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Research article

Potential removal of organic loads from petroleum wastewater and its effect on the corrosion behavior of municipal networks

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A potential and cost-effective treatment method utilizing thermally activated bentonite was evaluated for the treatment of highly loaded real petroleum processing wastewater (COD = 4500 mg/L) in order to reduce its COD and improve the corrosion properties. A save discharging COD limit of the treated effluent (800 mg/L) is achieved by using 6 g/L of calcinated bentonite after reaching the steady state (1 h of shaking) at pH 5. The durability of bentonite is proved. The corrosion behavior of the treated wastewater was investigated for mild steel by using electrochemical and weight loss measurements. The results proved that the corrosion rate of the wastewater was slightly reduced after the treatment process. More improvement of the corrosion resistance was achieved by adding sodium hexa-meta-phosphate (SHMP) corrosion inhibitor to the treated water. Tri-methyl ammonium bromide (CTAB) biocide was also added before discharging into municipal networks.

1. Introduction

Petroleum processing wastewater (PPW) is produced widely around the world, particularly in Middle East countries. Due to their toxicity, resistance to degradation and their solubility properties; conventional biological or chemical treatment technologies for petroleum wastewater do not reach the save discharging limits. The presence of these pollutants in the surroundings can be harmful to humans and the environmental system as well. This is because these agents can cause several mutagenic and/or carcinogenic effects (Koswojo et al., 2010). Physical technologies using different absorbents are effective in reducing organic compounds in wastewater. Although the activated carbon remains an expensive material, it remains the most common and broadly used adsorbent in the applications of wastewater treatment. From the cost point of view, researchers worked to find attractive alternatives to be widely used in real industrial wastewater treatment with reasonable cost effectiveness and local availability. Clays are considered 20 times cheaper than that of activated carbon. At the same time, the sustainability of the surrounding environment plays an important role in the use of low-cost adsorbents (Babel and Kurniawan, 2003; Hariani et al., 2015). The modified bentonite is used to get rid of methylene blue dye, the maximum adsorption of dye was found to be near to 100%. The ion exchange, protonation, hydrogen bonding and ion–dipole reactions describe the mechanisms of adsorption of organics onto clay minerals (Anirudhan and Ramachandran, 2015). The dyes are effectively removed from textile industry wastewater utilizing local bentonite. Moreover, bentonite is utilized for the removal of dissolved organic compounds in wastewater collected from paper mill industry (Gulgonul, 2012; Liu et al., 2013). Other researchers used successfully modified bentonite for removal of phenol from wastewater, which might be considered as an alternative strategy for existing conventional systems (Shen, 2002; Senturka et al., 2009; Hariani et al., 2015). The composite bentonite is very good adsorbent to remove phenol from aqueous solution and can be used to commercialize for treatment of wastewater contaminated with phenol pollutants in industrial scale. Furthermore, bentonite can act as a coagulant in addition to being an absorbent in the treatment of sewage wastewater for COD removal. The removal percentage reached more than 90% (Syafalni et al., 2013). The mild steel pipelines suffers from corrosion which results from discharged wastewater. Therefore, the corrosion control is very important to extend the duration time of these pipelines. Many authors reported the corrosion behavior and corrosion control of mild steel in different media (Ehteram and Aisha, 2008;

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Gheorghe et al., 2010; Mobin and Shabnam, 2010; Chinwko et al., 2014; Fang et al., 2011; Phadke et al., 2017). The handling of mild steel in acid, alkali and salt solutions is very important because the mild steel constitutes the major construction materials pipelines (Wang et al., 2012). However, the challenge here is how to reduce the steel pipelines degradation through discharging the treated wastewater, which is considered a severe corrosive environment. Inorganic and organic corrosion inhibitors are used to handle the corrosion process for mild steel in different severe media and the mechanism is depending on the structure of corrosion inhibitors and their adsorption properties (Finsgar and Jackson, 2014; Raja et al., 2016; Chigondo and Chigondo, 2016). The design and characteristics of the pipelines have higher effect of corrosion and microbial induced corrosion due to the water flow, however, quaternary ammonium salts are used as biocides and inhibitors (Diana et al., 2016; El-Shamy et al., 2009; El-Sayed et al., 2007; Neelam and Abhinav, 2014; Hongwei et al., 2015). In this study, the corrosion behavior of the untreated and treated wastewater were investigated and the corrosion inhibitor was used to improve the corrosion resistance. Biocide was then is tested to control the microbial growth as well as decrease the microbial corrosion. The sodium hexa-meta phosphate (SHMP) was used as corrosion inhibitor and cetyl tri methyl ammonium bromide (CTAB) was used as biocide. The corrosion behavior of the inhibitor and biocide are discussed in detail.

