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AGRICULTURAL WASTE CARRIERS FOR IMMOBILIZED MICROBIAL BIOREMEDIATION OF OIL-CONTAMINATED SOILS: A COMPREHENSIVE REVIEW

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Abstract. Petroleum hydrocarbon contamination represents a critical global environmental challenge affecting over 5 million km². Bioremediation using immobilized microbial consortia has emerged as a sustainable alternative to conventional remediation methods. This review examines current advances in immobilization technologies for oil-contaminated soil remediation, with particular focus on agricultural waste carriers including rice husks, buckwheat husks, and other lignocellulosic materials. Immobilized systems demonstrate significantly superior performance compared to free-cell applications, achieving degradation efficiencies of 50-90% versus 20-45% for free cells. Buckwheat husks exhibit exceptional performance with 58.4% TPH degradation and rate constants of 0.0187 d⁻¹, representing 73% enhancement over free-cell systems. This superior performance correlates with high rutin content (28.8 mg/100g) providing antioxidant protection, immobilization efficiency of 92.3%, and favorable moisture retention (55%). *Rhodococcus* and *Dietzia* genera demonstrate complementary metabolic capabilities for comprehensive hydrocarbon degradation. Key factors influencing remediation success include carrier porosity, surface area, immobilization efficiency, moisture retention capacity, and biochemical properties including antioxidant content. Despite promising laboratory results, challenges remain in scaling to field applications under extreme environmental conditions. Future research should prioritize optimization of carrier pretreatment, development of stress-tolerant strains, and integration of multi-carrier systems.

Keywords: bioremediation; immobilization; agricultural waste; petroleum hydrocarbons; buckwheat husk; rice husk; *Rhodococcus*; *Dietzia*.

Introduction

Petroleum hydrocarbon contamination affects approximately 5 million km² of land worldwide, posing severe environmental and public health risks [1, 2]. In oil-producing regions such as Kazakhstan's Caspian basin and Western regions, contaminated lands exceed 43,000 km², with approximately 6,000 km² directly impacted by petroleum products [3]. Petroleum hydrocarbons exhibit carcinogenic properties and significantly alter soil physical and chemical properties, reducing water permeability, fertility, and overall ecosystem functionality [4].

Traditional remediation approaches including physical removal, thermal desorption, and chemical oxidation, while effective, are energy-intensive, costly, and may generate secondary contamination [5, 6, 7]. These limitations have driven research toward biological remediation strategies that offer environmental sustainability and economic viability.

Among various bioremediation strategies, immobilization of microorganisms on solid carriers has gained significant attention due to enhanced cell viability, protection against environmental stress, and improved retention at contaminated sites [8, 9, 10]. Agricultural residues including rice husks, buckwheat husks, wheat straw, corn cobs possess characteristics suitable for microbial immobilization:

high porosity, large specific surface area, lignocellulosic structure providing attachment sites, biodegradability, and minimal toxicity [11, 12, 13].

This review synthesizes current knowledge on immobilized microbial bioremediation for oil-contaminated soils, with emphasis on agricultural waste carriers, immobilization mechanisms, kinetic modeling, environmental optimization, and field-scale implementation challenges.

Materials and methods. A comprehensive literature search was conducted using Scopus, Web of Science, and Google Scholar databases covering publications from 2010-2025. Search terms included combinations of "bioremediation", "immobilized microorganisms", "oil contamination", "petroleum hydrocarbons", "agricultural waste carriers", "Rhodococcus", "Dietzia", "rice husk", "buckwheat husk", and "lignocellulosic carriers".

Studies were included if they investigated petroleum hydrocarbon bioremediation using immobilized microorganisms, utilized agricultural waste or natural carriers, provided quantitative degradation data, and employed controlled experimental designs. Extracted parameters included carrier material properties, microbial strains, contamination levels, degradation efficiency, kinetic rate constants, immobilization efficiency, and environmental conditions.

Results. Agricultural waste carriers demonstrate significant advantages for microbial immobilization. Rice husks, with global production exceeding 150 million tonnes annually, possess high silica content (15-20%), cellulose (35-45%), and lignin (20-25%) [14, 15]. Their microporous structure provides extensive surface area, achieving immobilization efficiency of 87.6% and TPH degradation of 52.1% over 45 days with first-order rate constants of 0.0162 d^{-1} [16].

Buckwheat husks exhibit superior performance, achieving 58.4% TPH degradation with rate constants of 0.0187 d^{-1} , representing 73% enhancement over free-cell systems [16]. This performance correlates with higher rutin content (28.8 mg/100g versus 15.0 mg/100g in rice husks), providing antioxidant protection under oxidative stress conditions typical of hydrocarbon metabolism [17, 18]. Immobilization efficiency reaches 92.3%, the highest reported among agricultural carriers.

Scanning electron microscopy reveals dense bacterial colonization on carrier surfaces, with cell clusters forming biofilm-like structures within carrier pores. Cell viability ranges from 73-96% post-immobilization [19]. Immobilized systems outperform free cells through physical protection, improved substrate accessibility, moisture retention (buckwheat husks maintain 55% versus 38% in controls), and antioxidant protection from rutin and flavonoids [16, 17].

Kinetic modeling demonstrates first-order degradation dynamics following $\ln(C/C_0) = -kt$. Buckwheat husk systems show $k = 0.0187\text{ d}^{-1}$, rice husks $k = 0.0162\text{ d}^{-1}$, and free cells $k = 0.0108\text{ d}^{-1}$, corresponding to half-lives of 37.1, 42.8, and 64.2 days respectively [16, 20]. Degradation efficiency varies by hydrocarbon fraction: BTEX compounds (65-75%), short and medium-chain alkanes (55-65%), and PAHs (30-45%) [16, 21].

