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PRELIMINARY STUDY OF SURFACE TREATMENTS FOR PLATINUM ELECTRODES DESIGNED FOR OXIDATION–REDUCTION POTENTIAL DETERMINATIONS IN ACTIVATED SLUDGE

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ABSTRACT

Platinum electrodes with six different surface treatments (polishing, platinization, polypyrrole, polyurethane, cellulose acetate and Nafion) were tested for equilibrium exchange current densities and zero-current potential in treated water and activated sludge. Preliminary results show that platinization and polypyrrole treatment increase electron transfer rates, but polypyrrole film breaks up rapidly in activated sludge; polyurethane and cellulose acetate layers did not prevent fouling (and impaired performance) in activated sludge, but Nafion seemed more promising.

KEYWORDS

Electochemistry; platinum electrodes; oxidation-reduction potential; activated sludge.

INTRODUCTION

Platinum electrodes were shown to be potentially usable for the real-time monitoring of nitrification and denitrification processes in sewage treatment plants (Wouters-Wasiak *et al.*, 1993; Wareham *et al.*, 1994). They are much more sensitive to the redox variations of the environment than gold electrodes (Heduit *et al.*, 1993). Nevertheless, their use remains difficult due to the slow reaction rates at the interface and adsorption of species on the platinum surface (Heduit and Thevenot, 1992).

The increase of the electron exchange rates was attempted by a redox polymer layer obtained by *Pyrrole* electropolymerization on platinum (Polypyrrole) (Umana and Waller, 1986; Ikariyama *et al.*, 1987) and by electrolytic deposit of *platinum black* (platinization) intended to increase the rugosity and the active surface of the metal. Discrimination by size of the species capable of reaching the platinum was attempted by a

polyurethane layer (Bindra *et al.*, 1991), discrimination by size and (negative) charge by *cellulose acetate* (Wang *et al.*, 1988; Bindra *et al.*, 1991) or *Nafion* (Harisson *et al.*, 1988) layers.

METHODS

The electrochemical kinetics were assessed from the equilibrium exchange current densities determined by low-speed (1 mV/s) plotting of the potential-intensity curves (anode and cathode scans around the equilibrium potential) in treated water or aerated activated sludge and by plotting of the Tafel lines $|i|$ *vs* $(E\text{-}E_{i=0})$. The zero-current potentials were measured against a Saturated Calomel Electrode (SCE) using a high-impedance input millivoltmeter.

The exchange current densities and zero-current potentials determination were performed under the following conditions.

1. Immediately after treatment of the platinum surfaces (polishing, the mineral or organic deposit).

2. After treatment and immersion of the electrodes for 7 days in activated sludge alternately submitted to aerobic and mild anoxic conditions (> 100 m/VSCE).

3. After treatment and immersion of the electrodes for 24 hours in activated sludge maintained in anaerobiosis (- 200 mV/SCE).

RESULTS

Immediately after treatment of the platinum surface, the highest equilibrium exchange current densities were obtained with platinized electrodes or those coated with polypyrrole (Figure 1). Significantly lower rates were observed for the polished electrodes or those coated with cellulose acetate of Nafion. The polyurethane deposit gave the lowest exchange rate densities ($< 0.1\ \mu A.cm^2$).