2. Materials and methods

2.1. Materials

The bentonitic clay was brought from the Nile Company for mining. It was preprocessed by drying, grinding into powder and sieving (80- mesh). The drying process was carried out at 105 °C at lab oven GFL-7105, Gemini BV, Netherland. The chemical analysis of the bentonite is shown in Table 1. Adequate amount of a real petroleum industrial wastewater was collected from Qaroon Petroleum Company during a working day and preserved at 4 °C for further investigations. The pH was adjusted using Sigma-Aldrich HCl and NaOH. Filtration process was achieved utilizing Whatman membrane filters (0.45 μm). Particle size of bentonite was determined throughout the images taken by scanning electron microscope (SEM) at different magnifications using Quanta-250 FEG, USA. Mild steel electrodes were used for corrosion investigation.

2.2. Methods

Thermal activation of bentonite was carried out by calcination of native bentonite at programmable muffle furnace over a range of temperature from 50 °C to 500 °C in steadily raised temperature to reach 500 °C and reside at 500 °C for 30 min (Chagas et al., 2014). FTIR absorption spectra of the bentonite were recorded for the 350–4000 cm^{-1} range using Jasco-FTIR-Spectroscopy, Japan which is used for the illustration of active groups at the bentonite surface. Batch experiments were considered for all subsequent experiments. Experiments using activated and non-activated bentonite were done utilizing a lab-shaker for shaking the suspended solutions, Wiseshake, SHO-2D, South Korea. A pH-meter, WTW-inolab, Germany, was used for adjustment of the pH values of the suspensions. In 200 ml clean and dried glass reagent bottles, 100 ml of the wastewater was added, the chosen amount of bentonite was added, pH values of the wastewater samples were adjusted for desired value via HCl (1 M) and NaOH (1 M) for all experiments. The mixtures were shaked at 200 rpm using the shaker. After desirable contact time reached, samples were subjected to filtration, membrane filtration (0.45 μm) was considered, and then the filtrate was subjected to further analysis and characterizations. The produced sludge containing the clay is subjected to further analysis, drying-weighing-calcination-weighing in porcelain crucible. Following up the efficiency of the treatment was done using the measurements of COD. Wastewater characterizations were achieved according to the standard method (APHA et al., 2012).

The electrochemical measurements were carried out using a three electrode cell. A mild steel working electrode was embedded in an epoxy resin leaving 0.75 cm^2 exposed surface area. A platinum sheet was used as counter electrode and a saturated Calomel electrode (SCE) as a reference. The cell was connected to a Meinsberger Potentiostat/Galvanostat, Germany. The open circuit potential (OCP) of the electrode was recorded for 30 min to reach steady state potential. The potentiodynamic polarization measurements were recorded starting from −100 mV of the steady state potential with scan rate of 1 mV/S. Weight loss measurements were carried out on mild steel coupons for 2, 4 and 6 days in treated wastewater in presence and absence of inhibitor. Effect of biocide on the corrosivity of treated wastewater is also investigated.

3. Results and discussion

3.1. Physico-chemical characterizations of petroleum processing wastewater

The collected PPW was subjected to extensive physico-chemical characterizations to gain information about the wastewater quality. Table 2 represents the physico-chemical characterizations of the collected wastewater. Obviously from Table 2, the wastewater was highly loaded with organic pollutants (COD) which are hardly biodegradable (low BOD/COD ratio; about 0.16) and had a range of toxicity for the activated sludge. The measurement of the soluble COD showed nearly the same values of the total COD, the small amount of the total suspended solids (TSS) could be attributed to some inert materials like sand and/or dust. The measurements of the TSS for the treated effluents were not logical because the microfiltration process has been achieved for the treated effluent in order to remove the clay particles.

3.2. Respiration activity test for the wastewater to the activated sludge

Respiration activity test was carried out to determine the noxiousness number (NOX) which represents a total picture for the toxicity of the wastewater to the activated sludge. Fig. 1 represents the respiration activity test (Abdelfattah et al., 2016; NORM- DIN 8192:2007; Pagga, 1981) for the collected wastewater. From Fig. 1, low concentrations (20 ml/L or less) of the wastewater were not toxic for the activated sludge. In contrast, higher concentrations were toxic, the inhibition concentration for 50% of the activated sludge (IC_{50}) was 400 ml/L. The noxiousness number $(NOX)_{PPW} = 1/$

Table 1
Chemical Analysis for natural Bentonite.

Chemical Analysis	Percentage, %
SiO_2	49–55
Al_2O_3	20–24
Fe_2O_3	2.5–6.0
MgO	0.5–2.0
CaO	2.0–6.0
K_2O	1.2–1.4
Na_2O	1.1–2.4
Loss on ignition measured at 850 °C at 2 h	9.0–10