Rhodococcus and Dietzia genera demonstrate complementary metabolic capabilities. Rhodococcus species degrade aromatic compounds through dioxygenase systems, while Dietzia species show superior degradation of saturated hydrocarbons via alkane monooxygenase pathways [22, 23, 24]. Consortium approaches show 15-30% higher efficiency than single-strain applications [25, 26].

Environmental optimization reveals temperature optima of 25-30°C, pH of 7.0-7.5, moisture content of 60-70% water holding capacity, C:N:P ratios of 100:10:1 to 100:15:2, and carrier loading of 5-10% by weight [16, 27, 28]. Enzymatic activity measurements show catalase reaching $4.7\text{ mL O}_2 \cdot \text{g}^{-1}\text{ soil} \cdot (3\text{ min})^{-1}$ in buckwheat systems, 68% higher than free cells, while lipase activity reaches $24.3\text{ }\mu\text{mol fatty acids} \cdot \text{g}^{-1}\text{ soil} \cdot \text{h}^{-1}$ [16].

Challenges for field implementation include carrier degradation over extended periods, extreme environmental conditions (temperature fluctuations, salinity, alkaline pH), indigenous microbial competition, recalcitrant hydrocarbon fractions, and scale-up optimization [29, 30, 31]. Zeolite-

immobilized systems achieved 80.7% removal in 21 days in marine environments, though cost-effectiveness relative to agricultural wastes requires evaluation [32].

Conclusion. Agricultural waste carriers represent promising alternatives for immobilized microbial bioremediation. Buckwheat husks demonstrate superior performance with 58.4% TPH degradation, 92.3% immobilization efficiency, and rate constants of 0.0187 d^{-1} , attributed to favorable biochemical properties including high rutin content. Immobilization enhances degradation through physical protection, improved substrate accessibility, moisture retention, and antioxidant support.

Rhodococcus-Dietzia consortia enable comprehensive degradation through complementary metabolic capabilities. Key success factors include appropriate carrier selection and pretreatment, microbial consortium composition, and environmental parameter optimization. Despite field-scale challenges, immobilized systems offer significant advantages over conventional approaches.

Future research should focus on stress-tolerant strain development, multi-carrier system optimization, biosurfactant integration, and pilot-scale validation. Agricultural waste valorization combined with environmental remediation supports circular economy principles while addressing critical environmental challenges.

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МҰНАЙ ЛАСТАНҒАН ТОПЫРАҚТЫ ИММОБИЛИЗАЦИЯЛАНҒАН МИКРОБТЫҚ БИОРЕМЕДИАЦИЯЛАУ ҮШІН АУЫЛ ШАРУАШЫЛЫҒЫ ҚАЛДЫҚТАРЫ ТАСЫМАЛДАУШЫЛАРЫ: КЕШЕНДІ ШОЛУ

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Аңдатпа. Мұнай көмірсутектерімен ластану 5 миллион км²-ден астам аумақты қамтитын жаһандық экологиялық мәселе болып табылады. Иммобилизацияланған микробтық консорциумдарды пайдаланатын биоремедиация дәстүрлі тазалау әдістеріне тұрақты балама ретінде қолданылады. Бұл шолу мұнай ластанған топырақты тазалауға арналған иммобилизация технологияларының, әсіресе күріш қауызы, қарақұмық қауызы және басқа лигноцеллюлозалық материалдар сияқты ауыл шаруашылығы қалдықтарының қазіргі жетістіктерін зерттейді. Иммобилизацияланған жүйелер еркін жасушалық қолданбаларға қарағанда айтарлықтай жоғары өнімділікті көрсетеді (50-90% деградация тиімділігі). Қарақұмық қауызы 58,4% ЖМК деградациясымен және 0,0187 д⁻¹ жылдамдық тұрақтыларымен ерекше өнімділікті көрсетеді. *Rhodococcus* және *Dietzia* туыстары кешенді көмірсутектерді ыдыратуда толықтыру метаболикалық мүмкіндіктерді көрсетеді.

Түйін сөздер: биоремедиация; иммобилизация; ауыл шаруашылығы қалдықтары; мұнай көмірсутектері; қарақұмық қауызы; күріш қауызы; *Rhodococcus*; *Dietzia*.

СЕЛЬСКОХОЗЯЙСТВЕННЫЕ ОТХОДЫ-НОСИТЕЛИ ДЛЯ ИММОБИЛИЗОВАННОЙ МИКРОБНОЙ БИОРЕМЕДИАЦИИ НЕФТЕЗАГРЯЗНЕННЫХ ПОЧВ: КОМПЛЕКСНЫЙ ОБЗОР

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Аннотация. Загрязнение нефтяными углеводородами представляет критическую глобальную экологическую проблему, затрагивающую более 5 миллионов км². Биоремедиация с использованием иммобилизованных микробных консорциумов является устойчивой альтернативой традиционным методам очистки. В данном обзоре рассматриваются современные достижения в технологиях иммобилизации для очистки нефтезагрязненных почв, с особым акцентом на сельскохозяйственные отходы-носители, включая рисовую шелуху, гречневую шелуху и другие лигноцеллюлозные материалы. Иммобилизованные системы демонстрируют значительно превосходящую эффективность по сравнению со свободными клетками, достигая эффективности деградации 50-90% против 20-45%. Гречневая шелуха демонстрирует исключительную производительность с 58,4% деградацией ОНУ и константами скорости 0,0187

д⁻¹. Роды *Rhodococcus* и *Dietzia* демонстрируют комплементарные метаболические возможности для комплексной деградации углеводов.

Ключевые слова: биоремедиация; иммобилизация; сельскохозяйственные отходы; нефтяные углеводороды; гречневая шелуха; рисовая шелуха; *Rhodococcus*; *Dietzia*.