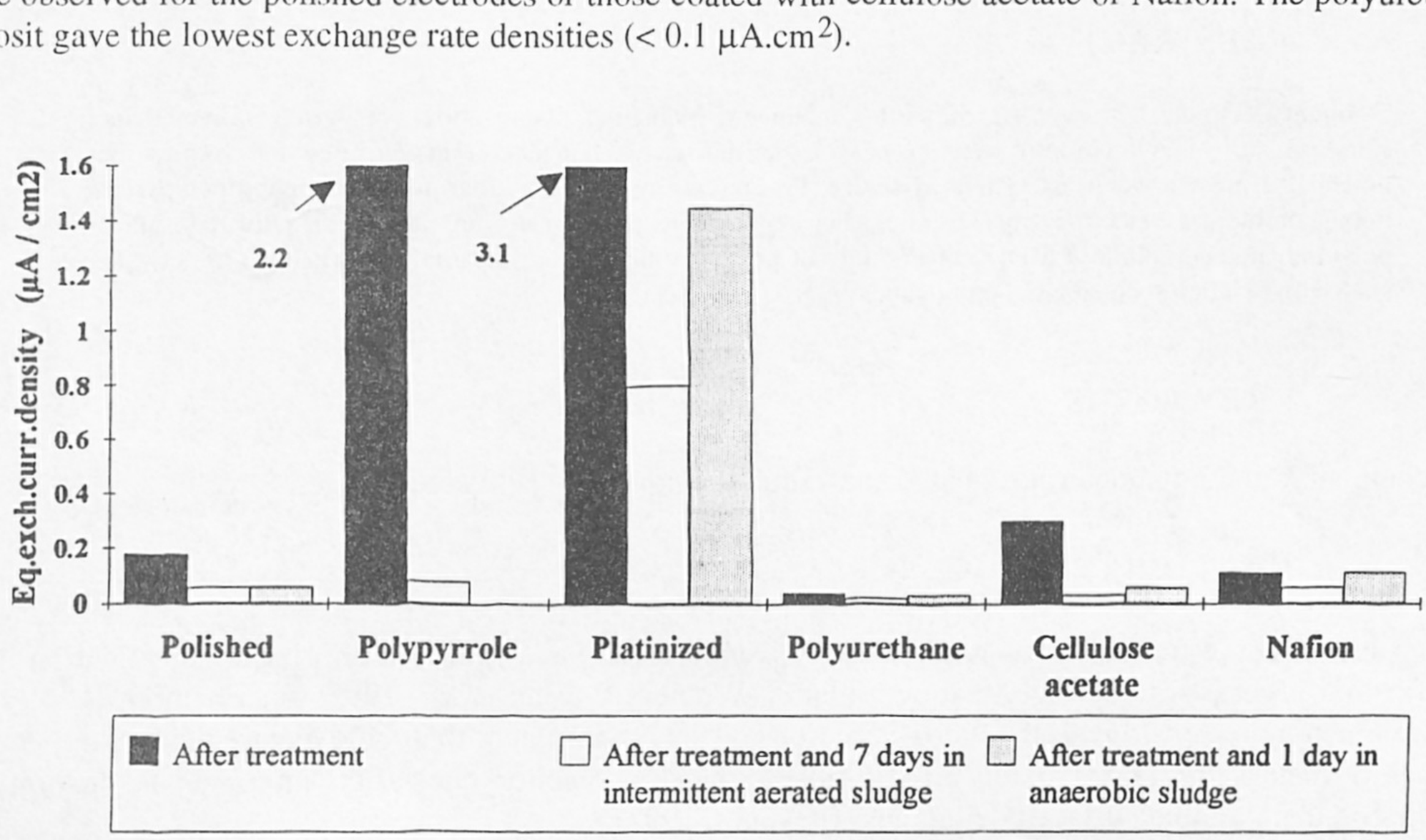

Fig. 1. Equilibrium exchange current densities in treated water or aerated activated sludge.

The equilibrium exchange current densities obtained after immersion of these treated Pt electrodes in the activated sludge alternately submitted to aerobic and anoxic sequences during 7 days reached only 10% to

55% of the initial current densities, with the exception of the polypyrrole layer (4%) which broke up rapidly in activated sludge.

After immersion of the electrodes in the anaerobic activated sludge, the exchange current densities obtained reached only 20% to 50% of the initial current densities, with the exception of Nafion. The platinized platinum electrode was found to maintain the highest equilibrium exchange current density value (1.45 $\mu A/cm^2$).

Immediately after Pt electrode treatment, the highest zero-current potentials were obtained after polishing or Nafion deposits (Figure 2). For the other deposits, potentials were found to be lower.

After immersion of the electrodes in the activated sludge alternately submitted to aerobic and anoxic sequences, the deviations from the former potentials were quite small for the polished electrodes and those coated with polypyrrole or Nafion. For the other deposits, the values observed were higher than the values observed immediately after treatment of the platinum surfaces.

When placed in anaerobiosis for 24 hours, potential show an under-estimation of approximately 200 mV when these electrodes were again dipped in an aerated solution, except for NAfion for which the drift was much lower (100 mV).

All these potentials are nevertheless significantly lower than equilibrium potential calculated, taking into account dissolved oxygen and pH within treated water or aerated sludge used for comparison (> 700 mV) (Heduit and Thevenot, 1989).

