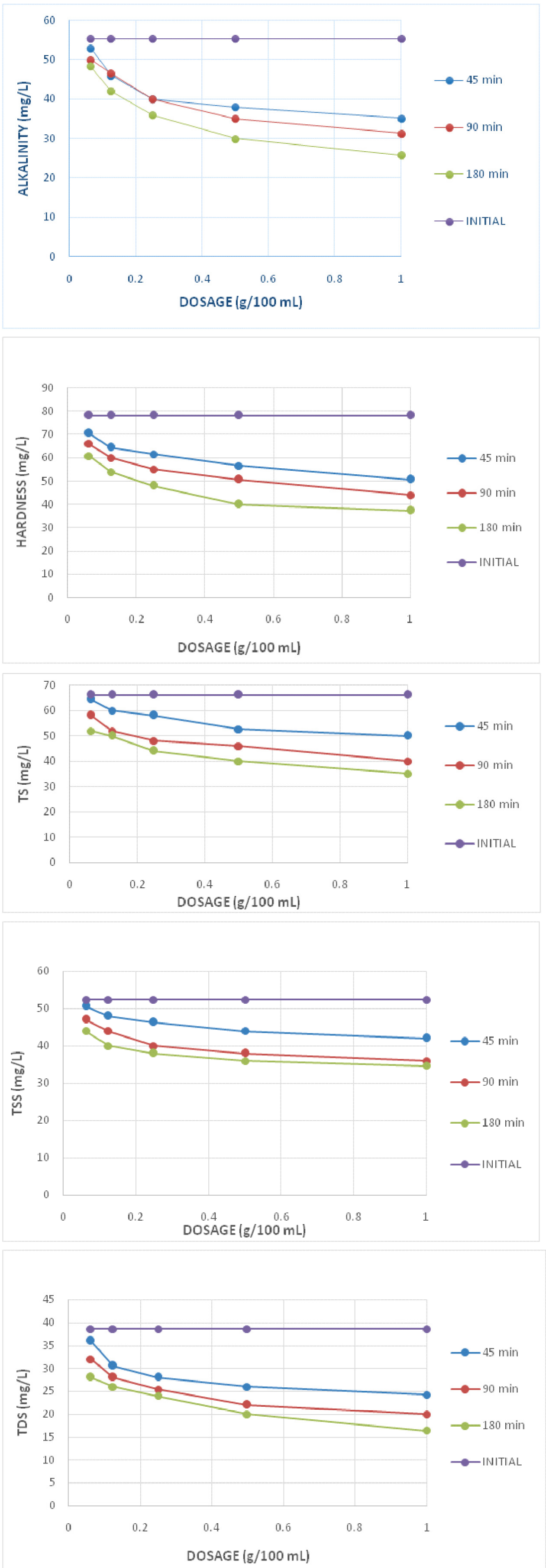

Fig. 2. Efficacy of fish scale adsorbent in the treatment of various water quality parameters of seafood processing industry effluent

minutes of contact time. Based on the results, it was proven that fish scale adsorbent is having the potential to reduce higher levels of alkalinity and hardness. But the %R is limited (<60 %), which might be due to the competition created between H^+ ions and Ca^{2+} and Mg^{2+} for adsorption sites. Similarly, Rolence et al. (2014), reported the hardness reduction capacity of coconut shell-activated carbon in synthetic hard water. Moreover, the involvement of adsorbent functional groups such as nitro (N-O), amine (N-H) and alkane (C-H) are likely to account for the adsorption of ions responsible for hardness onto the surface. In addition, the presence of oxygen-containing functional groups in adsorbent helps for the removal of TDS via complexation and ion exchange (Oh & Shin, 2015).

The FESEM analysis revealed the morphological changes occurring on the adsorbent surface before and after treatment with effluent. The raw adsorbent exhibited a porous surface at 50 µm resolution as shown in Fig. 3. The adsorbent surface was categorized into dark (organic) and white (inorganic) regions. The organic part consists of protein (carbon and oxygen) and the inorganic part consists of calcium and phosphorus (Zayadi & Othman, 2013). The pores on the adsorbent surface are very important for entrapping pollutants from effluent. After treatment, the adsorbent surface showed a rugged appearance at 5 µm resolution due to interaction with effluent during treatment. FTIR analysis was performed in order to identify the functional groups of adsorbent. The functional groups of the adsorbent undergo complexation and ionization mechanisms in effluent and aid in the treatment process. The identified functional groups before treatment and positions of shifted peaks in adsorbent after treatment are tabulated in Table 2. It was noticed that some functional groups in the adsorbent disappeared and shifted after treatment, which indicates the complete interaction of these groups during effluent treatment.

Two-way ANOVA was used to test the significance of adsorbent (at 5 % level) between increasing dosage levels and contact times in the effluent treatment process. The ANOVA result as given in Table 3 showed a significant difference ($p<0.05$) in the concentration of all parameters with increasing contact time and adsorbent dosage levels in seafood processing plant effluent. A good correlation between increasing dosage levels and the

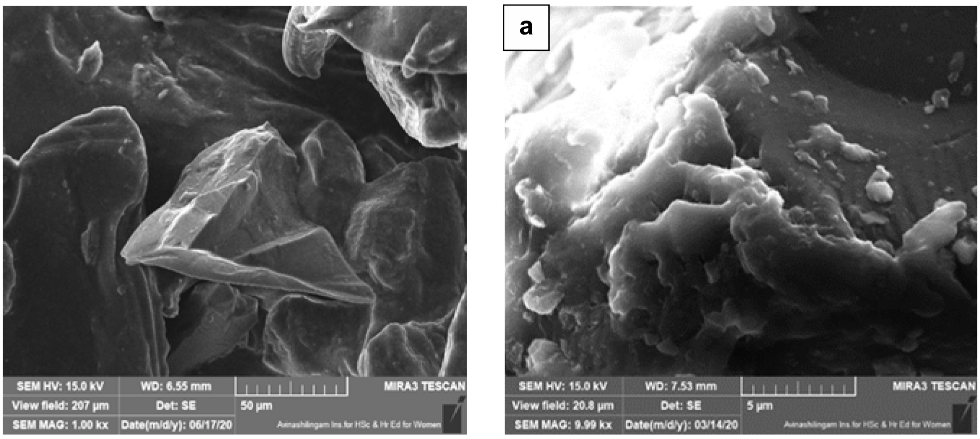

Fig. 3. FESEM micrographs of (a) raw adsorbent and (b) seafood processing effluent treated adsorbent

Table 3. Two-way ANOVA and correlation results obtained from effluent treatment with adsorbent

Parameters (Seafood processing industry effluent)	ANOVA p value (5 % significance level)							
	Dosage levels				Contact time			
	Mean sum of squares	F value	p value	Level of significance	Mean sum of squares	F value	p value	Level of significance
Alkalinity	141.37	8.26	0.002	+	333.00	19.47	6.63E-05	+
Hardness	163.93	8.34	0.001	+	820.89	41.76	1.26E-06	+
TS	92.93	8.16	0.002	+	463.93	40.77	1.43E-06	+
TDS	32.68	8.19	0.002	+	188.39	47.23	6.42E-07	+
TSS	47.96	8.11	0.002	+	236.67	39.99	1.59E-06	+

+ Significance at 0.05 %

Table 4. Correlation results obtained from effluent treatment with fish scale adsorbent

Parameters	Correlation (r) between increasing fish scale adsorbent dosage levels and percentage removal
Alkalinity	.979**
Hardness	.965**
TS	.920*
TDS	.951*
TSS	.861

**. Correlation is significant at the 0.01 level (2-tailed)
*. Correlation is significant at the 0.05 level (2-tailed)

corresponding %R of parameters was also observed using SPSS software (Table 4). Based on the results, it can be concluded that the fish scale adsorbent exhibited the best %R at 180 minutes contact time with the dosage of 1 g/100 mL of effluent. From the present study, it was concluded that waste fish scales can be effectively used as an eco-friendly adsorbent for the remediation of effluent which minimizes water pollution and also promotes solid waste management practices.

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