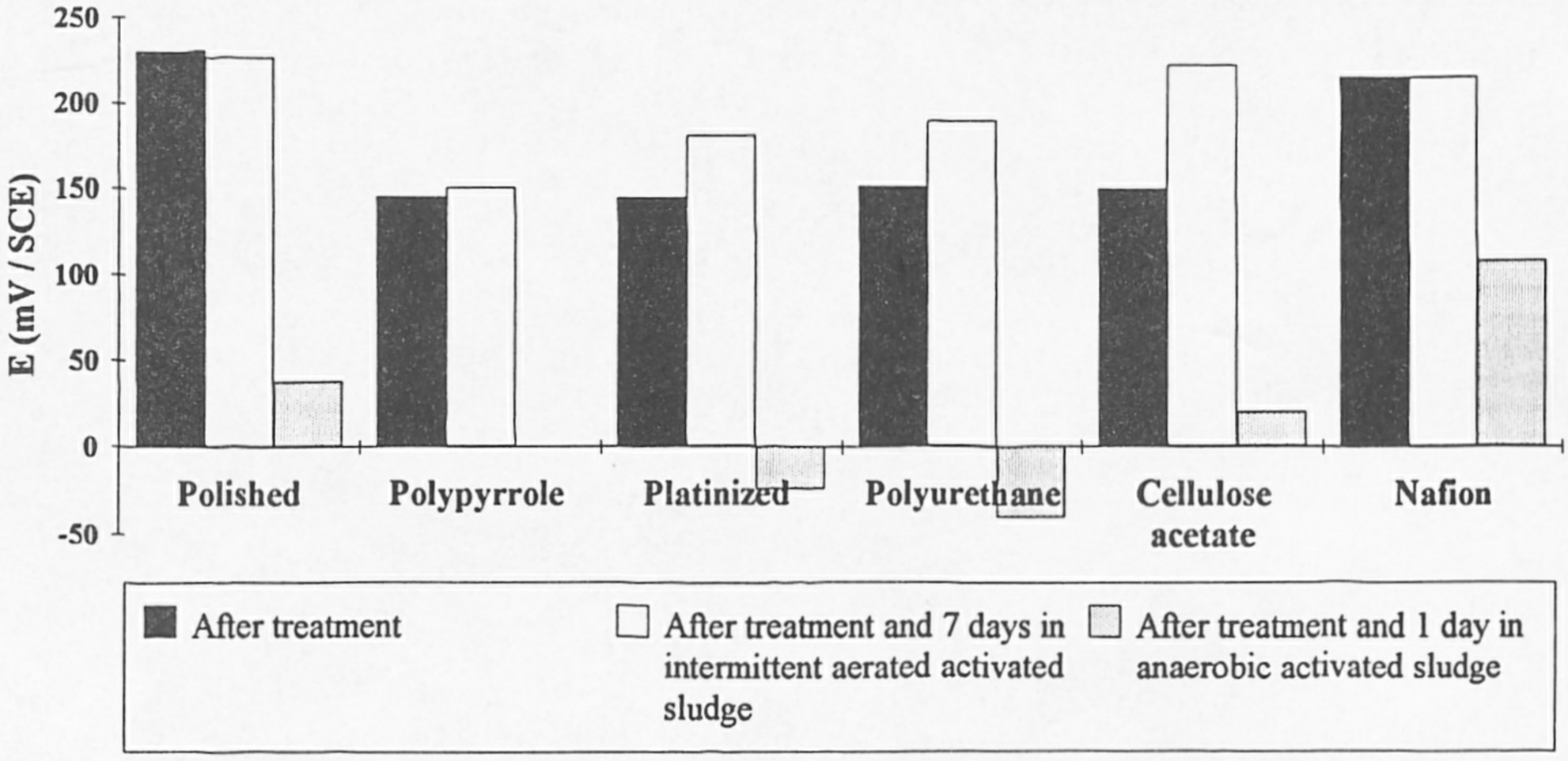

Fig. 2. Zero-current potentials in treated water or aerated activated sludge.

CONCLUSION

These preliminary studies show that the electrolytic deposits of platinum black or polypyrrole resulted in a significant increase of the electron transfer rates but that polypyrrole film was found to break up rapidly in activated sludge.

Under these experimental conditions, polyurethane and cellulose acetate layers did not prevent the platinum surface from fouling activated sludge: this contamination led to a decrease of the electron transfer rate and an under-estimation of the potentials when dipped into anaerobic sludge. Nafion deposit seems to decrease this drift and could be valuable in activated sludge; further study is in progress.

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